Kinetics, thermodynamic and equilibrium study of Cr(VI) adsorption from aqueous solutions by NCL coal dust

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Abstract–The waste material NCL coal dust was used as adsorbent for removal of Cr(VI) from aqueous solutions under batch adsorption experiments. The maximum removal of 99.97% was recorded at pH 2. The time required to attain equilibrium was found to be 60 min. Adsorption kinetics was described by the Lagergren equation. The value of the rate constant of adsorption was found to be 0.0615 min^{-1} at 16 mg dm^{-3} initial concentration and 298 K. The applicability of the Langmuir and Freundlich equations for the present system was also tested at different temperatures: 298, 313, and 328 K. Both thermodynamic parameters and temperature dependence indicated the endothermic nature of Cr(VI) adsorption on coal dust. The results showed that NCL coal dust is a promising adsorbent for the removal of Cr(VI) from aqueous solutions.

Key words: Coal Dust, Adsorption Dynamics and Isotherms, Cr(VI), Thermodynamic Parameters

INTRODUCTION

Water, air and solid waste (plastics) pollution due to the anthropogenic sources contribute a major share to the environmental degradation of ecosystems. Some heavy metals are essential in small amounts for the normal development of animals and plants, but most of them are toxic at higher concentrations. Heavy metals are introduced into the environment through natural phenomena and human activities [1]. The contamination of the existing water resources is increasing daily with rapid industrialization. The disposal of wastewater containing heavy metals is always a challenging task for environmentalists [2]. Chromium is well-known heavy metal contaminant in wastewater as well as ground water. There are two predominant forms of chromium: trivalent and hexavalent. Hexavalent chromium (Cr(VI)) is a highly toxic and carcinogenic pollutant in the aquatic environment [3]. Cr(VI) is more hazardous to animals than trivalent chromium [4,5], due to generally low solubility of its compounds [6]. Cr(VI) is a powerful epithelial irritant and confirmed carcinogen [7]. Chromium pollution in the environment occurs naturally from erosion and weathering of chromium-bearing minerals as well as chromium-bearing industrial wastewaters [8]. The extensive use of chromium and its compounds in leather tanning, ferrochrome, pigments, electroplating and photography has led to the increase in chromium content of wastewaters [9]. Therefore, the presence of Cr(VI) in water and wastewater has been of great public concern [10]. Cr(VI) causes skin-irritation, ulcer formation and chromatitis. Over-exposure to Cr(VI) leads to liver damage, pulmonary congestion and edema [11,12].

Various methods available for the removal of heavy metals and organic pollutants from industrial wastewater are precipitation, ion-exchange, electrochemical reduction, filtration and reverse osmo-sis. All these methods have the limitations of operational and/or economical feasibility [13]. Adsorption is a physico-chemical process, which has great potential for treating effluents containing undesirable components and renders them safe and reusable [14]. The major advantages of the adsorption process for water pollution control are low investment in terms of cost, simple design and easy operations [15]. On the basis of economic viability, the present communication is addressing the removal of Cr(VI) from aqueous solutions by using waste material Northern Coalfields Limited (NCL) coal dust. Batch adsorption technique has been adopted in removal of Cr(VI) from aqueous solutions. The effect of various important parameters, contact time, initial concentration, pH, adsorbent particle size, and temperature on removal of Cr(VI) has been discussed. The dynamics of adsorption and isotherm has also been reported.

EXPERIMENTAL

1. Materials

Coal dust was collected from the Northern Coalfields Ltd. of Singrauli, M. P., India and was used as an adsorbent without any pretreatment after passing through sieves to maintain desired particle sizes. The bulk density was measured by using a specific gravity bottle at room temperature. Physicochemical properties of NCL coal dust were analyzed by Fourier transform infrared (FTIR) spectrophotometer (Varian FTIR - 3100 spectrophotometer), XRD (Rigaku DMAX - III rotating diffractometer), and BET (Micromeritics Co., USA). An oven (S.M. Scientific Instruments Pvt. Ltd., New Delhi) was used for drying the adsorbent. All the chemicals used were of analytical reagent grade. The solutions were prepared using deionized water. The solution pH was measured with a pH meter (LI 120, Elico, India). Standard 0.1 N HCl and 0.1 N NaOH solutions were used for adjusting pH of the solutions.

