



## Removal of Chromium by a Low Cost Biosorbent (NTAC) from Polluted Waters: Synthesis, Characterization, Isothermal, Kinetic and Thermodynamic Studies

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### ABSTRACT

*A low cost biosorbent has been synthesized from the stems of "Tarennia asiatica" (NTAC) for the removal of chromium (VI) from contaminated waters by using batch adsorption method. Factors effecting the removal of chromium by the sorbent from chromium solution have been studied. Different adsorption isotherms have been applied to study the adsorption mechanism and the adsorption is physisorption. To study the rate and kinetics of adsorption some kinetic models have been applied. The correlation coefficient values indicate that the adsorption process can be fitted into Pseudo second order model. SEM, EDX techniques of the active carbon have shown a morphological change of the surface after adsorption and FTIR studies indicate the involvement of some surface functional groups in chromium (VI) adsorption. XPS analysis was studied to investigate the chemical compaction of surfaces of adsorbent. The effect of interfering ions has also been studied.*

**Keywords:** Removal of Chromium (VI); Batch adsorption technique; Inexpensive adsorbent; Surface characterization; Adsorption isotherms; Kinetic study

### INTRODUCTION

Contamination of water by toxic heavy metals like chromium, manganese, mercury etc. is the major environmental concern. Chromium finding place in many industries like leather tanning, photography, dye, electroplating and battery industries. Chromium is found hazardous to public health due to its carcinogenic properties [1,2]. Effluents from these industries contains considerable amount of chromium which is hazardous to human health is to be reduced to permissible limit (0.05 mg/lit) before letting out the effluents into natural waters to meet national regulation standards as well as to protect public health. Conventional methods [3-11] for removal of chromium have been reported. Due to operational demerits and cost intensive these methods are unaffordable for removal of chromium from effluent eaters. Hence non conventional methods such as adsorption methods like biosorbent [12], activated carbons [13-15], coconut fiber [16], Eucalyptus bark [17], fly ash [18], bone charcoal [19,20], Neem saw dust [21] which are cost effective and economic have been developed. In the present study the removal of chromium has been reported from effective inexpensive biosorbent synthesized from (NTAC). The carbonization has been done with nitric acid. SEM, EDX, XPS and FTIR techniques have been used to characterize the synthesized sample. Factors effecting the removal of chromium have been reported. Adsorption isotherms are applied to know the mechanism of adsorption. Kinetic studies are used to determine the rate of adsorption and kinetics of adsorption.

## EXPERIMENTAL PROCEDURE

### Preparation of NTAC (Activated Carbons)

Stems of *Tarenna asiatica* plant was collected and cut in to small pieces and air dried. It is washed with double-distilled water and treated with 0.1 N HNO<sub>3</sub>. It is electrically heated at 500°C the material was carbonized for 4 hours for activation. The carbonized material was washed with deionized water to remove excess acid and finally the activated carbon is dried in an air oven at 110°C. The activated carbon was sieved to an average diameter of about 0.01119 mm for adsorption experiments.

### Characteristics of the Nitric Acid Activated Carbons

Physicochemical characteristics of NTAC were studied by using standard methods and the results are presented in Table 1. The pH for the activated carbon adsorbent was determined using the Elico pH meter, model LI-120, and the pH<sub>ZPC</sub> was determined using the pH equilibrium method [22,23]. Particle size was determined using American Standard Test Method (ASTM) sieves [24]. Iodine number [25], decolorizing power [26] and other parameters such as apparent density, moisture, loss on ignition, ash, water soluble matter, and acid soluble matter were determined by using standard test methods [27,28]. The BET surface area [29] of the prepared activated carbon was determined by nitrogen gas adsorption analyzer at 77K using Quanta chrome Nova Win-Data Acquisition and Reduction for NOVA instruments version 10.01. The BET-N<sub>2</sub> surface area was obtained by applying the BET equation to the adsorption data. The acidic and basic groups on the surface area of active carbon adsorbent were estimated using the Boehm titration method [30,31]. Physicochemical characteristics of NTAC were studied and the results are presented in Table 1.

