Adsorptive Removal of Chromium(VI) from Aqueous Solution onto Fly Ash: Thermodynamic Study

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Abstract- **The objective of this study is to assess the uptake of hexavalent chromium Cr(VI) from aqueous solutions onto Fly ash. Fly ash samples were collected from Shri Ram fertilizers and Chemicals Ltd. (SRFC) Kota, Rajasthan. The study investigates the effect of temperature. Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$) were calculated. The $\Delta G°$ and $\Delta H°$ values for Cr(VI) adsorption on the fly ash showed the process to be spontaneous and endothermic in nature. The equilibrium data for the adsorption of chromium were analysed in the light of Langmuir and Freundlich isotherm models.**

Keywords: **Adsorption, batch method, langmuir, freundlich.**

I. INTRODUCTION

Heavy metal pollution of water has become a major environmental problem almost since the advent of agricultural and industrial revolution and today most water resources are still being contaminated with heavy metals released from domestic, industrial and other manmade activities (Khare & Singh, 2002; Hayat & Javed, 2008). The threat of toxic and trace metals in the environment is more serious than those of other pollutants due to their non biodegradable nature, accumulative properties and long biological half lives. It is difficult to remove them completely from the environment once they enter into it (Aderinola *et al*., 2009).

Chromium is essential to animals and human. Chromium in excess amounts can be toxic especially the hexavalent form. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials [1]. Chromium (Cr) besides lead, cadmium and copper is widely used for the production of colour pigments of textile dyes and is thus a common contaminant in textile factory effluents [2, 3, 4]. Chromium in its hexavalent form Cr(VI) is well known due to its health-related issues in humans including carcinogenic and mutagenic risks (Igwe and Abia 2006; Park and Jung 2001).

Fly Ash: Coal/Lignite based Thermal Power Generation has been the backbone of power capacity addition in the country [5]. Flyash is the term defined for the finely divided residues those results from the combustion of the ground coal. Primarily the flyash particles consist of Silica and Alumina; carbon and oxides of iron, calcium, magnesium, sulfur, titanium etc. being the secondary ingredients [6]. The chemical compositions of fly ash are high percentage of silica (61.1%), alumina (21.8%), Fe2O3 (4.69%), CaO (3.51%), SO3 (1.62%) [7, 8]. The location of the energy source, nature of fuel and size of the furnace determine the exact nature and quantity of these compounds [6]. Fly ash is one of the most abundant industrial waste materials and its major components make it as a potential material for the adsorption of heavy metal contaminants in water and wastewater [9]. The surface of fly ash is porous structure and it has a large specific surface area. Hence it can be used for the toxic metal ions, inorganic anions, organic compounds, and so on (Wang and Wu 2006).

As Shri Ram Fertilizers and Chemicals Ltd., Kota (SRFC) is located in Kota (Rajasthan). So, we used fly ash as an adsorbent for removal of Chromium.

II. MATERIAL & METHOD

The Batch test were carried out in 250 ml flask using fly ash as a sorbent. The fly ash samples were collected from the Shri Ram fertilizers & Chemicals Ltd., Kota (DCM). Chromium samples were prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in double-distilled water and used as a stock solution and diluted to the required initial concentration. A 1g fly ash was mixed with 100 ml of the aqueous solutions of various initial concentration (0.5mg/L, 1mg/L, 2mg/L, 3mg/L) of chromium (VI) in each flask. The stirring speed was kept constant at 120 rpm. The pH of the solution was measured with a HACH – pH meter. The effects of various parameters on the rate of adsorption process were observed by varying adsorbent concentration, initial Cr Concentration and pH of the solution. The solution volume (V) was kept constant. The measurements were made at the wavelength $\lambda = 540nm$,

which corresponds to maximum absorbance [10]. Using a mass balance, the concentrations of chromium (VI) at different time adsorbed in fly ash was calculated,

$q_t = \dfrac{(C_o - C_t)\ V}{M}$

Where q_t is the amount of chromium (VI) adsorbed onto the fly ash at time t, C_o is the initial concentration of chromium (VI), C_t is aqueous phase concentration of chromium (VI) at time t, V is the volume of the aqueous phase, M is the weight of fly ash.