2. Method

The Cr(VI) solutions were prepared by dissolving potassium di-

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chromate in deionized water. Batch adsorption experiments were carried out by shaking 100 mg of desired size of coal dust with 50 ml solution of known Cr(VI) concentration in each 250 ml conical flask placed in a thermostat provided with a shaking machine (REMI Equipments Ltd., Mumbai, India) at fixed temperature, pH and agitation speed of 125 rpm. The flasks were withdrawn after the desired contact time and the filtrates were analyzed for the remaining Cr(VI) concentration. A Systronics spectrophotometer (Systronics 166, Sr. No. 984, Ahmedabad, India) was used to determine the concentration of Cr(VI) in the filtrate. Dimethylglyoxime procedure [16] was used for the analysis.

RESULTS AND DISCUSSION

1. Physicochemical Characterization of Adsorbent

The physicochemical properties of coal dust are summarized in Tables 1-3. It is evident from Table 1 that coal dust is mainly comprised of oxides of silicon, aluminium and iron, while oxides of cal-

Table 1. Analysis of coal dust

Parameters	Value
pH	6.54
Conductivity (μs cm^{-1})	1231
Particle size (BSS)	105
Bulk density (g cm^{-3})	1.31
Water adsorption (%)	27.16
Apparent porosity (%)	43
Matter soluble in water (%)	6.38
Surface area (m^{2}g^{-1})	614.65
Proximate analysis	
Moisture (%)	4.37
Volatile matter (%)	11.53
Ash content (%)	13.98
Fixed carbon (%)	70.12
Chemical analysis	
Silica (%)	48.91
Alumina (%)	22.71
Iron oxide (%)	6.26
Calcium oxide (%)	1.25
Magnesium oxide (%)	1.01

Table 2. Important infra-red bands of coal dust along with their probable assignments

| Band position (cm^{-1})	Assignment
2924.35, 2849.12	C=C-H stretching
1749.59	C=O stretching
1647.36	C=C stretching
1615	Si-O-Al stretching
1590	Mg-O bend
1419.74, 1396.59	C-H deforming
1159.32, 1122.67, 773.52	Si-O stretching
590	Fe-O
315	Ca-O bend

cium and magnesium are present in traces. The adsorbent was analyzed by Indian Standard Methods of chemical analysis [17]. The surface area, bulk density, apparent porosity, etc. were also presented in Table 1. To determine the main function groups of coal dust participating in Cr(VI) adsorption, the important IR bands of coal dust along with their possible assignments are presented in Table 2. The strong bands at 2,924.35 and 2,849.12 cm^{-1} are indicative of the existence of alkyl chains C-H stretching vibration. The peak at 1,749.59 cm^{-1} is the result of C=O stretching vibrations and at 1,647.36 cm^{-1} is the characteristic peak of C=C stretching vibrations. The band at 1,615 cm^{-1} was assigned to Si-O-Al stretching vibrations. The presence of kaolinite, carbon (hexagonal system) and silica was identified by the X- ray diffraction pattern of coal dust d-spacing values (Table 3).

2. Effect of Contact Time and Initial Concentration

The removal of Cr(VI) by adsorption on coal dust increased with time and attained a maximum value at 60 min and thereafter remained constant. On increasing the initial concentration of Cr(VI) from 16 to 265.00 mg l^{-1} (Fig. 1), the percent removal decreased from 99.97 to 65.92% at 298±0.5 K, pH 2.00 and particle size of 105 micron. Although at a lower initial concentration of adsorbate the amount of adsorbate attained on the solid phase was smaller than the amount attained on adsorbent when higher initial adsorbate concentrations were used. The equilibrium was established in

Table 3. 'd' Values of coal dust (X-ray diffraction pattern)

d (A^0)	Possible components
3.54	Kaolinite
3.35	Carbon (hexagonal system)
2.08	Carbon (hexagonal system)
2.03	Carbon (hexagonal system)
1.54	Carbon (hexagonal system)
1.22	Carbon (hexagonal system)
3.34	Silica (quartz low)
4.26	Silica (quartz low)
1.82	Silica (quartz low)
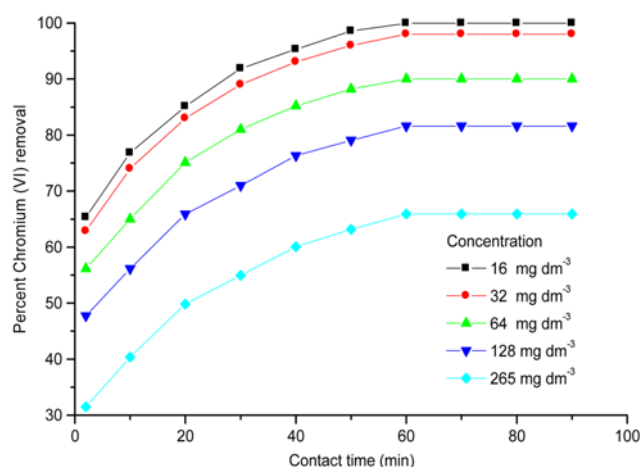
Fig. 1. Time variation of adsorption of Cr(VI) on carbon slurry at different initial concentrations. pH=2.00, particle size=105 micron, temperature=298±0.5 K, agitation speed is 125 rpm.

