Research Paper

Equilibrium Isotherm, Kinetic and Thermodynamic Studies of Cr (VI) onto Soil, Contaminated from Waste water of Textile Industry

* **Vijayvergiy Priya[1], Saxena Shweta[2]**
Department of Chemistry, M. B. P.G. College, University of Kota, Kota, INDIA

Abstract: *The aim of this work was to study the adsorption of Chromium on dye contaminated soil and to give the best suited kinetic model, adsorption isotherm and to evaluate thermodynamic parameters, which are helpful to understand the interaction of chromium with soil. Adsorption studies have been done using a batch adsorption technique. The change in Cr (VI) concentration due to adsorption was determined by 1,5 Diphenylcarbazide spectrophotometric method. The measurements were made at the wavelength λ=540nm. The concentrations of chromium (VI) at different time adsorbed in soil solids were calculated. Soil before adsorption and after adsorption was characterized using SEM results revealed that adsorption rate increases in increasing initial chromium concentration and temperature of adsorption medium. The positive values of ΔG^0 at all studied temperatures indicate that adsorption process is endergonic (non spontaneous). The values of ΔH^0 and ΔS^0 is found to be 14661.97 J/mol and 44.760 J/mol K respectively. The Langmuir and Freundlich isotherm were used to describe the adsorption equilibrium studies. The value of r^2 for Langmuir and Freundlich is 0.517 and 0.985 respectively. From kinetic experiments, it was obtained that the sorption process followed the intraparticle diffusion model.*

Keywords: Chromium, soil, kinetic model, thermodynamics, isotherms.

Introduction

Excessive quantities of Cr compounds are discharged in liquid, solid, and gaseous wastes into the environment and can ultimately have significant adverse biological and ecological effects [1]. Chromium is commonly found in the waste effluents from electroplating, metallurgical, tannery, and textile industry [2,3]. In the natural environment Cr occurs in different oxidation states ranging from II to VI, with Cr(III) and Cr(VI) as the most abundant species. Cr(III) is a required nutrient, whereas Cr(VI) has toxic effects [4,5]. Cr(VI) is approximately 100 times more toxic and 1000 times more mutagenic than Cr(III), which is known to be indispensable for animal nutrition [6, 7, 8].

Hexavalent Chromium exists as exceedingly soluble and highly toxic chromate ions, $Cr_2O_7^{2-}$ or $HCrO_4^-$, which can be contaminate aqueous ecosystems, causing serious environmental damage. The discharge of chromium in the water bodies is regulated to approximated 0.05 mg/dm^3, whereas that total of chromium is regulated at less than 2.0 mg/dm^3 [9, 10]. In the array of heavy metal ions, chromium is of special interest because it is an essential nutrient as well as a carcinogen[11]. Dietary deficiency of chromium (III) has found to cause faulty sugar metabolism [12], although in combination with insulin, it removes glucose from the blood and also plays a key role in fat metabolism[13]. On the other hand, chromium (VI) is lethal to human system because of its mutagenic and carcinogenic properties [14].

The maximum permissible limits of Cr(VI) in inland surface and drinking water are 0.1 mg/L and 0.05 mg/L, respectively [15, 16]. In order to comply with

this limit, it is essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels [17]. In Bhilwara, there are many Textile industries and according to study based on NGCM programme in Rajasthan certain areas of Bhilwara having Cr up to 160 to 190 ppm [18]. The objective of this study was to investigate the Cr (VI) sorption and migration into a soil which is contaminated by dye industry and find out best suited kinetic model and adsorption isotherms for sorption of Cr (VI) on soil.

Material and methods
Sample collection and treatment
The soil samples were collected from the process house, IV phase, RIICO industrial area, BHILWARA from a depth of 0-15 cm. The soil samples were dried in air for about three weeks. After drying the soil was sieved in order to obtain different particle size distribution (100-300 BSS).

Batch adsorption Experiments
The Batch tests were carried out in 250 ml flask using a contaminated soil as a sorbent. A stock solution of Cr (VI) is prepared by dissolving 2.8g of potassium dichromate $(K_2Cr_2O_7)$ in 1000 ml double-distilled water and this solution is diluted as required to obtain solution containing different initial concentration (5-50mg/L). A 2g soil was mixed with 100ml of the aqueous solutions of various initial concentrations (5mg/L, 10mg/L, 20mg/L, 30mg/L and 50mg/L) of chromium (VI) in each flask.

