



## Anion Exchange Sorption of Chromate from Aqueous Solutions by Activated Carbon

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### Abstract

Water decontamination from chromium (Cr) is of prime importance because of its carcinogenic nature. The sample of activated carbon was characterized by surface area analyzer, SEM/EDX, TGA, FTIR and PZC. This study was focused on adsorption of hexavalent chromium from the aqueous phase onto activated carbon. Both the temperature and pH had a positive effect on the chromate uptake by activated carbon. The chromate uptake at different pH values followed the trend: pH 2 > pH 3 > pH 4 > pH 5 > pH 7 > pH 8. The sorption maxima at pH 2 was explained on the basis of electrostatic attraction between the negatively charged chromate anions and positively charged surface of the activated carbon. Different models were tested to access the sorption maxima and to probe into the chromate adsorption mechanism. The thermodynamic parameters suggested that heat is needed to shift the hexavalent chromium from solution to the solid surface. It was concluded that the anion exchange sorption was involved in removing the chromate anion from the aqueous system into the surface of activated carbon.

**Keywords:** Chromate, Activated carbon, Anion exchange, Sorption.

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### Introduction

Water pollution caused by heavy metal has become a serious threat to the human being for the last 20 years [1]. Numerous people die each year all over the world because of the diseases caused by drinking water. Heavy metals is believed to be one of the major causes of water pollution [2, 3] and consequently, these heavy metals enter into the food chain and create a severe risk to living organism due to their long bio-accumulation [4].

Millions of people die on account of the diseases caused by drinking water contaminated with heavy metals [3,5]. Chromium (Cr) is highly toxic metal on account of its carcinogenic nature

[6,7]. Chromium generally exists in the Cr (0), Cr (III) and Cr (VI) oxidation states [8, 9]. The Agency for Toxic Substances and Disease Registry (ATSDR) depicted that the salts of Cr (VI) are relatively more toxic due to their mobilities than Cr (III) [10,11]. The hexavalent chromium exists in different forms of  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  in aqueous phase [12, 13].

Different industrial processes such as electroplating, surface finishing, metal fabrication, metal extraction and manufacture of batteries are seen to be the major contributors of chromium to the atmosphere [14, 15]. Several researchers

studied the chromium adsorption from aqueous solution [16, 17] using different adsorbents to reduce the concentration of chromium in the aquatic environment. The materials used for the decontamination of water from the dyes and hexavalent chromium include kaolinite, sand, goethite, activated alumina, activated organic resins and zeolite etc. [18, 19].

According to a survey, more than one billion people are unable to access to safe drinking water. Due attention is required for the decontamination of water from heavy metals in general and chromium in particular because of its carcinogenic nature. Activated carbon is a good choice to be used for the decontamination of water from chromate anion because of its high surface area and excellent performance as compared to its counterparts reported in the literature [20]. Activated carbon can be used as a capable materials for the cleansing of water from toxins. Though, the adsorption of chromate on carbon materials has been studied previously. However, the mechanism of adsorption and thermodynamic studies of chromium (VI) adsorption from aqueous solution onto activated carbon have not been given due attention. The present study not only focuses to probe into the mechanism of chromate adsorption onto activate carbon but also to evaluate the thermodynamic feasibility of the process.

### Materials and Methods

Research grade reagents were used throughout the experimental work. Commercial activated carbon and ( $K_2Cr_2O_7$ ) were purchased from Merck. All the working solutions were prepared in deionized water.

### Characterization

The surface area of the activated carbon (AC) was determined by Quantachrome NOVA 2200e surface area analyzer. The powder sample was also analyzed using the X-ray diffractometer, model JDX-3532 with Mn filtered Cu-K $\alpha$  radiations. The X-rays patterns were taken at 2 $\theta$

values ranging from 10 – 80 °C with step size 0.30° and a step time 5 s. The scanning electron microscopy (SEM) was carried out to study the surface morphology of AC. Energy dispersive X-ray (EDX) analyses were conducted by the EDX model INCA 200. Thermogravimetric analysis (TGA) of AC was performed to determine the weight of a sample as a function of temperature by thermal Analyzer model Perkin Elmer 6300. The sample was heated at a rate of 10 °C per minute starting from 30 °C to 1000 °C. FTIR analyses of AC before and after chromate adsorption were performed by Infrared spectrophotometer, model Shimadzu 8201PC. Salt addition method was applied to determine the PZC [21].

