

Adsorption of Chromium (VI) From Aqueous Solution by Activated Carbon- TiO₂ Nanocomposite

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ABSTARCT: Activated carbon was prepared from Typha AngustataL. It was characterized by XRD, SEM and IR .The Effect of various parameters such as P^H, adsorbent dosage, contact time, Initial concentration and temperature was studied. Based on linear regression analysis, The data obtained from the batch studies showed a good compliance with the Langmuir, Freundlich, Tempkin and D-R models. The studies showed that the activated carbon can be used as a good adsorbent for the removal of hexavalent chromium from aqueous solution.

KEYWORDS: Activated carbon- TiO₂Nanocomposite, adsorption, kinetics, Langmuir and Freundlich isotherm, hexavalent chromium.

I.INTRODUCTION

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr (III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent [1]. Due to its high solubility, Cr (VI) is the most hazardous, since it can accumulate in the food chain and cause several ailments [2,3].

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction, and evaporation, etc. [4]. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium (VI). Among all these, adsorption is the most promising technique and a feasible alternative[5].

A variety of materials have been tried as adsorbents for Cr (VI) and a number of studies have been reported using adsorbents like granular activated carbon [2] Soya cake [6], rubber tyres and sawdust [8], activated sludge [9], unmodified natural clay [7]lingocellular substrate[10], fly ash [11], rice husk based activated carbon [12], etc. Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [13, 14].

In addition information concerning the adsorption of chromium onto TyphaAngustata.L has not been reported. In view of the health problems caused by Cr (VI), the present study was performed to evaluate activated carbon as adsorbents for the removal of Cr(VI) from polluted water by systematic evaluation of the parameters involved such as Chromium concentration. Furthermore, the Freundlich and Langmuir adsorption isotherms were applied to study adsorption and to calculate isotherm parameters.

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II. MATERIALS AND METHODS

A. PREPARATION OF ACTIVATED CARBON: In the present study, Typha Angustata L flowers were collected from the perundurai, at Erode (Dt) in Tamilnadu. They were cut into small pieces and dried for 25 days. The flowers were dried and burnt in the muffle furnace at 450-500°C and kept it for half an hour. The collected carbonized material was ground well and sieved to a smaller particle size. Activated carbon has been stored in plastic vessels for the further experiment. The sample was sieved into a smaller particle size of 0.15 to 0.25 mm and was used.

B. PREPARATION OF Ac- TiO₂-NC: Activated carbon (3g) was allowed to swell in 15 ml of water-free alcohol and stirred for 2 hours at 25°C to get a uniform suspension. At the same time, the titanium dioxide (3g) was dispersed into water-free alcohol 15 ml then the diluted titanium dioxide was slowly added by dropping it into the suspension of AC and stirring continued for another 5 hours at 25°C. Then 5 ml alcohol mixed with 0.2 ml deionized water was added slowly and stirring continued for another 5 hours at 25°C. The suspension was then kept overnight for 10 hours at room temperature and the precipitate obtained was carefully dehydrated in a vacuum oven for 6 hours at 80°C to a characteristic of the Ac- TiO₂-NC were determined.

C. ADSORBATE SOLUTION: A stock solution of Cr (VI) was prepared in 1000 ml deionised water using 2.8300 g dried K₂Cr₂O₇. The working solution was obtained by diluting the stock solution with deionised water, and P^H was adjusted to the desired values according to the following experimental design with 1M HCl and 1M NaOH solution. Chromium ion concentrations were determined at characteristic wave length (λ_{max} = 540 nm) with a double beam UV- visible spectrophotometer.

D. CHARACTERIZATION OF ADSORBENT: Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of pure activated carbon and that of AC – TiO₂ Nano composition. Fig 1(a&b).

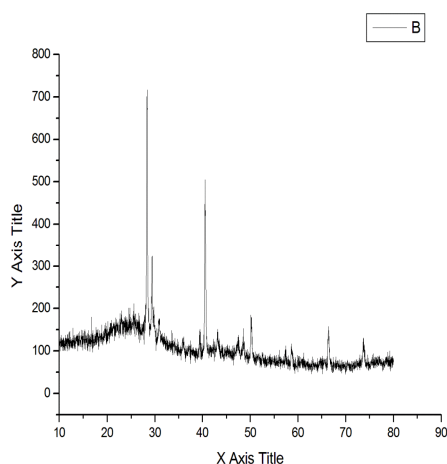


Figure 1(a). Carbon

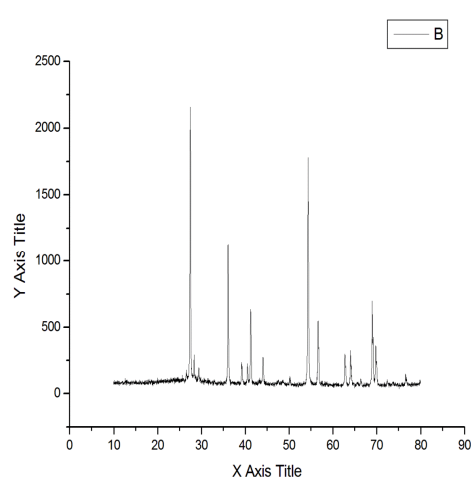


Figure 2(b). carbon+TiO₂

Show characteristic peaks at 28° and 30°. Which confirm the presence of AC – TiO₂ phase in the Nano composite.

The surface morphology of the adsorbent was visualized using scanning electron microscopy (SEM) figure 2(a&b). The diameter of the composite ranges from 10 μm to 1 μm.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 10, October 2016

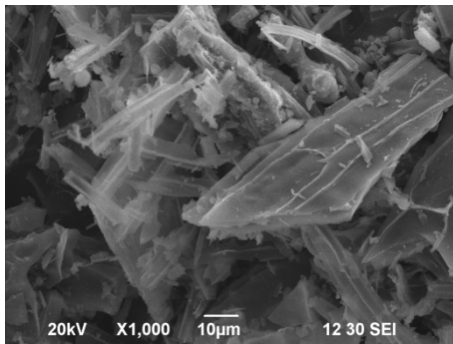


Figure 2 (a). Carbon

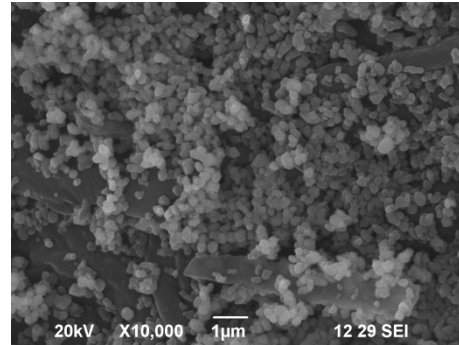


Figure 2 (b) AC-TiO₂ - NC

FT-IR spectroscopy: The absorption bands are due to the stretching and bending vibration of the group. The frequency of carbon peak 617.22cm^{-1} and TiO₂ peak 655.80cm^{-1} .

