

# Removal of Chromium(VI) from Aqueous Solution by Fly Ash: Thermodynamic and Kinetic 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. The study also investigates the effect of temperature. Thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated. The  $\Delta G^\circ$  and  $\Delta H^\circ$  values for Cr(VI) adsorption on the fly ash showed the process to be spontaneous and endothermic in nature. The adsorption data follow the Langmuir model better than the Freundlich model and the adsorption equilibrium was described well by the Langmuir isotherm model.

**Keywords:** Adsorption, batch method, point of zero charge, kinetics.

## 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 man-made 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). With increased use of a wide variety of metals in industries and in our daily life, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other

within the food chain (Sadasivan & Tripathi, 2001). Chromium is one of the toxic heavy metals (Kotaś and Stasicka 2000). The toxicity of chromium is related to its valence, and hexavalent chromium is more toxic than trivalent chromium, easily absorbed, and accumulated in human body. Trivalent chromium and hexavalent chromium can be converted into each other. The sources of chromium pollution include chromium ore processing, metal surface treatment, leather tanning, dyeing, and other wastewater discharges.<sup>1</sup> The discharge limit for chromium from industries is less than 1 mg/L. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L.<sup>2</sup>

### **Fly Ash**

Coal fly ash is an industrial by-product generated during the combustion of coal and it is the main solid waste discharged from coal-fired power stations. With the development of the power industry, the fly ash emissions of coal-fired power plants increased year by year (Scheetz and Earle 1998; Wang *et al.* 2014). Fly ash has great potential in water treatment (Blissett and Rowson 2012; Keng *et al.* 2014) because of its low cost, unique physical, and chemical properties. Fly ash is a kind of porous loose solid aggregate, and its main components are Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, CaO, and so on.<sup>1</sup> Fly ash has a good adsorption effect on cations, especially heavy metal ions (Cho *et al.* 2005). The adsorption characteristics of heavy metals using various particle sizes of bottom ash were reported by Shim *et al.*<sup>3</sup> In another study, fly ash from a coal-fired power plant was used for the removal of Zn(II) and Ni(II) from aqueous solutions; it is proved to be effective as activated carbon at high dosages.<sup>4</sup>

As Kota Super Thermal Power Station (KSTPS) is situated 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 Kota Super Thermal Power Station, Kota. Chromium samples were prepared by dissolving a known quantity of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) 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 contact time, adsorbent concentration, initial Cr Concentration and pH of the solution. The solution volume (V) was kept constant. The measurements were made at the wavelength  $\lambda = 540\text{nm}$ , which corresponds to maximum absorbance<sup>5</sup>. Using a mass balance, the concentrations of chromium(VI) at different time adsorbed in fly ash was calculated,

$$q_t = \frac{(C_0 - C_t) V}{M}$$

Where  $q_t$  is the amount of chromium(VI) adsorbed onto the fly ash at time  $t$ ,  $C_0$  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.

### POINT OF ZERO CHARGE

The pH at which the sorbent surface charge takes a zero value is defined as point of zero charge (pHpzc). At this pH, the charge of the positive surface sites is equal to that of the negative ones. The knowledge of pHpzc allows one to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pHs higher than pHpzc, sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pHpzc, solid surface is positively charged and could interact with negative species.<sup>6</sup> The experiment to determine the point of zero charge of the fly ash was carried out by the pH drift method and it was obtained at 5.8

### III. 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.<sup>7</sup> Earlier studies<sup>8</sup> and<sup>7</sup> showed similar results with zeolite prepared from raw fly ash (ZFA) and tea factory waste (TFW) respectively.