### Adsorption studies

The stock solution of 1000 ppm chromium was prepared from  $K_2Cr_2O_7$  which was then diluted to the desired concentration of chromium in the range of 10-150 ppm. During the adsorption experiments, 0.1 g AC was added into 30 ml chromium solutions of different concentrations. The initial pH of the suspension was fixed at a desired pH value by standard solutions of either nitric acid or sodium hydroxide. The system was equilibrated for 24 h at 120 rpm. The final pH of each suspension was recorded. After the filtration, the concentrations of chromium in the filtrates were determined by the atomic absorption model Perkin-Elmer Analyst 800. Similar adsorption experiments were conducted at different temperatures. Moreover, the pH effect on the uptake of chromium by AC was investigated by varying the pH from 2 to 8 at 298K.

Chromium adsorption was computed from the difference of the initial and the final concentration of the chromium in aqueous solution using the following mathematical relationship:

$$q_e = \frac{V_L(C_o - C_e)}{1000m} \quad (1)$$

where  $q_e$  refers to the amount of chromium adsorbed ( $\text{mol g}^{-1}$ ),  $V_L$  is the volume of solution (ml),  $m$  is the amount of AC (g),  $C_o$  and  $C_e$  are the initial and final chromium concentrations ( $\text{mol L}^{-1}$ ). The solid samples of AC were air dried and subjected to EDX and FTIR analyses for the confirmation of chromate adsorption.

## Results and Discussion

### Characterization

The BET surface area of the activated carbon (AC) determined by the Quantachrome model NOVA 1200e was found to be  $177\text{m}^2/\text{g}$ , which is similar to the one previously recorded by Borah *et al.* [22].

The XRD image indicates that the sample of AC is amorphous in nature and its PZC value is found to be 3.2 Fig. 1. Similar PZC values for different materials have been recorded in the literature [22, 23]. As expected, the EDX spectrum of AC indicates that the sample contains only carbon and oxygen Fig. 2.

A close inspection of the IR spectrum Fig. 3 of AC reveals smaller peaks at  $1701$ ,  $1589$ , and  $1384\text{cm}^{-1}$  which can be assigned to the vibration of C=O groups as was suggested by Rao *et al.* [24]. These peaks are most probably due to the existence of carboxyl group available on the surface of virgin AC. The band at  $3387\text{ cm}^{-1}$  represents the water molecules absorbed into the solid surface as this band is assigned to the OH stretching vibration [25]. The peak at  $2345\text{ cm}^{-1}$  is attributed to the evacuation of  $\text{CO}_2$  while the bands at  $1544$ ,  $1680$  - $1720\text{ cm}^{-1}$  are assigned to the C=O and C=C linkages as proposed by the Calahorro *et al.* [26].

The SEM micrograph Fig. 4 of AC reveals that the particles of activated carbon are irregular in shape and lack a definite morphology. Mostly the particles of AC are in the aggregated form and its external surface area seems to be porous in nature [27].