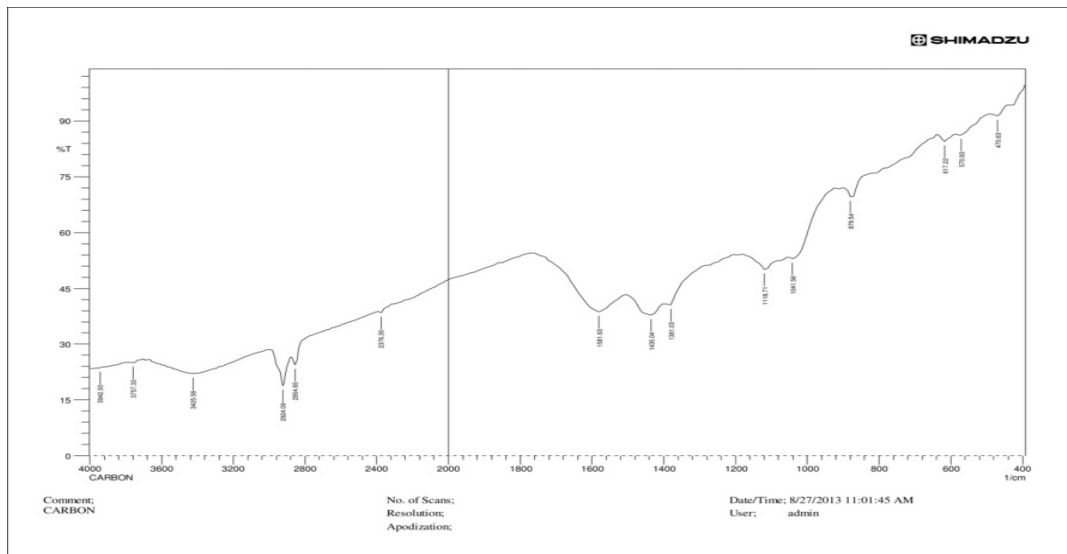


Figure 3 (a) Carbon

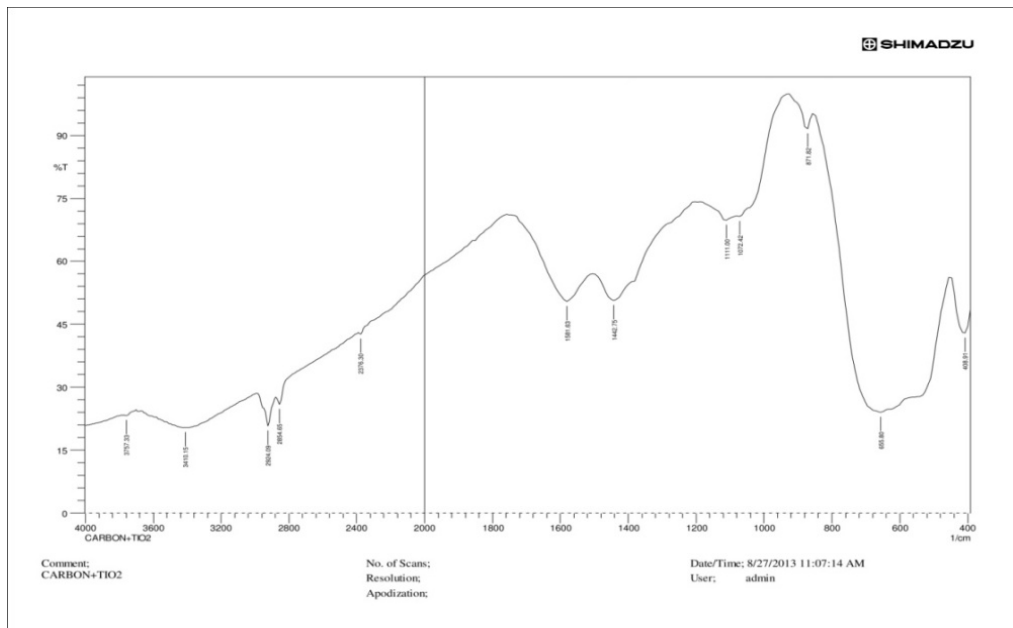


Figure 3 (b).Carbon+TiO₂.

III. BATCH ADSORPTION STUDIES

Batch adsorption experiments were also performed by agitation 0.1g of the adsorbent with 50ml of chromium solution the P^H containing different initial concentration form 10 to 40mg/L at 30°C. After the established contact time (2h) was attained, the suspension was filtered, and supernatant was analyzed for the metal concentration of 10 to 40mg/L and the adsorbent dosage of 0.1g. The pH values was adjusted in the range of 4-9 by using dil. HCl and NaOH solution. Experiments were carried out by varying the adsorbent amount from 0.1 to 1.0g with Cr(VI) concentration ranging from 10 to 40mg/L. The concentration of Cr(VI) in the solution was determined spectrophotometrically by developing a purple-violet colour with 2 drops of phosphoric acid and 1,5-diphenyl carbazide in acidic solution as complexing agent. The absorbance of the purple-violet colored solution is read at 540nm.[15]

The percentage removal of metal and amount of metal adsorbed on AC- TiO₂ -NC was calculated by equation (1) and (2) respectively.

$$\% \text{ removal} = \frac{100[C_0 - C_e]}{C_e} \text{-----(1)}$$

$$q_e = \frac{[C_0 - C_e]V}{W} \text{----- (2)}$$

Where q_e is the quantity of metal adsorbed on the adsorbent at the time of equilibrium (mg/g), C₀ and C_e are the initial and equilibrium concentration (mg/l). V is the volume of solution, W is the weight of adsorbent(g).

IV. RESULTS AND DISCUSSION

A. EFFECT OF CONTACT TIME AND INITIAL METAL CONCENTRATION: The effect of contact time shows that equilibrium is achieved faster 10 to 210 min with Nanocomposite. It is observed that in both cases the percentage removal of Cr(VI) ion increase with increase in metal ion concentration Fig (4). The rate of adsorption is very fast initially with about 96% of the total lead being removal within few minutes followed by a increased rate with the approach of equilibrium. The removal rate is high initially due to the presence of the binding sited which gradually become saturated with time resulting in increases rate of adsorption as equilibrium approached finally attain.