III. RESULT AND DISCUSSION
A. TEMPERATURE VARIATION
To study the effect of this parameter on the uptake of Cr(VI) ions by fly ash, we selected the following temperature: 30˚, 40˚ and 50˚C. The Chromium concentration was maintained 2mg and adsorbent amount 1gm. The adsorption of Cr(VI) increased when temperature was increased from 30˚ to 50˚C (Fig 1).

The temperature also remarkably influenced the equilibrium metal uptake. The increase in the equilibrium sorption of Cr(VI) with temperature indicates that Cr(VI) ions removal by adsorption on fly ash favours a high temperature. This may be a result of increase in the mobility of the large Cr(VI) ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface [11]. Earlier studies [11] and [12] showed similar results with tea factory waste (TFW) zeolite prepared from raw fly ash (ZFA) respectively.
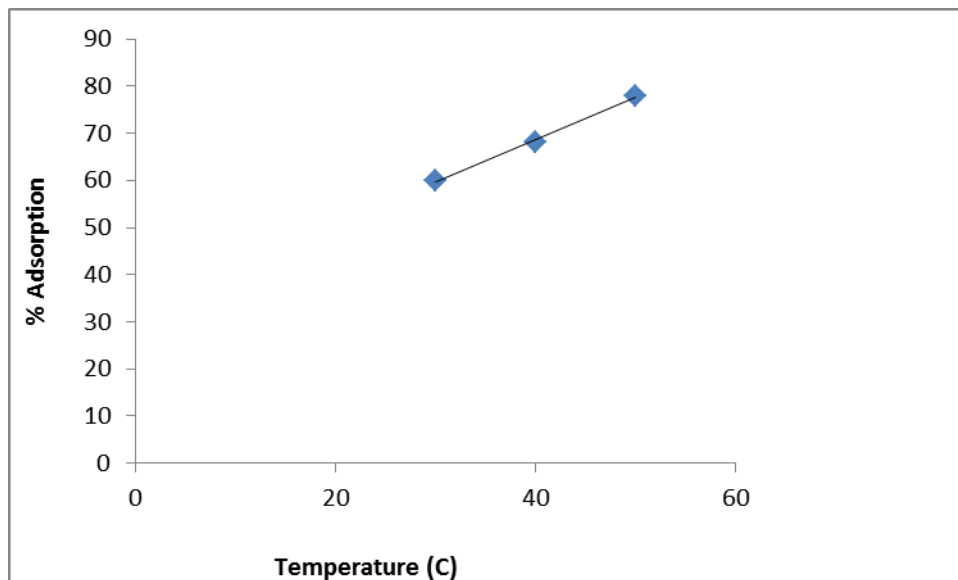

Figure 1: Effect of Temperature on adsorption of Cr (VI)

B. THERMODYNAMIC PARAMETERS
Thermodynamic parameters such as enthalpy change (ΔH˚), free energy change (ΔG˚)
and entropy change (ΔS˚) can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation.

$$\Delta G° = -RT \ln K_C \qquad\qquad (1)$$

where ΔG˚ is standard free energy change, K_C is the thermodynamic equilibrium constant without units, T is the absolute temperature in Kelvin, and R is the gas constant.

$$\Delta G° = \Delta H° - T\Delta S° \qquad\qquad (2)$$

The Gibbs free energy indicates the spontaneity of the adsorption process, where higher negative values reflect a more energetically favourable adsorption process. Values of ΔG˚ was found to be -1.020, -1.962, -3.399 KJ/mol for the temperature 30˚, 40˚ and 50˚C respectively. The negative ΔG° values obtained for various systems in this study confirm the feasibility of the adsorbent and spontaneity of adsorption [13]. The changes in enthalpy (ΔH˚) and entropy (ΔS˚) were determined from the slope and intercept of Vant Hoff's linear plots of ln K_C vs 1/T (Figure 2). The enthalpy change, ΔH˚, and the entropy change, ΔS˚, for the sorption processes are calculated to be 33.959 KJ mol^{-1}