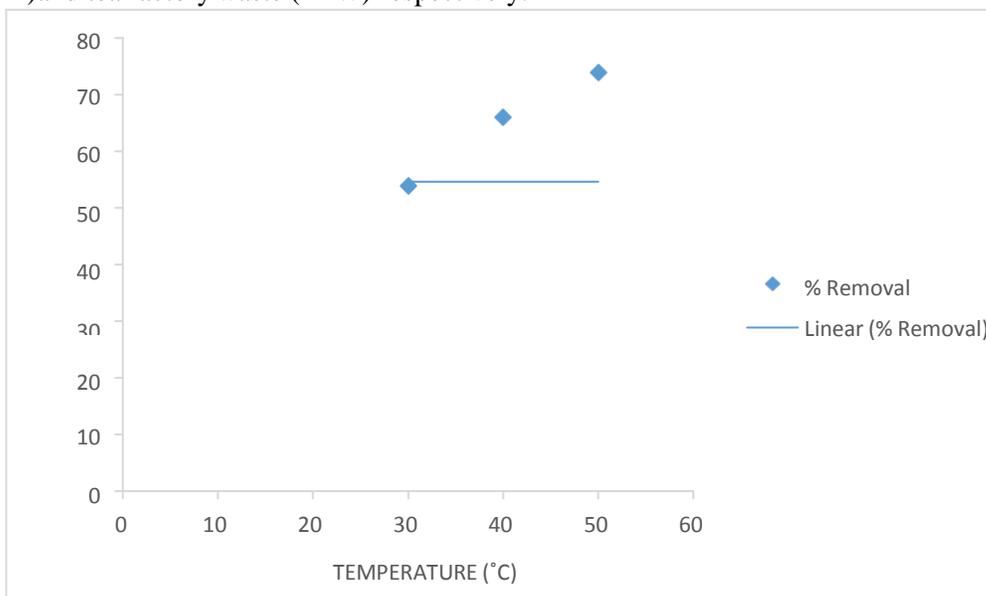


Figure 1: Effect of Temperature on adsorption of Cr (VI)

#### IV. THERMODYNAMIC PARAMETERS

Thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation.

$$\Delta G^\circ = -RT \ln K_C \quad (1)$$

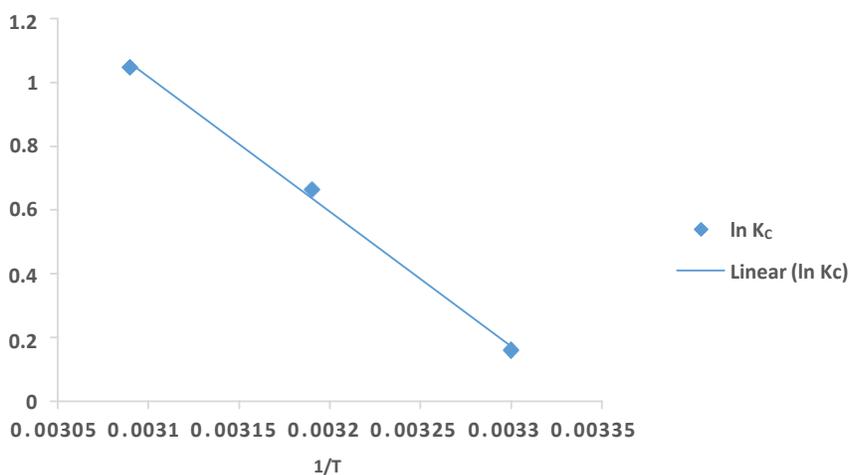
where  $\Delta G^\circ$  is standard free energy change,  $K_C$  is the thermodynamic equilibrium constant without units,  $T$  is the absolute temperature in Kelvin, and  $R$  is the gas constant.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