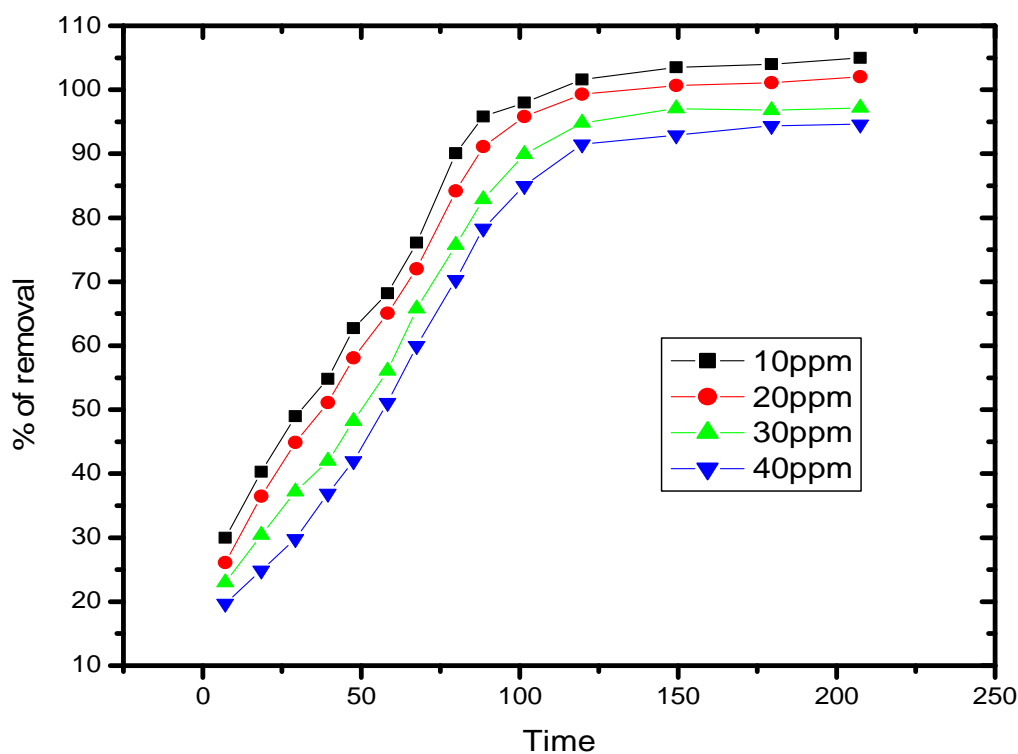


Figure 4:contact time

B. EFFECT OF ADSORBENT DOSAGE: Figure(5) shown the effect of adsorbent dosage on the removal of chromium. It is clear from the figure that as the adsorbent dosage increases, the adsorption also increases. The removal of chromium (about 94%) was achieved for an adsorbent dosage of 1g of the adsorbent.

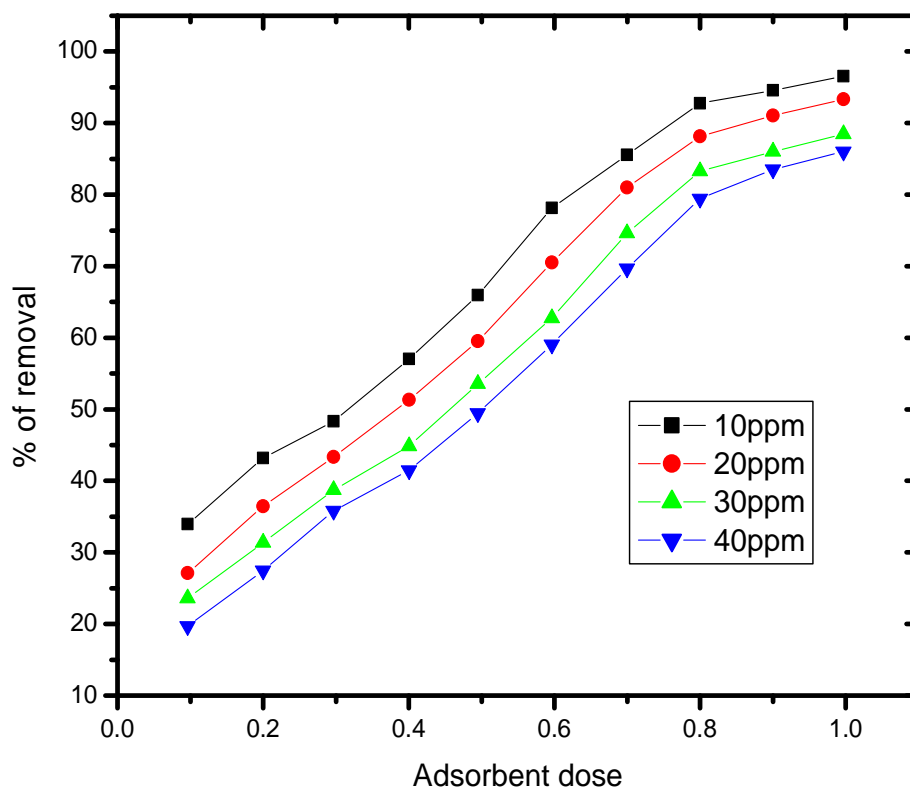


Figure 5: Adsorbent dosage

C. EFFECT OF TEMPERATURE: Temperature studies showed fig (6) at different temperature 30°, 34°, 38°, 42° and the results. It is observed that adsorption of chromium ions increases with increasing temperature showing the process to be endothermic.