60 min and was independent of Cr(VI) concentration in water. Similar results have been reported by other workers for other adsorbate-adsorbent system [18-20]. When the adsorbent dose was increased from 1.0 to 8.0 g l^{-1}, complete removal of Cr(VI) took place at initial concentration of 128 mg l^{-1}. The curves of Fig. 1 are clear, continuous, single and smooth, indicating formation of a monolayer of adsorbate on the adsorbent surface. The higher % removal of Cr(VI) in lower concentration ranges has industrial application as in most of the effluents a lower concentration of Cr(VI) is encountered.

3. Effect of pH

The effect of pH on removal of Cr (VI) was studied in the pH range of 2 to 10 at initial concentrations of 16 to 265 mg dm^{-3} with adsorbent particle size of 105 micron for 90 min at 298±0.5 K (Fig. 2). The agitation speed was kept constant at 125 rpm. Fig. 2 clearly shows that pH plays a major role in the Cr(VI) adsorption. For each initial concentration value studied the percent removal was observed to decrease as the pH increased from 2 to 10. Furthermore, there is a steep rise in adsorption of Cr(VI) as the pH decreases from 10 to 2. This indicates that the sorption capacity of the adsorbent is pH dependent [12]. The decrease of the adsorption at higher pH may be attributed to the hydrolysis of Cr(VI) in the solution, as pH may affect the surface charge of adsorbents as well as the degree of ionization of different pollutants.

4. Effect of Particle Size

The removal of Cr(VI) was found to increase from 77.85 to 85.13% as the particle size decreased from 297 to 44 micron for initial concentration of 128 mg dm^{-3} at pH 2 and temperature of 298±0.5 K (Fig. 3). The higher adsorption with smaller adsorbent particles may be attributed to the fact that smaller particles provide a larger surface area. The equilibrium time was found to remain unaffected by the adsorbent particle size.

5. Effect of Temperature

The adsorption of Cr(VI) by coal dust having particle size of 105 micron was found to increase from 90.02 to 95.03% when the temperature was increased from 298 to 328±0.5 K for fixed initial concentration of 64 mg dm^{-3} at pH 2 and agitation speed of 125 rpm (Fig. 4). Increase in percent removal of Cr(VI) with increase in temperature indicated the process to be endothermic.

6. Adsorption Dynamics

Adsorption dynamics gives an idea about solute uptake rate, which controls the residence time of the solute at the solid-solution interface. Thus, the study of adsorption dynamics becomes quite significant in wastewater treatment. This study was done by conducting the batch adsorption of Cr(VI) with different initial concentrations on coal dust in a shaking machine operated at a fixed agitation speed, fixed particle size of adsorbent and desired temperature, as described in the experimental method. The widely used kinetic model [21] was expressed by using the Lagergren equation Eq. (1):
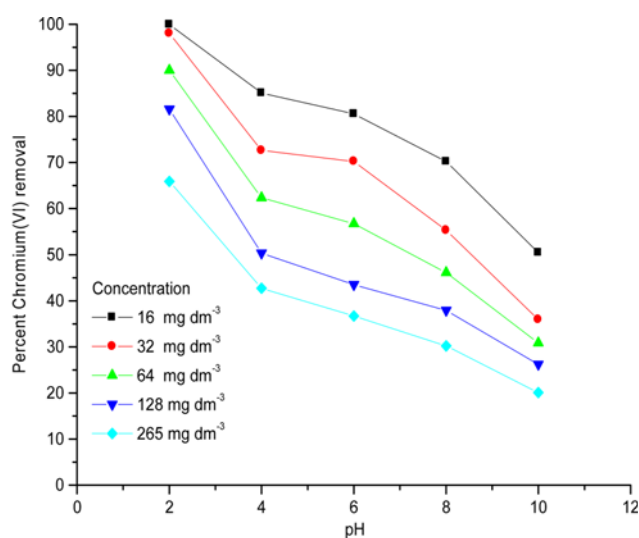
$$\log(q_e - q) = \log q_e - (k'/2.303)t \qquad (1)$$