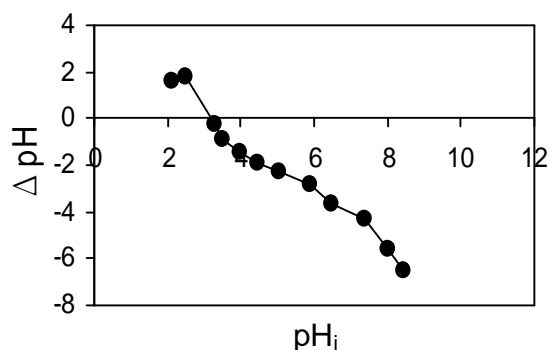


Figure 1. Point of zero charge (PZC) of AC

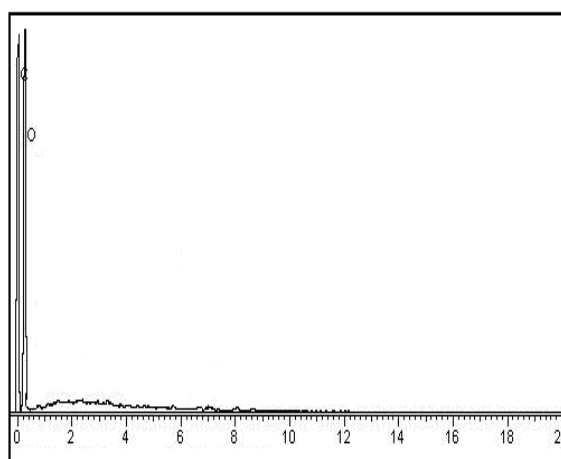


Figure 2. EDX spectrum of AC

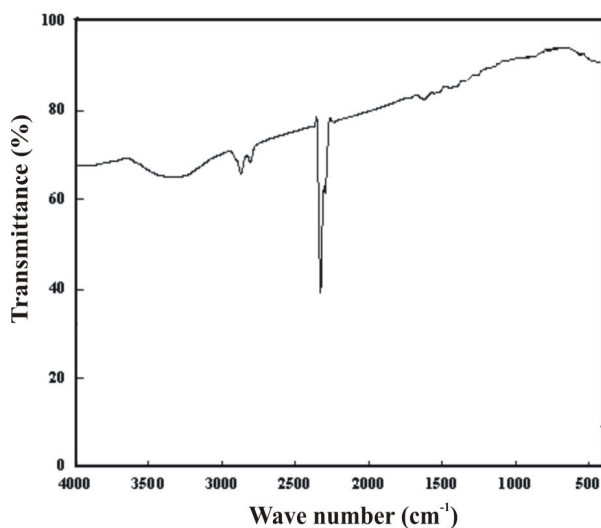


Figure 3. FTIR spectrum of AC.

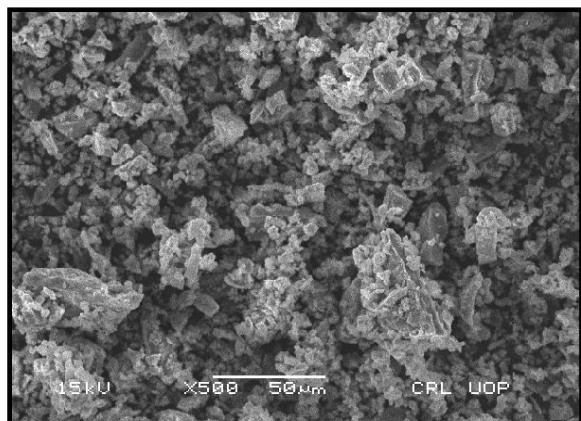


Figure 4. Scanning electron micrograph (SEM) of AC

### Adsorption studies

#### Effect of media dosage, concentration of chromate and temperature on adsorption

Adsorbent dose has a significant effect on the extent of chromate adsorption. The effect of adsorbent dosage on chromate adsorption was studied in a batch system using AC dose of 0.1-1.00 g and initial chromate concentration 100 mg/L at 298 K. The results are shown in Fig. 5 which indicate that the equilibrium amount of chromate ions adsorbed decreased with increase in AC dosage. At a low adsorbent dose, the adsorption sites are exposed and the adsorption is faster resulting in higher adsorption capacity. On the other hand, the low adsorption capacity at higher dose is due to the decrease in the availability of adsorption sites because of the aggregation of adsorbent particles.

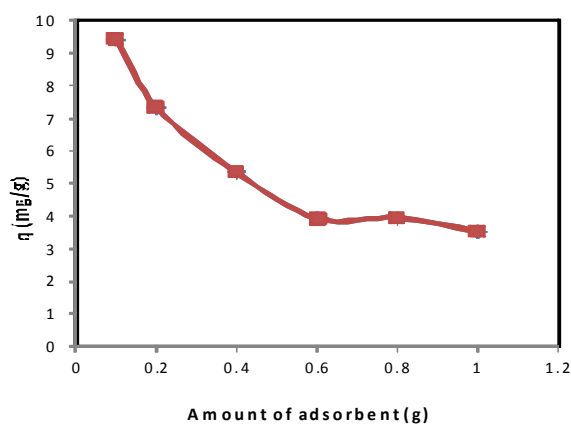


Figure 5. Effect of media dosage on chromate adsorption by AC at pH 5

Temperature role is important in the adsorption of both anion and cation from aqueous solution to the solid substrate. The influence of temperature (293K, 303K, 313K, and 323K) on the anion exchange sorption of chromate by the virgin sample of AC Fig. 6 was also investigated. It was observed that temperature has a profound effect on the chromate adsorption. The uptake of chromate is found to increase from  $24 \times 10^{-5}$  to  $50 \times 10^{-5}$  mol/g when the temperature of the system is raised from 293K to 323 K. The increased uptake of Cr (VI) with rise in temperature reflects that the process of adsorption is endothermic and further suggests that heat energy is needed to divest and transport the chromate anions from the aqueous phase into the solid surface. Similar results for the adsorption of metal anions by different adsorbents have been reported elsewhere [28, 29].