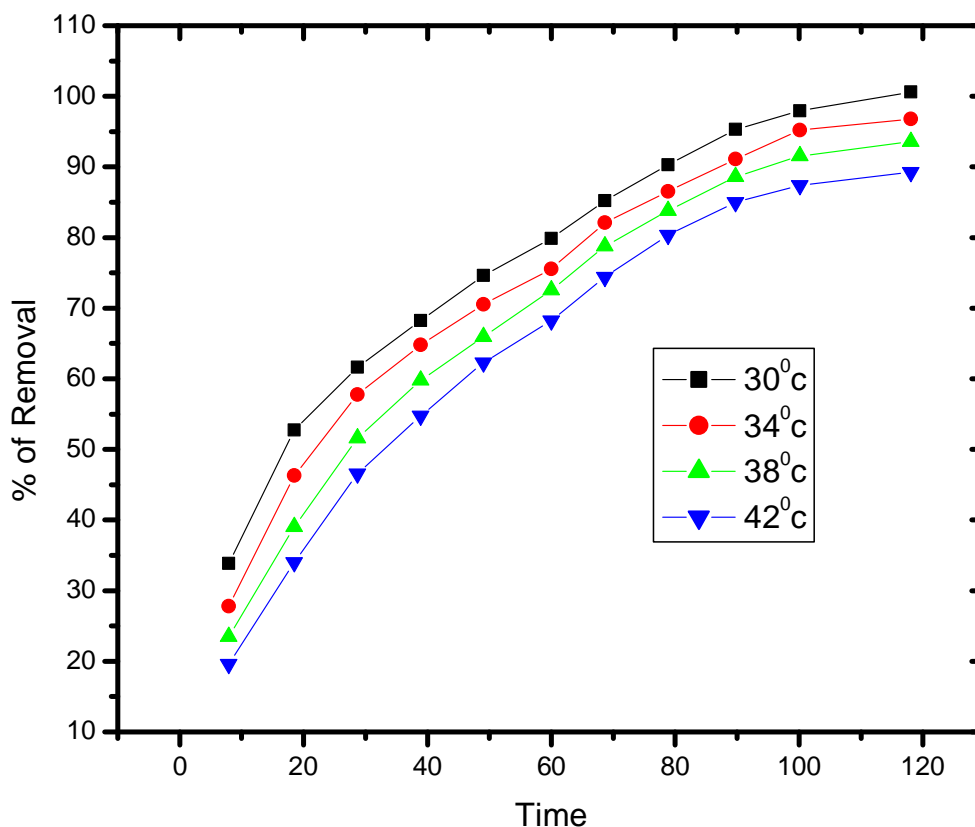


Figure 6: Effect of Temperature

D. EFFECT OF PH: The effect of pH on the adsorption of Cr(VI) by activated carbon was studied at pH values of 3 to 9 with the adsorbate various concentration of 10-40mg/L maintaining the adsorbent dose at 0.1g and the contact time at 2 hours for nanocomposite. The residual Cr(VI) ions were analysed with atomic absorption spectrophotometer. From this figures it is clear that chromium adsorption efficiency is highest at P^H 7-9 with Nanocomposition P_{ZPC}^H for the Nanocomposition was determined as 8.0.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 10, October 2016

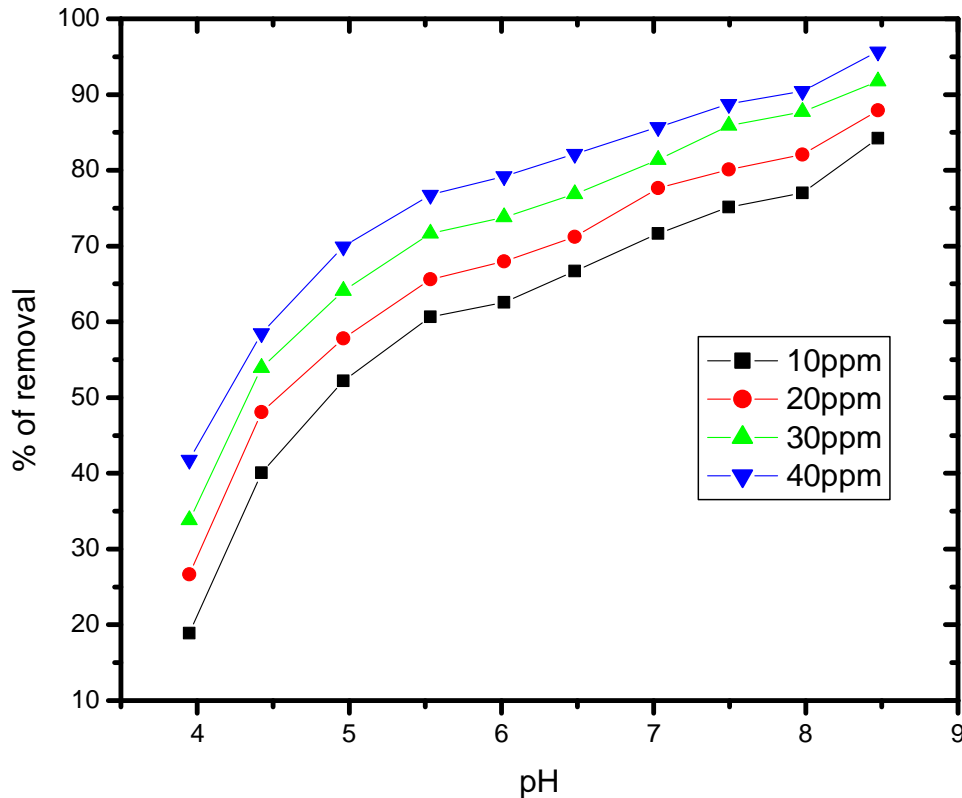


Figure 7:Effect of pH

E. ADSORPTION ISOTHERM: The adsorption isotherm were analyzed using Langmuir , Freundlich, Tempkin and Dubinin – Radhuskevich isotherm.

i. Langmuir adsorption isotherm: The Langmuir adsorption isotherm is often used for adsorption of the solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all the isotherms describing adsorption, and it is often expressed as

$$q_e = \frac{Q^0 R_L C_e}{1 + K_L C_e}$$

The above equation can be rearranged to create the following linear form

$$\frac{c_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0}$$

Where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/L) and C_e is the equilibrium concentration of the adsorbate (mg/L), and q_0 and 'b' are Langmuir constants related to adsorption capacity and rate of adsorption respectively.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 10, October 2016

As required by equation plotting C_e/q_e against C_e gave a straight line, indicating that the adsorption of heavy metal on the nanocomposite follow the Langmuir isotherm fig (8). The Langmuir constant ' K_L ' can be evaluated from the slope and intercept of the linear graph.