Fig. 2. Equilibrium adsorption Cr(VI) on carbon slurry at different pH values. Particle size=105 micron, temperature=298± 0.5 K, agitation speed=125 rpm, contact time is 90 min.
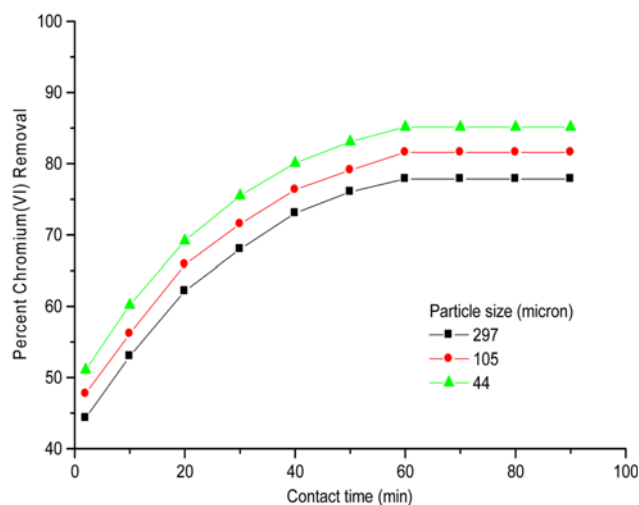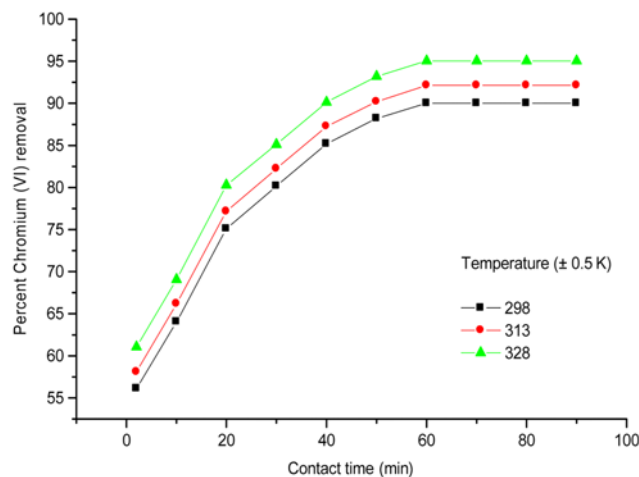

Fig. 3. Time variation of adsorption of Cr(VI) on carbon slurry at different particle sizes. Initial concentrations=128 mg dm^{-3}, pH=2.00, temperature=298±0.5 K, agitation speed is 125 rpm.

Fig. 4. Time variation of adsorption of Cr(VI) on Carbon slurry at different temperatures. Initial concentrations=64 mg dm^{-3}, pH=2.00, particle size=105 micron, agitation speed is 125 rpm.

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg g^{-1}), q is the amount of solute adsorbed at any time t (mg g^{-1}), and k′ is the adsorption rate constant. The plots of log $(q_e - q)$ vs. t at different concentrations of Cr(VI), i.e., 16 to 265 mg L^{-1}, at 298±0.5 K and pH 2, are shown in Fig. 5. A straight line is obtained for each value of initial concentration, indicating that the process of removal is governed by Lagergren's equation. The slope of this plot gives the value of the adsorption rate constant k′.

The values of k′ for all initial concentrations are similar, i.e., independent of initial concentration of adsorbate, indicating that the system follows first-order rate kinetics (Table 4).

7. Adsorption Isotherms

The Langmuir constants Q^0 and b are related to adsorption capacity and apparent heat change, respectively [22]. The values of Q^0 and b at different temperatures were determined from the slope and intercept of the linear plots of Ce/q_e vs. Ce (Fig. 6). The equilibrium concentration (Ce) of adsorbate decreases with increasing temperature showing that the adsorption is favored at higher temperature. This is supported by the values of adsorption capacity (Q^0) and apparent heat change (b), which increase with increase in temperature (Table 5). The applicability of the Langmuir isotherm in the present system indicates the monolayer coverage of Cr(VI) on the outer surface of the coal dust.