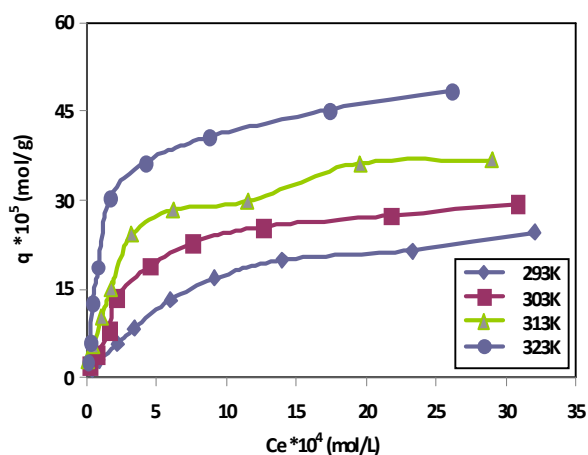


Figure 6. Effect of temperatures on chromate adsorption by AC at pH 5

#### pH effect on adsorption

The pH of the system drastically changes the adsorption capacity of the materials. It is due to the changes in both the speciation of chromium and surface charge properties of the substrate. The adsorption isotherms at different pH values have been presented in Fig. 7. The uptake of chromate anions at different pH value follows the trend: pH 2 > pH 3 > pH 4 > pH 5 > pH 7 > pH 8. The sorption maxima at pH 2 can be explained on the basis of strong electrostatic attraction between the

positively charged surface and negatively charged chromate anions.

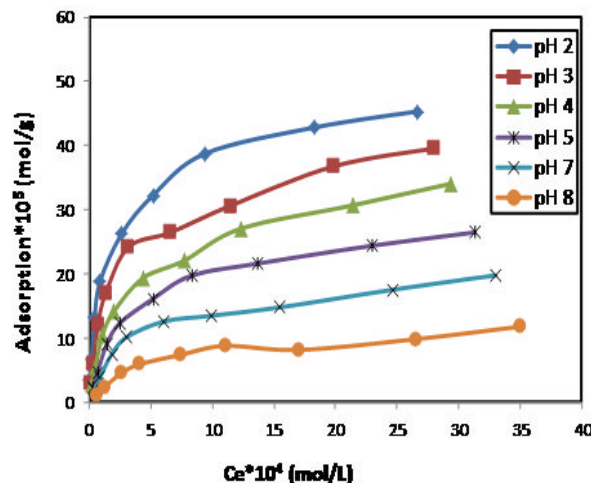
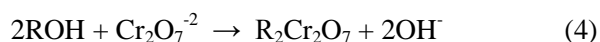


Figure 7. Effect of pH on chromate adsorption by AC at 303K

The increase in final pH further reveals that adsorption is accompanied by the release of hydroxyl anion from the surface to the aqueous phase. From the changes in pH of solution, the following mechanisms may be proposed for the adsorption of chromate onto the activated carbon.



where R represents the solid matrix. The similar adsorption mechanism was described for the uptake of arsenate using binary mixed oxides of iron and silicon [30].

### Adsorption isotherms

The following adsorption isotherms were used to investigate the mechanism and sorption capacity of adsorbent.

The Langmuir's isotherm [31] assumes monolayer formation on the surface of adsorbent

with no interaction between the sorbed molecules. The Langmuir's isotherm defines the equilibrium set up between the activated carbon and remaining concentration of chromate anions in solution. The most extensively used form of the Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_b} + \frac{C_e}{q_{\max}} \quad (6)$$

where  $C_e$  and  $q_e$  refer to the chromate anions ( $\text{mol L}^{-1}$ ) and the amount of chromate sorbed ( $\text{mol.g}^{-1}$ ) respectively,  $K_b$  represents constant ( $\text{L mol}^{-1}$ ) which is linked to the binding energy of sorption,  $q_{\max}$  refers to the monolayer sorption capacity of AC ( $\text{mol.g}^{-1}$ ). The plots of  $C_e/q_e$  vs.  $C_e$  are straight lines Fig. 8 and monolayer sorption capacity derived from the Langmuir model is consistent with its experimental values which illustrate that the Langmuir model is the best fit to the sorption data. Higher values of the binding energy constant indicate a stronger interaction between the surface and chromate anions Table 1. Both the sorption capacity ( $X_m$ ) and apparent binding energy constant ( $K_b$ ) increase with temperature rising from 293K to 323K which also indicates the chromate adsorption onto AC is an endothermic process.