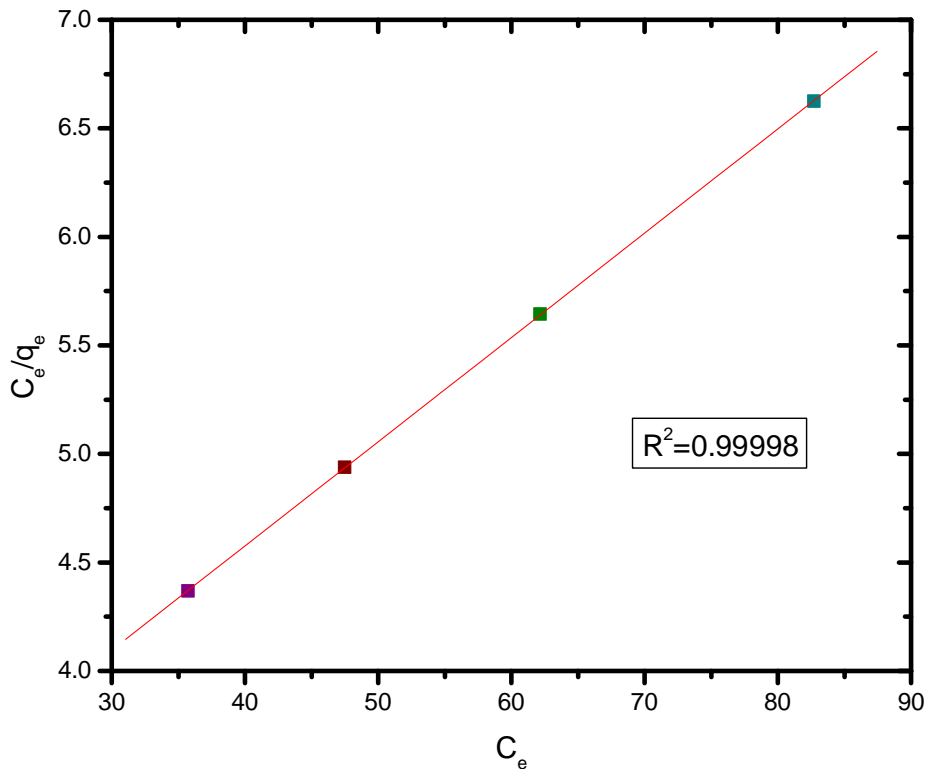


Figure 8: Langmuir adsorption isotherm

The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L defined by

$$R_L = \frac{1}{1 + K_L C_0}$$

Where ' C_0 ' is the initial solute concentration of adsorbate [mg/L]. ' K_L ' is the Langmuir adsorption constant (L/mg). R_L value lies between 0 and 1 indicates favourable adsorption (Norrozi B, serial, G.A, Arami M (2007)).

ii. Freundlich Isotherm: The Freundlich isotherm (1906) is earliest known relationship describing the adsorption equation which is often expressed as heterogeneous surface energies (mckay et al. 2006).

$$q_e = K_f C_e^{1/n}$$

The equation is conveniently used in the linear form by taking the logarithmic of both sides.

$$\log q_e = \log k_f + 1/n \log C_e$$

Where q_e is the amount of metal adsorbed in mgL^{-1} . C_e is the equilibrium concentration (mgL^{-1}), K_f and n were Freundlich constant. (mg/g, L/mg) related to adsorption capacity and adsorption intensity of the sorbent respectively.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 10, October 2016

The plot of $\log q_e$ Vs $\log C_e$ yields a straight lines which indicating the confirmation of the freundlich isotherm for adsorption fig (9).The values of n indicates favourable adsorption when $1 < n < 10$.

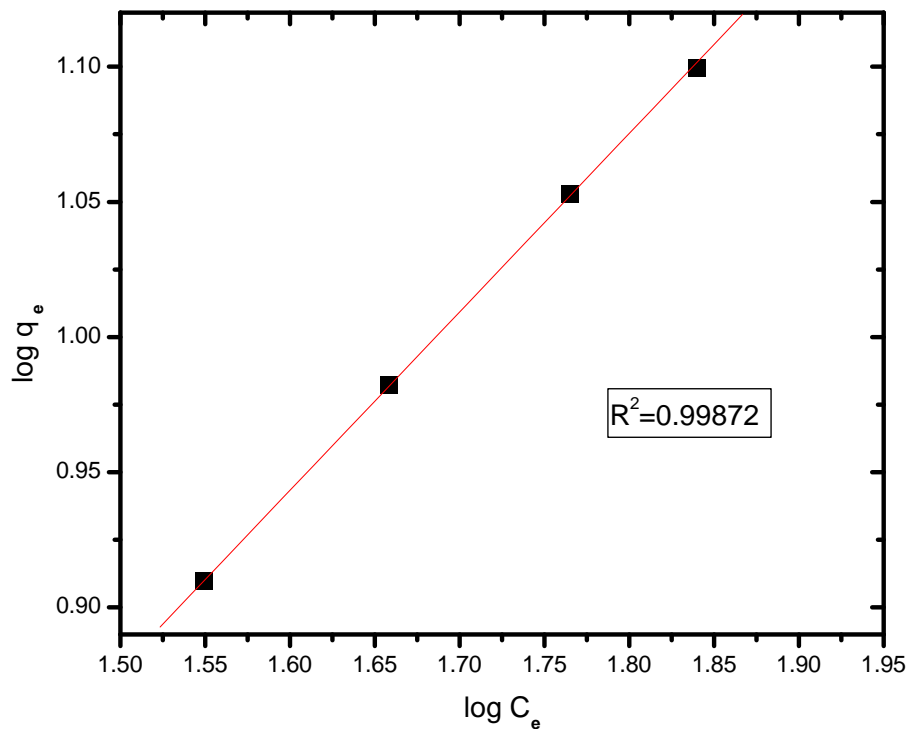


Figure 9: Freundlich isotherm

iii. Tempkin isotherm: Tempkin isotherm is represented by the following equation

$$q_e = \frac{RT}{b} \ln[AC_e]$$

Equation can be expressed in its linear form as

$$q_e = B \ln A + B \ln C_e$$

Where B is a constant related to the heat of adsorption (J/mol) and A is the Tempkin isotherm constant, corresponding to the maximum binding energy (L/mg). A plot of q_e vs $\ln C_e$ is shown in Figure(10).