and 0.1152 KJ mol^{-1} K^{-1} respectively. The positive values of ΔH^o indicate the endothermic adsorption process and the positive value of ΔS^o indicate an increased randomness at the solid- solution interface [14].
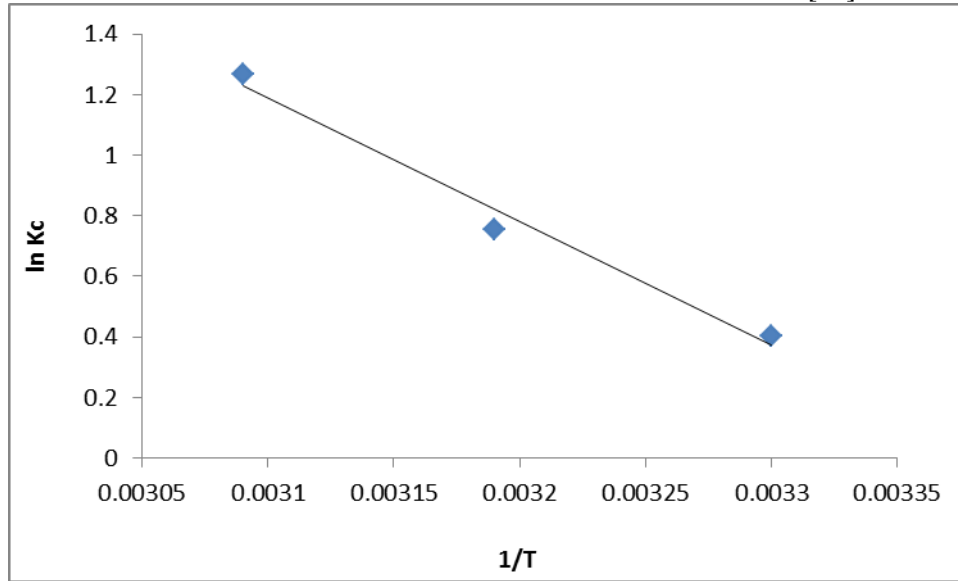

Figure 2: Plot of ln K_C vs. 1/T for Chromium(VI) adsorption

C. ADSORPTION ISOTHERMS

The adsorption equilibrium information is the most important part of information in understanding an adsorption process [12]. For solid–liquid adsorption system, the adsorption behavior can well be described by adsorption isotherm model (Tella *et al*., 2014). The adsorption isotherm can indicate the distribution of adsorbate molecules between the solid phase and the liquid phase at equilibrium. Equilibrium is said to be established when the concentration of adsorbate in bulk solution is in dynamic balance with that on the liquid adsorbate interface (Aksu, 2002). It is significant to understand the adsorption behavior in order to describe adsorption process using appropriate adsorption isotherm model. Therefore,
the distribution of Cr(VI) ions between the adsorbent and solution was determined by Langmuir and Freundlich adsorption isotherms by fitting the equilibrium adsorption data into
their respective isotherm equations [15].

(a) Langmuir Isotherm

Adsorption studies were carried out with a fixed initial adsorbent dose (1g) and varying adsorbate concentration, and applicability of the data to the Langmuir adsorption isotherm was tested. It was found that the data obtained fitted well into the linearised Langmuir adsorption isotherm, which is given by

$$\frac{Ce}{Qe} = \frac{1}{Qo\,b} + \frac{Ce}{Qo} \qquad\qquad (3)$$

where Ce is the equilibrium concentration and qe is the amount adsorbed per gram of adsorbent at equilibrium; Qo and b are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of Qo and b were calculated from the slope and intercept of the graph (Fig. 3) [11].
The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L, which describes the type of isotherm:

$$R_L = \frac{1}{1 + bCo} \qquad\qquad (4)$$

where Co is the initial concentration of Cr(VI). Thus, R_L is a positive number whose magnitude determines the feasibility of the sorption process. The process is irreversible if $R_L = 0$, favorable if $0 < R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$ [17]. The value of dimensionless separation factor R_L obtained in between 0 to 1, so we can say that the Langmuir isotherm model is best suited.
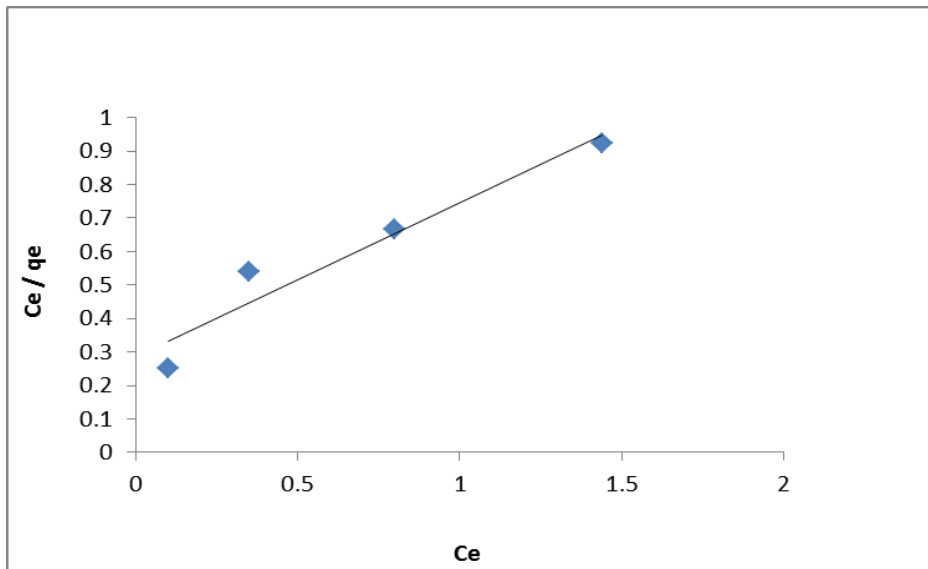
Figure 3: The linear Langmuir isotherm plot for adsorption of Cr(VI)

(b). Freundlich Isotherm

The adsorption data of chromium is also analysed by a Freundlich model. The logarithmic form of the Freundlich model is given by the equation (5):

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg l^{-1}), and K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively [18].
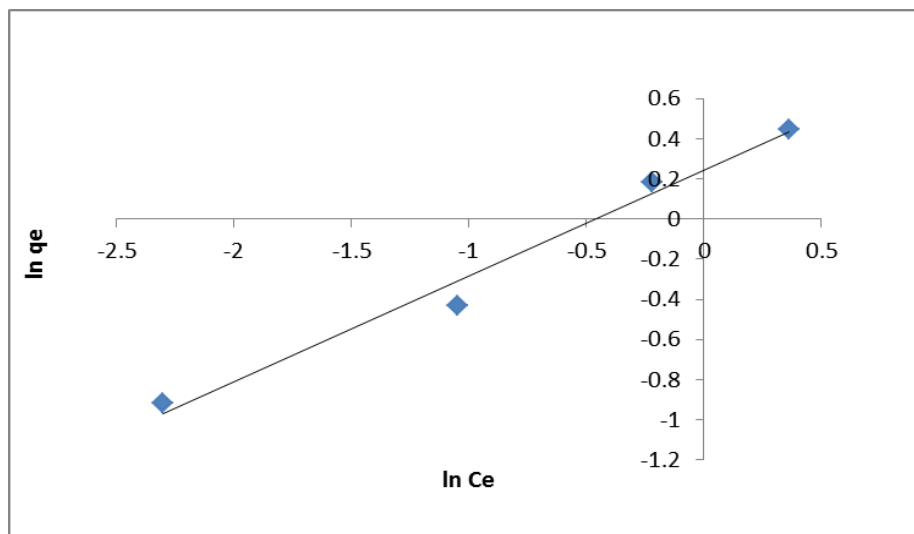

Figure 4: The linear Freundlich isotherm plot for adsorption of Cr(VI)

IV. CONCLUSION

Fly ash has been shown to be an effective adsorbent for removal of Cr(VI) from aqueous solutions. Increase in percentage of adsorption with increase in temperature indicates that the process is endothermic in nature and so high temperatures favour the adsorption process. Thermodynamic parameters showed that the sorption of Cr(VI) ions onto Fly ash was feasible, spontaneous and endothermic under studied conditions. Adsorption follows both Langmuir and Freundlich adsorption isotherms.

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