Table 1: Physicochemical characteristics of NTAC

S No	Parameter	Value
1	Apparent density, (g/ml)	0.225
2	Moisture content, (%)	6.8
3	Loss on Ignition (LOI), (%)	83.56
4	Ash content, (%)	6.31
5	Water soluble matter, (%)	0.69
6	Acid soluble matter, (%)	0.62
7	Decolorizing power, (mg/g)	360
8	pH	2.1
9	pH <sub>ZPC</sub>	6.12
10	Iodine number, (mg/g)	486.3
11	Particle size(μ)	45
12	BET Analysis - Surface area, m <sup>2</sup> /g	Before
		After
		194.6
		183.4
13	Surface functional groups (meq/g)-Boehm Titration	
I	Carboxyl	1.251
II	Lactonic	1.1
III	Phenolic	1.362
IV	Carbonyl	1.405
V	Total basic groups	6.85

### Adsorption Experimental Procedure

#### Preparation of reagents:

All chemicals and reagents are used of analytical grade. Double distilled water is used in the preparation of solutions. Adsorption studies were carried out by batch method using a test solution of 50 mg/lit of chromium (VI) ions. From this 50 mg/lit chromium ion solution, 100 ml of solution was pipetted out into a 250 ml iodine flask at room temperature 30 ± 1°C. A weighed quantity of the prepared active carbon adsorbent was added and the solution pH was adjusted using dilute HCl or NaOH and was measured with digital pH meter using a combined glass electrode. The solution was shaken in an orbital electronic shaker at 120 rpm. Iodine flask was removed from the shaker at the end of desired contact time. The adsorbent was filtered after allowing the solution to settle the adsorbent for 2 to 4 min. The filtrate was analyzed for the concentration of free chromium (VI) ions present in the solution and was determined spectrophotometrically by developing a purple violet colour with 1,5 diphenyl carbazide [32] in acidic solution as a complexing agent. The absorbance was measured at 540 nm.

**Chromium ion analysis:**

The percentage removal of Chromium (VI) ion and amount adsorbed (in mg/g) were calculated using the following equations.

$$\% \text{ Removal (\%R)} = \frac{(C_i - C_e)}{C_i} \times 100$$
$$\text{Amount adsorbed (q}_e\text{)} = \frac{(C_i - C_e)}{m} V$$

Where,  $C_i$  = Initial concentration of the chromium (VI) solution in mg/lit;  $C_e$  = Equilibrium concentration of the chromium (VI) solution in mg/lit;  $m$  = mass of the adsorbent in grams;  $V$  = Volume of chromium (VI) test solution in liters

The same procedure has been followed, to study the effect of adsorbent dosage, pH of the chromium (VI) solution, agitation time, initial concentration of chromium (VI) solution, particle size, temperature and in presence of foreign ions on the adsorption of chromium (VI) onto NTAC.

**Methods used for Surface Characterization****FTIR:**

The functional groups on activated carbon, NTAC are identified by using Fourier Transform Infrared spectroscopy (FTIR). It was measured by using BRUKER VERTEX 80/80v FTIR spectrometer, Bruker AXS, Inc., Madison, WI, USA Optical resolution of  $<0.06 \text{ cm}^{-1}$ , with automatic and vacuum compatible beam splitter changer (BMS-c) option. The instrument used to record the FTIR spectrum with KBr pellet as reference.

**SEM:**

The surface morphology of the activated carbon sample of NTAC was studied by scanning electron microscopy. The microphotographs of NTAC were recorded using LEO 1420 VP Compact variable pressure digital SEM, manufactured by Leo Electron Microscopy Ltd. (Cambridge, UK; beam voltage 500 to 2000 V, Magnifications 250 to 65,000 X, Resolution 3 nm at 1000 V).

**EDX:**

EDX will give the chemical composition on the surface of the activated carbon (NTAC). These are due to large part of the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum and was recorded for NSAC using BRUKER EDX Two-dimensional VANTEC-500 detector.

**XPS:**

X-ray Photoelectron Spectroscopy (XPS) is used for chemical analysis and is one of the most widely used analytical technique for surface analysis because it can be applied to a broad range of materials and provide valuable quantitative information of the surface of the material being studied. The spectrum for NTAC was observed from ESCA LAB 250Xi X-ray Photoelectron Spectrometer.

**RESULTS AND DISCUSSIONS****The Fourier Transforms Infrared (FTIR) Spectroscopy**

The Fourier transforms infrared (FTIR) spectra of NTAC is represented in Figure 1 before adsorption and in Figure 2 after adsorption of chromium (VI) ion. The Fourier transform infrared (FTIR) spectroscopy analysis of NTAC before and after adsorption of chromium (VI) confirmed the occurrence of chromium (VI) adsorption on active carbon as there are some changes like shifts and decreases in the percentage of transmittance in the FTIR spectra of the solid surface in the range  $4000 \text{ cm}^{-1}$  to  $500 \text{ cm}^{-1}$ . The FTIR spectra shows the adsorption band at  $3864 \text{ cm}^{-1}$  and  $3211 \text{ cm}^{-1}$  corresponding to the stretching vibration of O-H and N-H respectively and the adsorption bands at  $1793 \text{ cm}^{-1}$  (carboxylic) and  $1681 \text{ cm}^{-1}$  (carboxylate) are responsible functional groups for metal ion sorption [33]. Strong peaks at  $2944 \text{ cm}^{-1}$  and  $2862 \text{ cm}^{-1}$  corresponding to stretching vibrations (symmetric and asymmetric) of aliphatic C-H, [34-37] bending vibrations of methylene and methyl peaks due to inplane bending vibration of C-H of methylene group [38-40], peaks due to C-O stretching in alcohols, phenols, lactones, ethers, esters, acids, epoxides [39-47], peaks due to out of plane deformation vibration of C-H groups in aromatic structures [48-50] have been observed. The adsorption process is of physisorption but not chemisorption due to the absence of C-Cr peak.