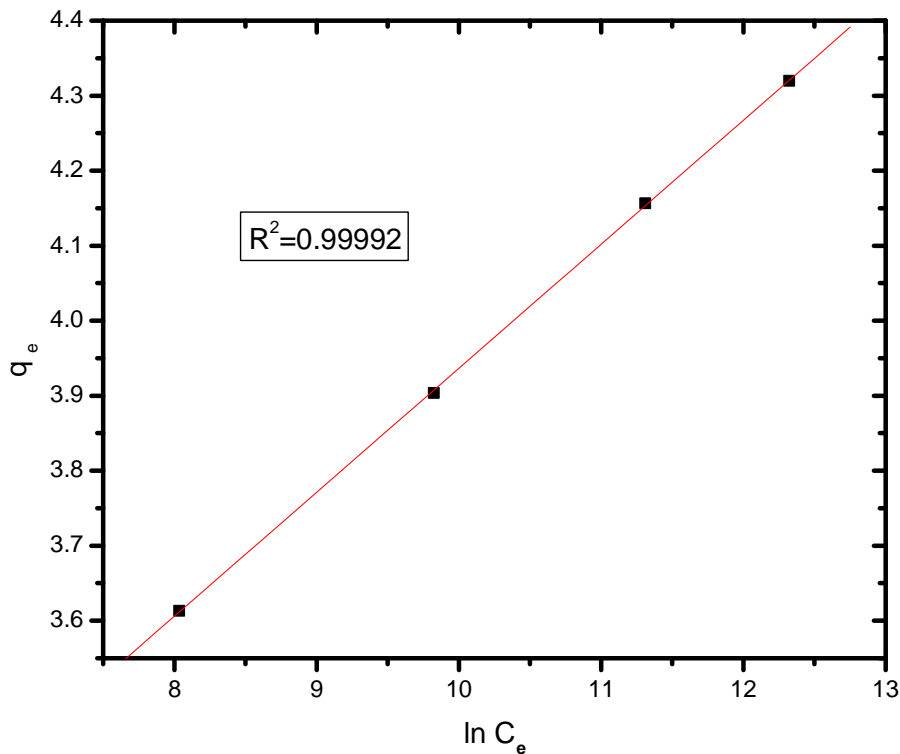


Figure10: Tempkin isotherm

iv. Dubinin-Radushkevich isotherm: The equilibrium data was further subjected to the D-R isotherm model to identify the nature of adsorption processes. The linear form of D-R isotherm equation is given by the equation [19].

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/g), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to adsorption mean free energy (mol^2/J^2) and ε is the Polanyi potential.

$$\varepsilon = RT \ln (1 + 1/C_e)$$

The D-R isotherm model did not fit the equilibrium data as the R^2 value.

$$E = 1/\sqrt{2\beta}$$

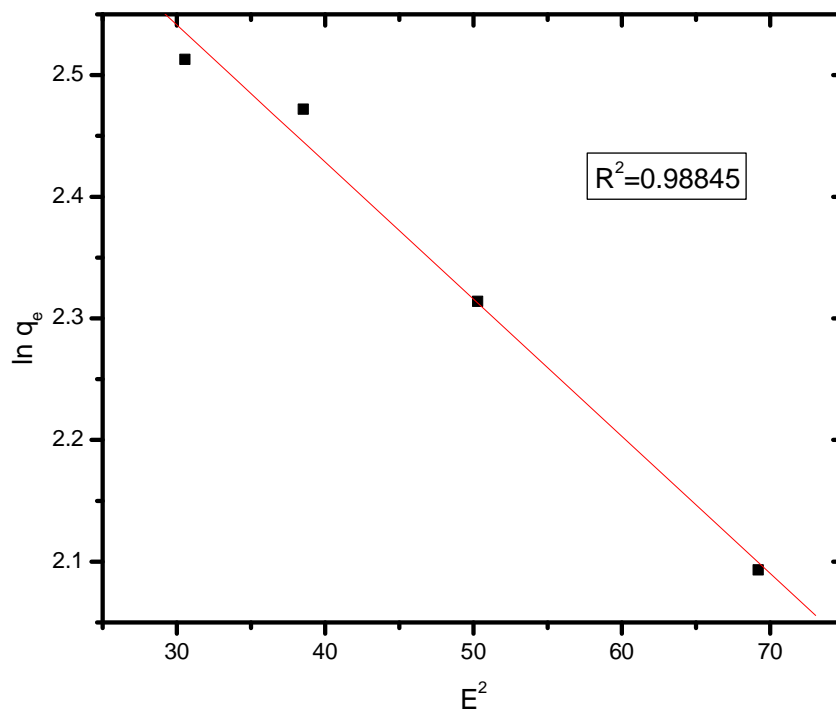


Figure 11. D-R isotherm

Table 1: Results of isotherm plots for the adsorption of Chromium on AC-TiO₂ AC

Initial metal Concentration	Langmuir isotherm				Freundlich isotherm		
	Q ₀ (mg/g)	b(L/mg)	R ²	R _L	K _f	N	R ²
60	20.833	0.018	0.9999	0.4807	0.94	1.515	0.9987
80				0.4098			
100				0.3571			
120				0.3164			

F. ADSORPTION: KINETICS: The kinetics of adsorption of Chromium by the nanocomposite and the kinetic models of pseudo first order, pseudo second order, and Intraparticles diffusion model were considered.

i. Pseudo First order kinetics: In integrated form of the pseudo first order kinetics model can be represented as $\log(q_e - q_t) = \log q_e - (K_1/2.303)t$

Where q_e is the amount of metal adsorbed at equilibrium (g/mg). q_t is the amount of metal adsorbed at time (mg/g) and k_1 is the pseudo first order rate constant k_1 and q_e (ther) can be calculated from the slope and intercept of the graph. The q_e (ther) and q_e (exp) value are shown in table(2). The adsorption process does not follow first order kinetics.