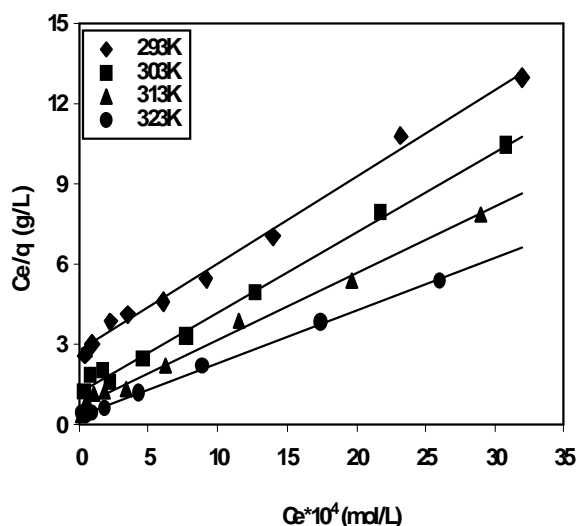


Figure 8. Langmuir's isotherms for chromate adsorption by AC at different temperatures at pH 5

Dubinin-Radushkevich (D-R) model [32] can be used to explore the adsorption mechanism and its linear form is given as follows:

$$\ln qe = \ln q_{max} - \beta \varepsilon^2 \quad (7)$$

where  $\beta$  is the adsorption energy, and  $\varepsilon$  refer to Polayni potential which is calculated from the following relationship.

$$\varepsilon = RT \ln \left( 1 + \frac{1}{Ce} \right) \quad (8)$$

Table 1. Langmuir's constants for chromate adsorption by AC at pH 5.

Adsorbent	T (K)	R <sup>2</sup>	R <sub>L</sub>	K <sub>b</sub> x10 <sup>-2</sup> (g/L)	q <sub>max</sub> x 10 <sup>-5</sup> (mol/g)
AC	293	0.993	0.305	12.00	30.58
	303	0.994	0.181	23.88	33.42
	313	0.994	0.119	38.63	39.88
	323	0.998	0.085	56.82	50.89

The values of  $q_{max}$  (mol.g<sup>-1</sup>) and  $\beta$  (mol<sup>2</sup>.kJ<sup>-2</sup>) are obtained from the intercepts and the slopes of  $\ln qe$  against  $\varepsilon^2$  plots Fig. 9. The linear plots of  $\ln qe$  vs.  $\varepsilon^2$  show the applicability of D - R isotherm and the mean free energy (E) is computed according to the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

The values of R<sup>2</sup>,  $\beta$ ,  $q_{max}$  and E determined from the plots of  $\ln qe$  vs.  $\varepsilon^2$  for chromate sorption by AC are given in Table 2. The reported value of mean free energy (E) for an ion exchange process is in the range of 8-16 kJ mol<sup>-1</sup>. In the present case, the mean free energy values for chromate adsorption by AC range from 8.63 – 11.04 kJ mol<sup>-1</sup> which strongly supports that anion-exchange mechanism is involved in removing chromate anion from aqueous solution through AC. The D.R model

further elaborates the mechanism of chromate adsorption to be anion exchange as was proposed on the basis of pH changes after chromate adsorption, according to reaction 3. It is concluded from the above observation that the chromate sorption is accompanied by the hydroxyl anions released from the surface. The present findings are also consistent with those reported for arsenate sorption onto metal oxide [30].