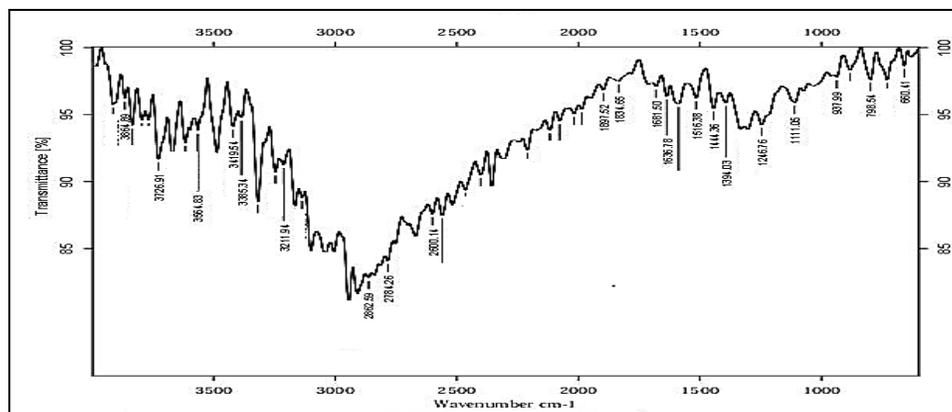


Figure 1: FTIR spectra of NTAC before adsorption of chromium (VI) ion

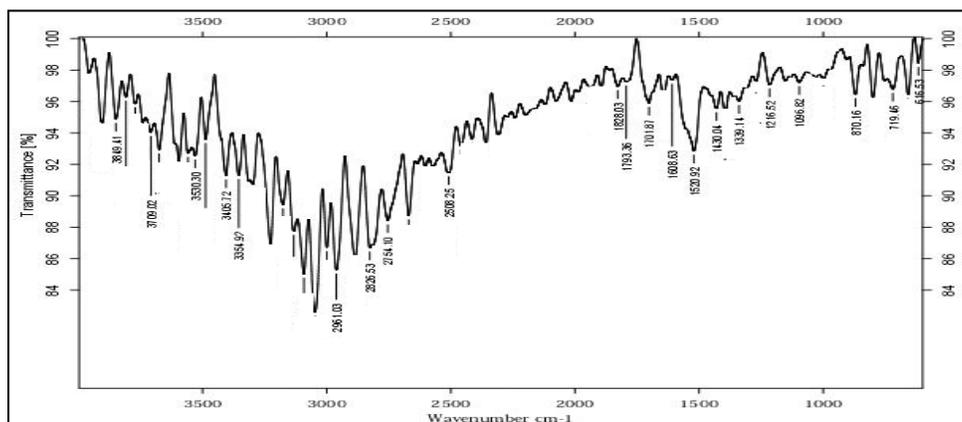


Figure 2: FTIR spectra of NTAC after adsorption of chromium (VI) ion

### Scanning Electron Micrographs (SEM)

SEM has been studied to know the surface characteristics of the adsorbent, NTAC such as size, shape and shape of the particles, pore size characteristics of the surface, the relative amounts of elements and their arrangement is also known from this studies. The SEM photographs were recorded before and after adsorption and are presented in Figure 3.