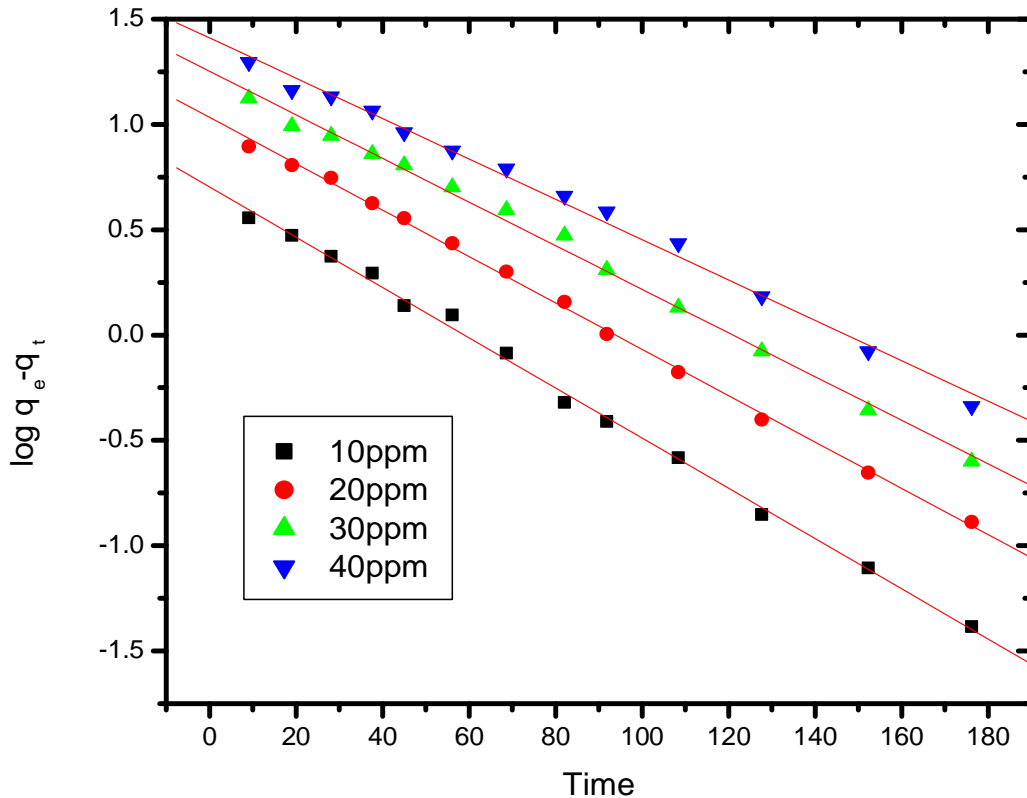


Figure 11: Pseudo first order

ii. Pseudo-second order kinetic model: The integrated form of I order

$$1/q_e + q_t = 1/q_2 + K_2 t$$

The linear pseudo second order kinetic equation is given as

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t$$

where k_2 is rate constant of second order adsorption ($g\ mg^{-1}\ min^{-1}$). As expected the plot of t/q_t vs t Figure (12) was linear. The values of q_e and k_2 can be calculated from the slope and intercept. The q_e (the) and q_e (exp) values are shown in Table 2. The calculated q_e (the) values are in consonance with q_e (exp) with high correlation coefficient values. The adsorption of NC-Tio2 –AC followed pseudo-second order kinetics.

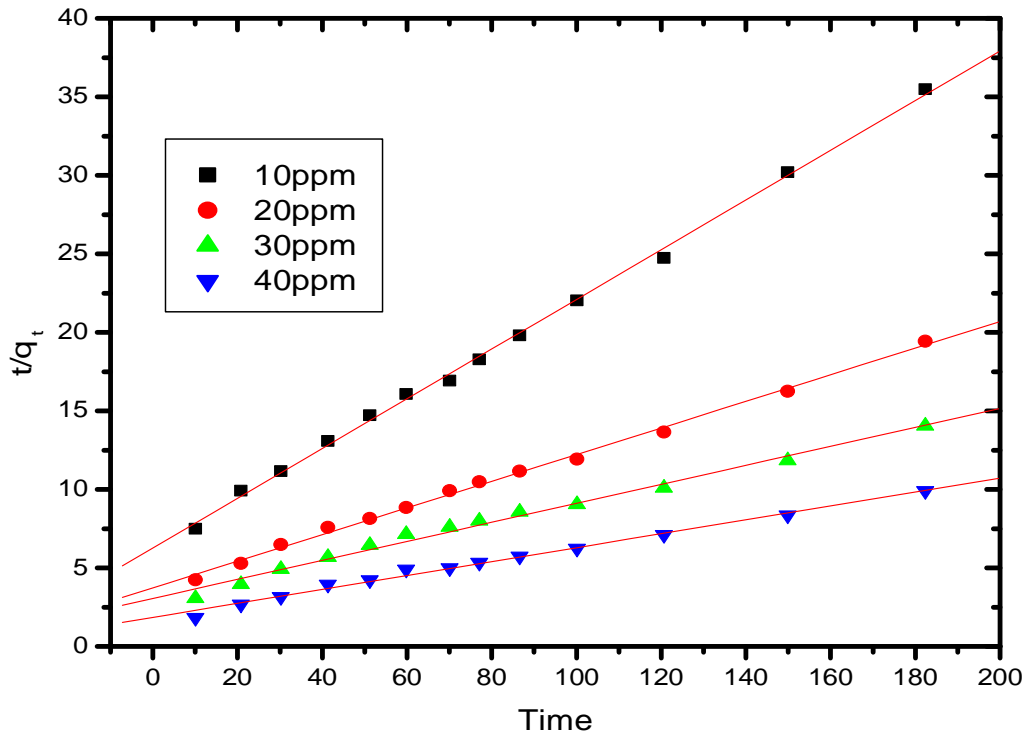


Figure 12: Pseudo second order

iii. **Intraparticle diffusion** : The Intraparticle diffusion model used here refers to the theory proposed by Weber and Morris based an intraparticle diffusion coefficient K_{id} is defined by the equation,

$$q_t = K_{id} t^{1/2} + C$$

Where K_{id} is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), C is the intercept (mg/g) can be calculated by plotting q_t vs $t^{1/2}$ and the results are given in Figure (13) and Table 2. The linear portion of the plot does not pass through the origin. Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion.