The stirring speed was kept constant. The flasks were shaken at a constant rate, allowing sufficient time for adsorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with heavy metal ions over the course of the experiments. The study was performed at room temperature to be representative of environmentally relevant condition. The effects of various parameters on the rate of adsorption process were observed by varying initial Cr Concentration, and Temperature of the solution. The solution volume (V) was kept constant. The change in Cr (VI) concentration due to adsorption was determined spectrophotometrically according to standard methods [19]. The measurements were made at the wavelength λ=540nm, which corresponds to maximum absorbance [20]. A purple-violet colored complex was developed in the reaction between Cr (VI) and 1, 5-diphenylcarbazide in acidic condition. Using the equation (1), the concentrations of chromium (VI) at different time adsorbed in soil solids were calculated,

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

(1)

Where q_t is the amount of chromium (VI) adsorbed onto the natural soil 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 natural soil.

Characteristics of Soil
The tests were Performed with the help of the CEG test house and research centre, Jaipur and RARI, Durgapura Jaipur and given in Table 1.

Table 1. The Characteristics of the soil

S. No.	Parameters	Soil
1	pH	8.2
2	Conductivity(dS/m)	0.21
3	Organic Carbon	0.18 %
4	Phosphate (per Kg)	24
5	Potash (per Kg)	254
6	Clay Content	3.67 %
7	Sand Content	72.57 %
8	Silt Content	23.76 %

Results and Discussion
Effect of initial Cr (VI) concentration
The effect of different initial concentration of Chromium (VI) onto soil is presented in figure 1.
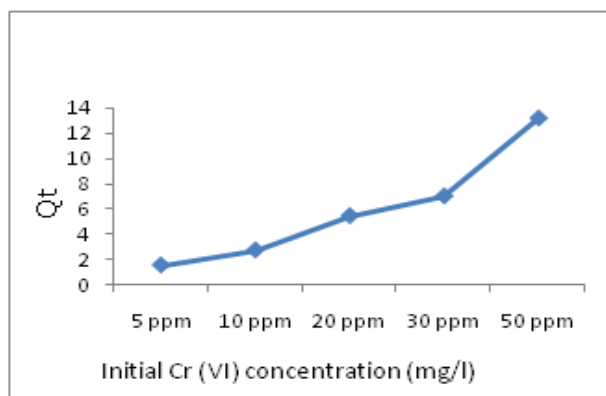
Figure 1: Effect of initial Cr (VI) concentration on adsorption of Cr (VI) (conditions: amount of soil 2gm/100ml, volume of sorption medium 100 ml, particle size , 100 BSS, temp: 30^{0}C

Five different concentrations of 5, 10, 20, 30, and 50 mg/l for Cr (VI) were selected to investigate the effect of initial concentration of Cr (VI) onto soil. The temperature was maintained at 30°C and the amount of Soil 2 gm. It was found that the adsorption increases with increase in initial concentration of Chromium (VI). This may be due to the availability of more number of Cr (VI) ions in solution for adsorption to the available sites [21].

Kinetic models

Several kinetic models have been applied to examine the controlling mechanism of chromium adsorption.The pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model and elovich equation were used for testing dynamic experimental data at 2g of soil and the different initial concentrations of Cr (VI) were 5, 10, 20, 30 and 50 mg L^{-1} at 30^{0}C temperature. The pseudo-first-order kinetic model of Lagergren is given as [22].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1^{'}}{2.303}t \qquad (2)$$

where qe and qt (mg g-1) are the amount of Cr (VI) adsorbed at equilibrium and at time t (min), respectively, and K_1 (min^{-1}) is the adsorption rate constant.

The pseudo-second-order kinetic model can be expressed as [23].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where $k2$ (g mg^{-1} min^{-1}) is the rate constant of second order equation.

The intraparticle diffusion equation [24] can be written by following equation

$$q_t = K_{id}t^{1/2} + C \qquad (4)$$

Where qt is the amount of dyes adsorbed onto adsorbent at various times t (mg/g), C is
the intercept and K$_{id}$ is the intraparticle diffusion rate constant (mg g^{-1}min^{-1}).
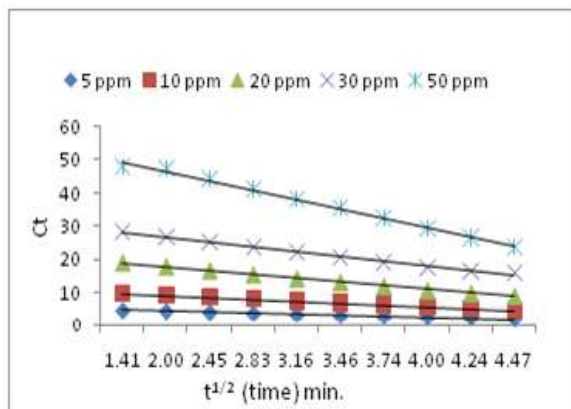
The Elovich model equation is generally expressed as [25].
:

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \times t^{1/2} + I \qquad (5)$$

Where α is the initial adsorption rate (mg·g^{-1}·min^{-1}), β is the desorption constant (g·mg^{-1}) during any one

experiment. On simplification equation becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (6)$$

Figure 2: Intraparticle diffusion model for adsorption of Cr(VI) onto soil

If Cr(VI) adsorption fits the Elovich model, a plot of qt vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$.