The distribution coefficient ( $K_C$ ) values increased with temperature, indicating the endothermic nature of adsorption. A plot of Gibbs free energy change,  $\Delta G^\circ$ , versus temperature,  $T$  (K); was found to be linear. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of the plots. The thermodynamic parameters enthalpy change,  $\Delta H^\circ$ , entropy change,  $\Delta S^\circ$ , are shown in Table 1. The enthalpy change,  $\Delta H^\circ$ , and the entropy change,  $\Delta S^\circ$ , for the sorption processes are calculated to be 35.126 KJ mol<sup>-1</sup> and 0.1174 KJ mol<sup>-1</sup> K<sup>-1</sup>, respectively. Values of  $\Delta G^\circ$  was found to be -0.403, -1.725 KJ/mol and -2.809 kJ/mol for the temperature 30°, 40° and 50°C respectively. The negative values of  $\Delta G^\circ$  at various temperatures indicate the spontaneous nature of the adsorption process. The positive value of  $\Delta S^\circ$  indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process. In addition, the positive value of  $\Delta H^\circ$  indicates that the adsorption is endothermic<sup>7</sup>.

**Table 1: Van't Hoff equation and calculated values of  $\Delta H^\circ$  and  $\Delta S^\circ$  of Cr(VI) adsorption**

Van't Hoff Equation	Equation of line with correlation coefficient	Slope	Intercept	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (KJ mol <sup>-1</sup> K <sup>-1</sup> )
$\ln K_C = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R$	$Y = -4224.9x + 14.115R^2 = 0.9974$	-4224.9	14.115	35.126	0.1174



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

## V. ADSORPTION ISOTHERMS

The adsorption equilibrium information is the most important part of information in understanding an adsorption process.<sup>8</sup> 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<sup>9</sup>.

### [A] 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 (3)

$$\log q_e = \log KF + 1/n \log C_e \quad (3)$$

where  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mg l}^{-1}$ ), and  $KF$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively<sup>10</sup>.

### [B] 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

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

where  $C_e$  is the equilibrium concentration and  $q_e$  is the amount adsorbed per gram of adsorbent at equilibrium;  $Q_0$  and  $b$  are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of  $Q_0$  and  $b$  were calculated from the slope and intercept of the graph (Fig. 3).<sup>11</sup>

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor,  $RL$ , which describes the type of isotherm:

$$RL = \frac{1}{1 + bC_0} \quad (5)$$

where  $C_0$  is the initial concentration of Cr(VI). Thus,  $RL$  is a positive number whose magnitude determines the feasibility of the sorption process. The process is irreversible if  $RL = 0$ , favorable if  $RL < 1$ , linear if  $RL = 1$  and unfavorable if  $RL > 1$ .<sup>12</sup> The value of dimensionless separation factor  $RL$  obtained in between 0 to 1, so we can say that the Langmuir isotherm model is best suited.

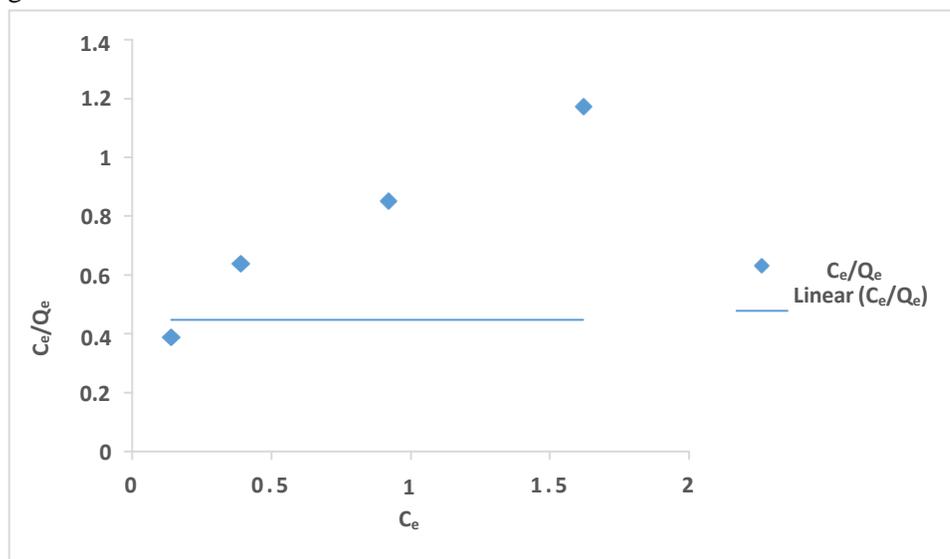


Figure 3: The linear Langmuir isotherm plot for adsorption of Cr(VI)