The plot of log q_e vs. log Ce yields a straight line (Fig. 7), indicating the applicability of the Freundlich isotherm in the concentra-
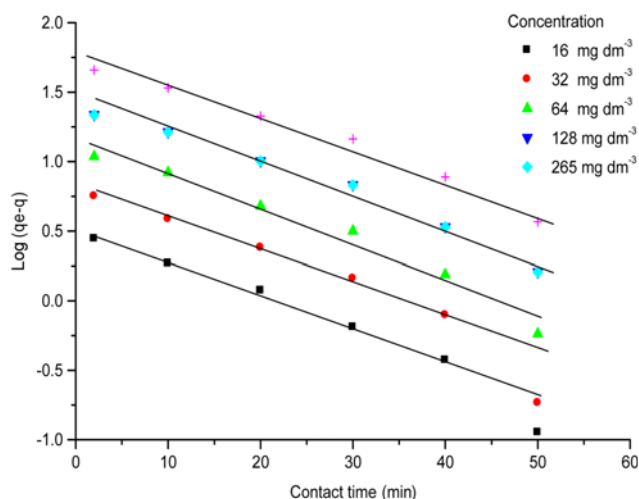

Fig. 5. Rate constant plot for adsorption of Cr(VI) on carbon slurry at different initial concentrations. pH=2.00, particle size= 105 micron, temperature=298±0.5 K, agitation speed is 125 rpm.

Table 4. Rate constant at different initial concentrations

Concentration of Cr(VI) (mg dm^{-3})	16	32	64	128	265
Rate constant (min^{-1}×10^{-2})	6.15	6.01	5.89	5.16	4.49

pH: 2.00, temperature: 298±0.5 K, particle size: 105 micron

Table 5. Various constants of Cr(VI) on coal dust at different temperatures

Parameters	Values at different temperatures		
	298±0.5 K	313±0.5 K	328±0.5 K
Langmuir constants			
b	0.0671	0.0763	0.1403
Q^0	77.5194	113.6364	185.1852
R^2	0.9784	0.9946	0.9982
Freundlich constants			
K_F	50.8512	53.8642	57.0558
n	7.8927	9.1075	9.7847
R^2	0.9952	0.9928	0.9812
Kc (dm^{3}g^{-1})	4.4747	5.8532	9.5684
ΔG^0 (kJ mol^{-1})	−0.8874	−1.0991	−1.4722

pH: 2.00, particle size: 105 micron, contact time: 90 min, agitation speed: 125 rpm
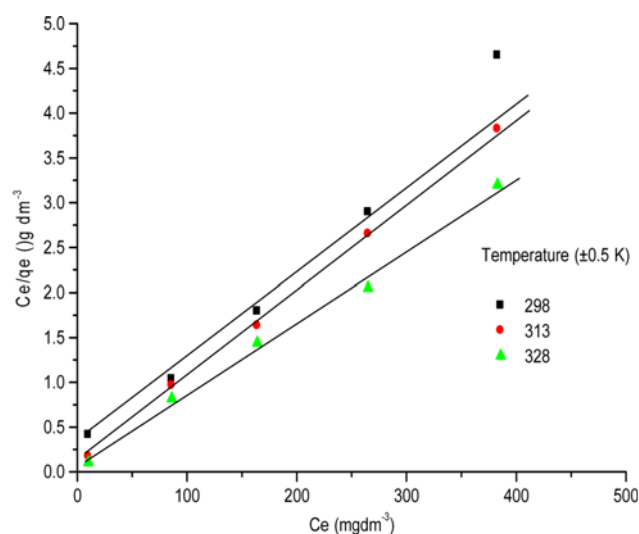

Fig. 6. Langmuir isotherm for the adsorption of Cr(VI) on carbon slurry at different temperatures. pH=2.00, particle size= 105 micron, agitation speed=125 rpm, contact time is 90 min.
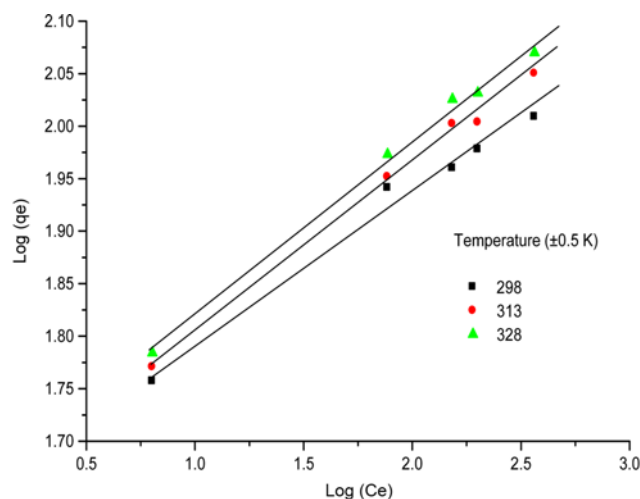