The calculated values of regression coefficient (r^2) of different kinetic models are presented in the Table 2. The correlation coefficients for pseudo-first-order kinetics are higher than that for the pseudo-second order kinetics. This suggests that the present system can be represented better by the pseudo-first-order model.

The plot of qt verses t$^{1/2}$ for the intraparticle diffusion for the adsorption of Cr(VI) (Figure 2) has been tested to obtain the diffusion rate parameters. The values of correlation coefficient of different kinetic models are given in Table 2. The correlation coefficient for the intraparticle diffusion are between 0.9579 and 0.9835 which are higher than the pseudo second order kinetics , so indicates that intra particle diffusion model is best fits in the present system.

Effect of Temperature

The effect of temperature on the sorption of Cr(VI) was investigated at different temperature 30, 35, 40 and 45°C at pH 2.0 and 2 g of soil into 250mL of conical flask containing 100ml of 5 ppm of Cr(VI) solution. The adsorption of Cr(VI) at different temperature shows an increase in the adsorption capacity when the temperature is increased as given in Figure 3. This indicates that the adsorption reaction is endothermic in nature.

The predicted cause for improvement in adsorption with increase in temperature may be due to the formation of new binding sites on and near the surface of adsorbent as a result of breaking of some internal bonds. Increase in the kinetic energy of adsorbate was also thought as another possible reason for the increase in adsorption that facilitated diffusion of adsorbate within pores of adsorbent [26].

Table 2: R² values of different kinetic models

Kinetic model name	R²				
	5 ppm	10 ppm	20 ppm	30 ppm	50 ppm
Pseudo first order	0.9456	0.9119	0.9074	0.8184	0.8938
Pseudo second order	0.4145	0.7327	0.3760	0.2598	0.4651
Intra particle diffusion	0.9787	0.9756	0.9835	0.9863	0.9579
Elovich equation	0.9068	0.8999	0.9160	0.9269	0.8674

Table 3. Values of standard Gibb's free energy of adsorption at different temperature

Temperature (^{0}C)	Temperature T (K)	K_c	$\Delta G^0 = -RT \ln K_c$ (J/mol)
30	303 K	0.170241	1077.179
35	308 K	0.212251	779.2794
40	313 K	0.250751	639.7319
45	318 K	0.319672	380.005

Table 4: Van't Hoff Equation and calculated values of ΔH^0 and ΔS^0

Van't Hoff Equation	Slope	Y Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
$\ln Kc = -\dfrac{\Delta G^0}{RT} = -\dfrac{\Delta H^0}{RT} += -\dfrac{\Delta S^0}{R}$	-1760.83	5.392578	14661.9737	44.760250
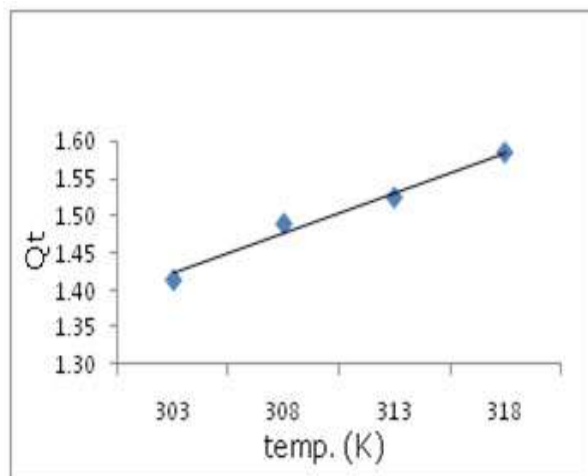
Figure 3: Effect of temperature on Cr(VI) sorption onto soil, (conditions: initial concentration of Cr(VI), 5ppm, amount of soil, 2gm/100ml, volume of sorption medium, 100ml)

Calculation of thermodynamic parameters
The Standard Gibb's Free Energy was evaluated by following equation:

$$\Delta G^0 = -RT \ln K_c \qquad (7)$$

Where R is the universal gas constant (J mol^{-1} K^{-1}), Kc is the thermodynamic equilibrium constant, and T is temperature of the system in Kelvin The equilibrium constants K_c was evaluated at each temperature using the following relationship

$$K_c = \frac{C_{Ae}}{C_e} \qquad (8)$$

Where C_{Ae} is the amount adsorbed on solid at equilibrium and C_e is the equilibrium concentration. The estimation of standard Gibb's free energy of adsorption at different temperature is shown in Table 3 .The positive values of ΔG^0 at all studied temperatures indicates that adsorption process is endergonic (non spontaneous).