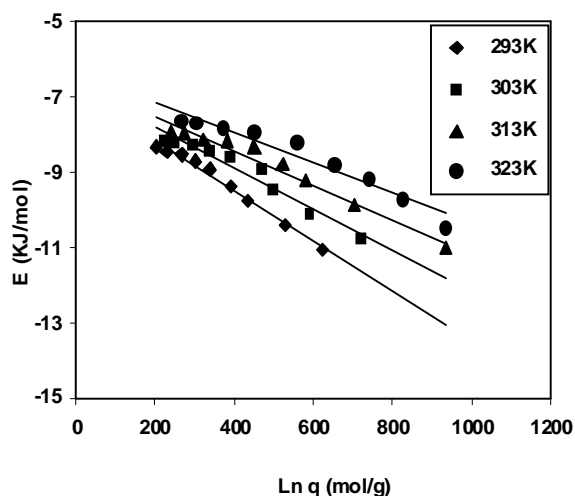


Figure 9. D-R isotherms for chromate adsorption by AC at different temperatures at pH 5

Table 2. D-R constants for chromate adsorption by AC at pH 5.

Adsorbent	T (K)	R <sup>2</sup>	$\beta$ (mol <sup>2</sup> .kJ <sup>-2</sup> )	E (kJ mol <sup>-1</sup> )
AC	293	0.989	-6.7	8.64
	303	0.951	-5.5	9.53
	313	0.971	-4.6	10.4
	323	0.939	-4.1	11.0

### Thermodynamic parameters

The entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) changes were calculated using the vant Half equation in the form:

$$\ln K_b = \Delta S/R - \Delta H/RT \quad (10)$$

The free energy change ( $\Delta G$ ) was calculated from the following mathematical expression:

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

where  $K_b$  is the binding energy constant ( $L.g^{-1}$ ),  $R$  is the molar gas constant ( $J. mol^{-1} K^{-1}$ ), and  $T$  (K) is the absolute temperature. The plots of  $\ln K_b$  vs.  $1/T$  Fig. 10 reveal that equation 10 is best applied in the present case. The values of  $\Delta H$  and  $\Delta S$  Table 3 are positive. The  $\Delta H$  value is greater than 40 kJ/mol which reveals that the process of adsorption is chemical in nature and further illustrates that greater heat energy is needed to shift the hexavalent chromate to the surface of AC. The findings of this study are contrary to the results observed for the adsorption chromate, where the  $\Delta H$  value was reported to be negative and process of adsorption was exothermic. Besides, the current values are in also good agreement with the results reported for several exchangers. Moreover, negative  $\Delta G$  values that adsorption of Cr (VI) onto AC is favourable. As expected, the positive value of  $\Delta S$  can be assigned to the spontaneous nature of the chromate adsorption. It further illustrates that the chromate anions removes the hydration sheath at the solid - liquid interface which is responsible for the increased entropy of the system. The magnitude of  $\Delta S$  value is comparable to the reported values in literature.

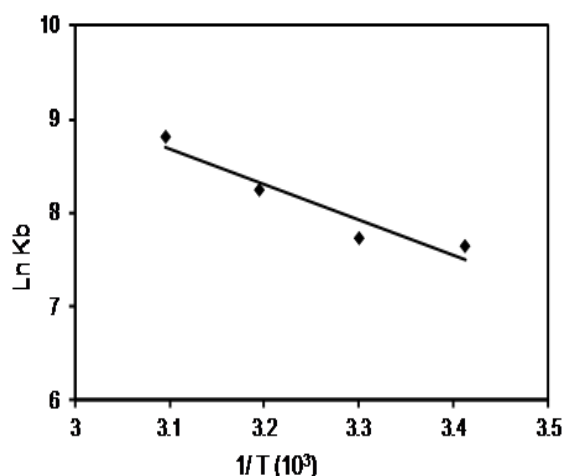


Figure 10. Plot of  $\ln K_b$  vs.  $1/T$  for chromate adsorption by AC at pH 5

Table 3. Thermodynamic parameters for chromate adsorption by AC at pH 5.

Adsorbent	T (K)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/molK)
AC	293	-57.99	40.62	198
	303	-59.98		
	313	-61.96		
	323	-63.94		

## Conclusion

The uptake of chromate on activated carbon is observed to be depend upon the temperature and pH. The maximum sorption of chromate is observed at pH 2. Both D-R and Langmuir models are the best choices to explain adsorption data. The anion exchange sorption was involved in removing the chromate anion from the aqueous system into the surface of activated carbon. The thermodynamic studies confirmed that the entropy ( $\Delta S$ ) is the main controlling factor for the chromate adsorption onto the AC.

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