Fig. 7. Freundlich isotherm for the adsorption of Cr(VI) on carbon slurry at different temperatures. pH=2.00, particle size= 105 micron, agitation speed=125 rpm, contact time is 90 min.

tion range studied. Values of K_F and n (Table 5) also indicate that the amount of adsorbate adsorbed per gram of adsorbent increases with temperature, which further proves the endothermic nature of the adsorption in the present adsorbate-adsorbent system. The parameters n and K_F are the measure of adsorption capacity and adsorption intensity of Cr(VI) on the adsorbent. The values of n presented in Table 5 represent good adsorption as suggested by Rengaraj et al. [23]. The data thus obtained makes it clear that the adsorbent is efficient in removing Cr(VI) from the aqueous solutions.

8. Thermodynamic Parameters

Thermodynamic parameters, e.g., the free energy change (ΔG^0), and the enthalpy change (ΔH) [24,25], were calculated from the following Eqs. (2)-(3):

$$\Delta G^0 = -RT \ln K_c \tag{2}$$

$$b = b' e^{-\Delta H/RT} \tag{3}$$

where k_c is the equilibrium constant, T is absolute temperature, R is a gas constant, b is the Langmuir constant while b′ is another constant. The equilibrium constant K_c can be given by Eq. (4):

$$K_c = C_{Be}/C_{Ae} \tag{4}$$

Where C_{Be} is the equilibrium concentration of Cr(VI) on the adsorbent (mg g^{-1}) and C_{Ae} is the equilibrium concentration of Cr(VI) in solution (mg dm^{-3}). Eq. (4) can also be written as and given by Eq. (5):

$$\ln b = \ln b' \frac{\Delta H}{RT} \tag{5}$$

The value of ΔH, calculated from the slope of the straight line obtained from the plot between in b vs. 1/T (Fig. 8), was found to be 2.1216 kJ mol^{-1}. The value of ΔG^0 increases (Table 5) with rise in temperature, which indicates that adsorption is favored at higher temperatures. Both the thermodynamic parameters, ΔH and ΔG^0, provide support for the endothermic nature of the adsorption process.

CONCLUSIONS

The NCL waste material (coal dust) can be used as an effective
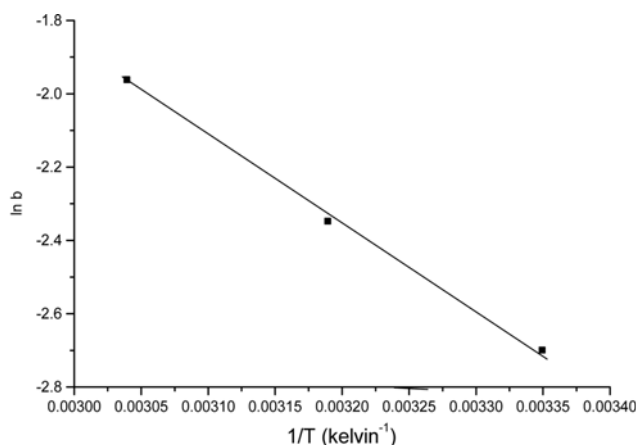
Fig. 8. Plot of ln b vs. 1/T for enthalpy change for the adsorption of Cr(VI) on carbon slurry at different temperatures. pH= 2.00, particle size=105 micron, agitation speed=125 rpm, contact time is 90 min.

adsorbent material for bringing the Cr(VI) concentration in wastewater to acceptable limits by maintaining the optimum conditions of pH, temperature and adsorbent dose. The carbonyl and carboxyl groups may be responsible for adsorption of Cr(VI) on NCL coal dust from aqueous solutions. The adsorption isotherm for the adsorption of Cr(VI) follows both the Langmuir and Freundlich isotherms. Thermodynamic parameters indicate the endothermic nature of adsorption process. The data obtained in the present study can be used for abatement of Cr(VI) concentration from wastewater using NCL waste material as the adsorbent.

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