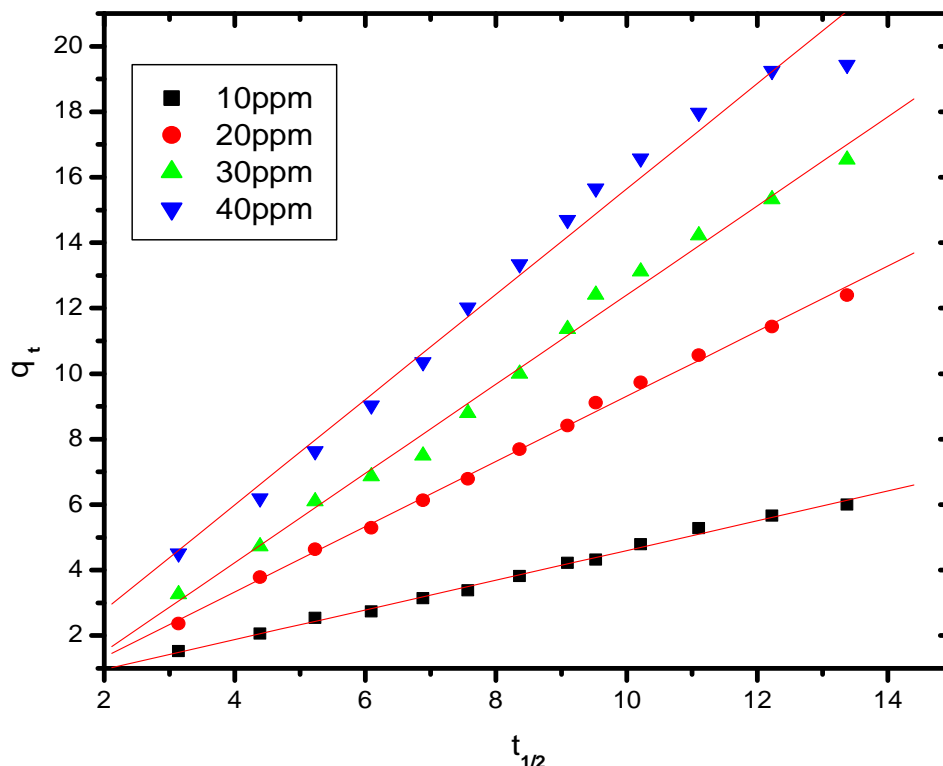


Figure13:Intraparticle diffusion

Table 2: The Kinetic Parameter for the adsorption of Chromium by AC-TiO₂-NCAdsorbent

Initial metal concentration	Pseudo first order				Pseudo second order				Intraparticle diffusion		
	K ₁	q _{e,exp}	q _{e,cal}	R ²	K ₂	q _{e,exp}	q _{e,cal}	R ²	K _{id}	C	R ²
10	0.02745	4.943	5.043	0.9974	0.0039	4.943	6.321	0.9982	0.4536	0.0629	0.9956
20	0.0253	10.201	10.809	0.9984	0.0019	10.201	11.792	0.9916	0.995	0.6452	0.9940
30	2.885	14.573	17.906	0.9954	0.0017	14.573	16.666	0.9994	1.3613	1.2132	0.9932
40	0.021	19.053	25.72	0.9933	0.0010	19.053	22.573	0.9916	1.6074	0.4348	0.9936

G. THERMODYNAMIC PARAMETERS: The thermodynamic parameters for the sorption process could be determined from the experimental data obtained at various temperatures using the equation

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where K_c is the Langmuir constant related to the energy of adsorption, R is the gas constant and T is the absolute temperature (K). the adsorption process such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 10, October 2016

(ΔS°). Suggest endothermic and spontaneous nature of sorption process of the absorption of chromium onto to AC-TiO₂.NCat all temperatures investigated.

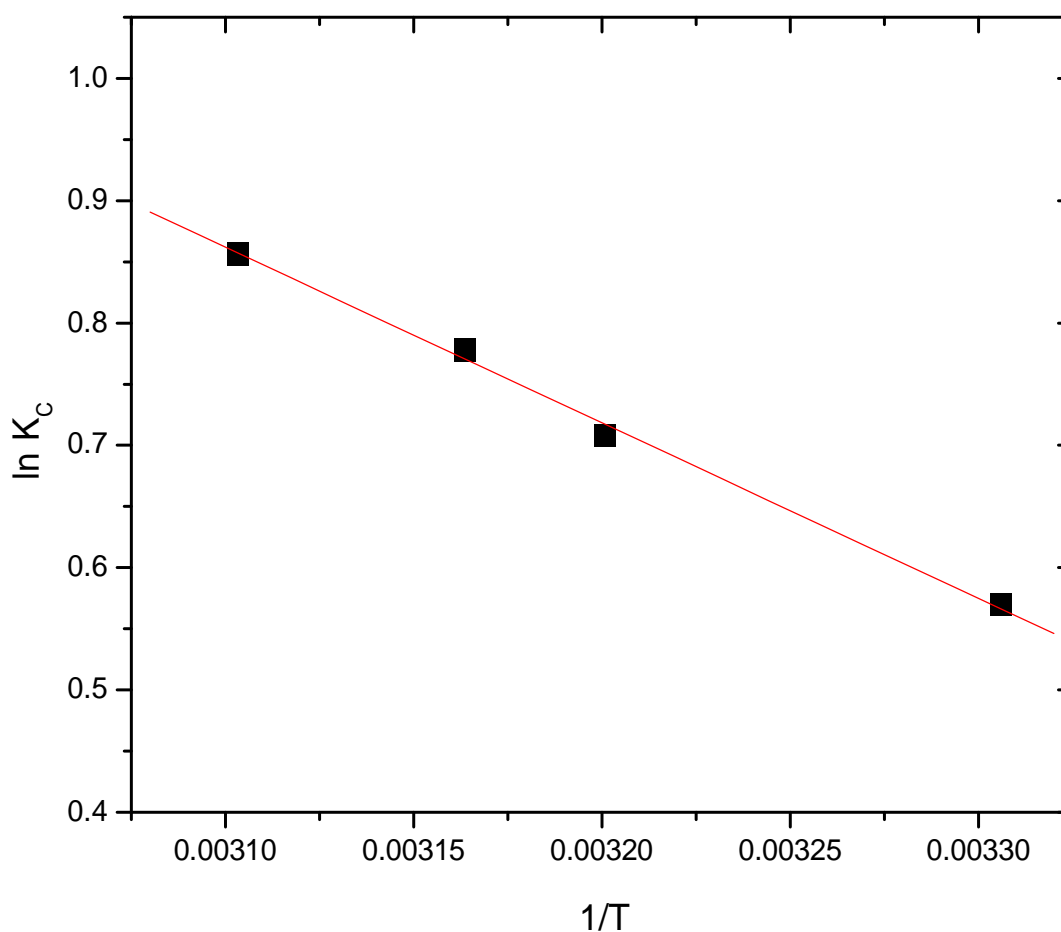


Figure14:Thermodynamic parameter

V. CONCLUSION

Batch adsorption studies carried out demonstrated the removal of chromium using AC- TiO₂-NC to be strongly dependent on contact time and initial metal concentration, adsorbent dose, pH and temperature. The experimental data of the adsorption under study were evaluated using Freundlich, Langmuir, Tempkin and D-R isotherm. The kinetic results was best described by pseudo second order equation. Thermodynamics data indicated that the adsorption of Cr(VI) onto activated carbon is endothermic, chemisorptions can be pointed out as the controlling mechanism.

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Vol. 5, Issue 10, October 2016

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