## VI. KINETICS

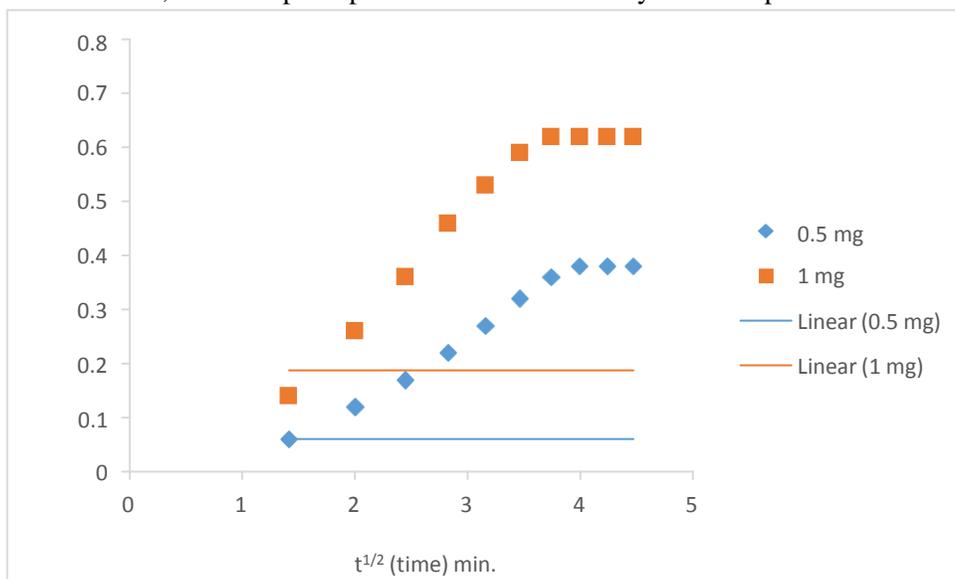
The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to determine the mechanism of Cr(VI) adsorbed onto Fly ash, several commonly used adsorption kinetic models were employed to discuss the controlling mechanism.<sup>13,14</sup> Several kinetic models such as zero order, first order, second order, pseudo-first-order, pseudo-second-order, intra-particle diffusion and elovich equation model have been applied to find out the adsorption mechanism.<sup>8</sup> The intraparticle diffusion model is used to explain diffusion mechanism of adsorption process.<sup>15</sup> The intraparticle diffusion model can be described as follows.<sup>16</sup>:

$$qt = K_{id} (t)^{1/2} + C \quad (6)$$

where  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{h}^{-1/2}$ ) and  $C$  is the intercept. The value of  $C$  relates to the thickness of the boundary layer. The larger  $C$  implies the greater effect of the boundary layer. According to Eq. (6), if adsorption mechanism follows the intraparticle diffusion model, the plot of  $qt$  against  $t^{1/2}$  should show linear relationship. Slope

$K_{id}$  and intercept  $C$  will be obtained by linear fitting analysis. The plot of  $qt$  versus  $t^{1/2}$  is given in Fig.4. The value of rate constant of Morris–Weber transport,  $K_{id}$ , calculated from the slope of the linear plot are shown in Fig. 4. The rate constant  $K_{id}$  was calculated from the slope of the straight line with a correlation factor.<sup>8</sup>

In applying all the kinetic models the value of  $R^2$  was obtained maximum and the standard error of estimation (SEE) value was minimum for the intra-particle diffusion model. So it can be seen, the adsorption process was controlled by the intra-particle diffusion model.



**Figure 4: Intraparticle diffusion equation plot for Chromium(VI)**

## VII. 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. The adsorption data fitted well to the Langmuir adsorption isotherm and the intra-particle diffusion model. The point of zero charge (PZC) of fly ash was at 5.8.

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