The plot of ln K_c versus 1/T for determining the values of ΔH^0 and ΔS^0, given in Figure 4. The values of ΔH^0 and ΔS^0 is found to be 14661.97 J/mol and 44.76 J/mol K respectively, given in Table 4. The positive value of ΔH^0 again confirms that the adsorption is endothermic. The positive value of ΔH^0

and ΔS^0 tells the adsorption reactionwas unfavorable for enthalpy but favorable for entropy. The positive value of ΔS^0 revel increased randomness at the solid/solution interface during adsorption and the system became more disordered through adsorption process.

Isotherms

An adsorption isotherm was used to characterize the interaction of sorbent molecule with the adsorbent material. Sorption equilibrium is usually described by an isotherm equation whose parameter expresses the surface properties and affinity of the sorbent at fixed temperature, and initial metal concentration. Langmuir sorption isotherm is well known of all isotherms describing sorption [27] and it has been applied in many sorption processes [28]. It is represented as:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q_m b} + \frac{C_{eq}}{Q_m} \qquad (9)$$
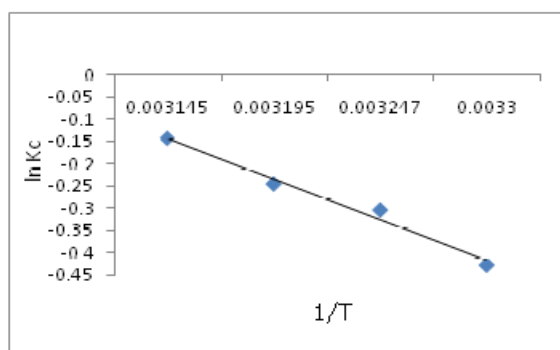
**Figure 4: Plot of ln K$_c$ versus ln 1/T**

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/L), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of Ceq/ Qeq vs. Ceq suggest the applicability of the Langmuir isotherms. The values of Qm and *b* were calculated from slope and intercepts of the plots, which are listed in Table 5.

The well known linear form of Freundlich model is expressed by:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \times \ln C_e \qquad (10)$$

where Ce is the equilibrium concentration of the adsorbate (mg/L) and qe is the amount of adsorbate

adsorbed per unit mass of adsorbent (mg/g). K_F(L/mg) and 1/n are Freundlich constants representing the adsorption capacity and intensity of adsorption, respectively. The values of K_F and n were obtained from the slope and intercept of the plot of log q_e verses log C_e and are given in Table 5. The value of n is greater than unity, indicating that Cr (VI) ions were favourably adsorbed on the activated carbons investigated. Results revealed that Freundlich adsorption isotherm was the best model for the metal ions adsorption onto soil with R^2 of 0.985.
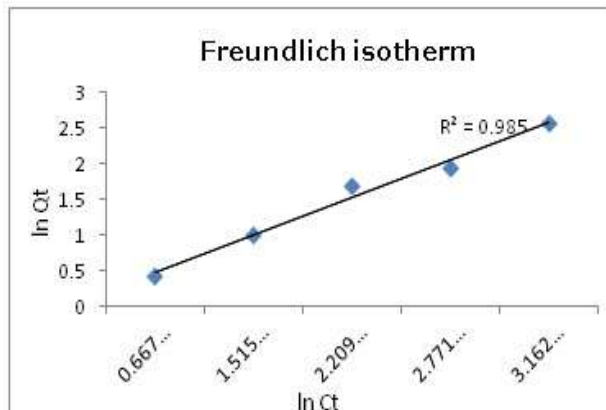
Figure 5: Freundlich isotherm for Cr(VI) adsorption onto soil

Conclusion

The result indicates that the adsorption increases with increasing initial chromium concentration and temperature. The positive value of ΔH confirms that the adsorption is endothermic. The positive value of ΔH and ΔS tells the adsorption reaction was unfavourable for enthalpy but favourable for entropy.

Among the kinetic models, the intra particle diffusion model was considered the best to explain the behavior of the adsorption process because the average R^2 of intra particle diffusion model is the highest among other models (pseudo first order average R^2=0.8954, pseudo second order average R^2= 0.4496, Elovich equation R^2 = 0.9034, intra particle diffusion average R^2=0.9034). Freundlich isotherm is best fits among Langmuir and Freundlich. The present study will helpful to understand the parameters which affect the migration of Chromium in the soil of contaminated area.

Rajasthan, RARI Durgapura Jaipur and CEG Test House and Research Centre for helping in soil analysis.

Table 5: Table 5 Values of Langmuir and Freundlich Constants

Langmuir		
b (L/mg)	q_e (mg/g)	R^2
0.1306	6.135	0.517
Freundlich		
K_f (mg/g)(L/mg)$^{-1/n}$	n_f	R^2
0.895	1.9011	0.985

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