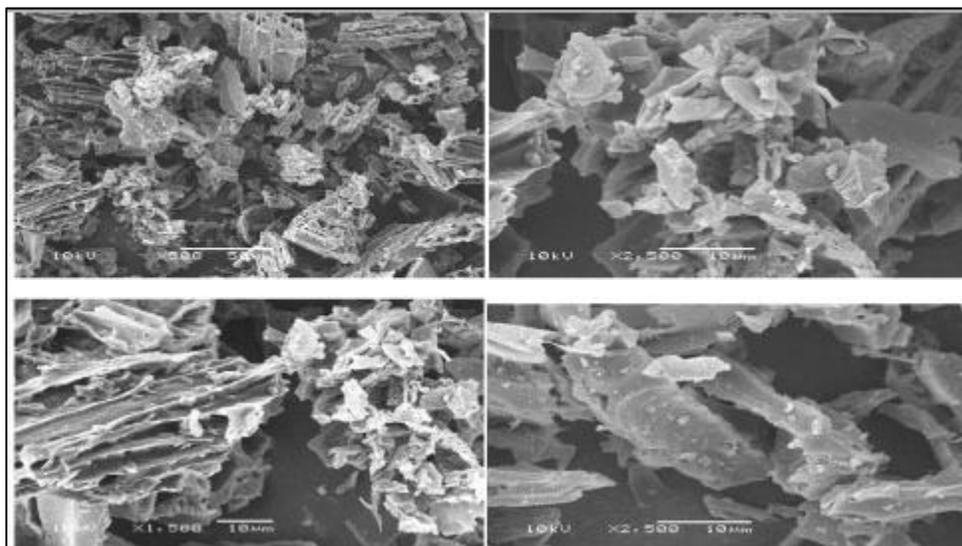


Figure 3: SEM analysis of NTAC before (left) and after (right) absorption at X5000 and X6000 magnifications

From the above studies it is informed that a well-developed surface area was observed in a randomly distributed pore size in all micrographs.

### Analysis of EDX

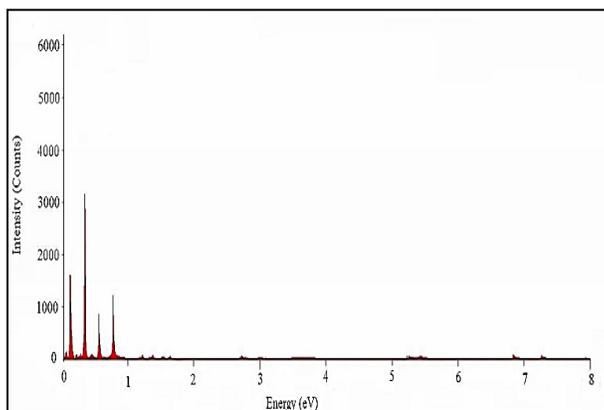


Figure 4: The EDX spectra of NTAC before chromium adsorption

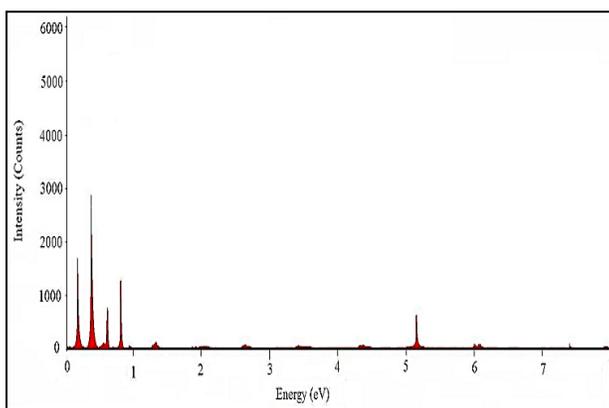


Figure 5: The EDX spectra of NTAC after chromium adsorption

To study the chemical composition of the activated carbon the Energy-dispersive X-ray spectroscopy (EDX) studies were carried out for the activated carbon, NTAC. Figures 4 and 5 represent the untreated and chromium ion treated EDX of the activated carbon. The presence of carbon, oxygen and a small amount of nitrogen has been observed on analyzing the spectra with other elements. By comparing Figures 4 and 5, we observe an extra peak at 5.2 in Figure 5 representing chromium after the adsorption which concludes there is chromium adsorption. The analysis results were shown in Table 2.

Table 2: Elemental analysis of NTAC before and after adsorption of chromium (VI) ion

EDX- Elemental Analysis (before)					EDX- Elemental Analysis (after)					
Composition	CK	NK	OK	CrK	Total	CK	NK	OK	CrK	Total
Energy(eV)	0.3	0.5	0.7	1.1		0.3	0.5	0.7	5.2	
Wt%(Mass ratios)	69.5	7	23.5	---	100	66.4	8.7	19	5.9	100
At%(Atomic percentages)	70.2	7.1	22.7	---	100	65.6	8.6	19.8	6	100

### Photoelectron Spectrometer (XPS)

The XPS reports were studied to investigate the chemical composition of surfaces of adsorbent (NTAC) before and after with chromium treatment. XPS counts electron ejected from a sample surface on irradiation by x-rays. XP spectra have different regions for surface analysis of elements. The survey scans of NTAC before treatment exhibit the peaks between 285-290; 390-400; 528-535 indicate the presence of carbon, nitrogen and oxygen elements on the surface of the sample (Figures 6 and 7).

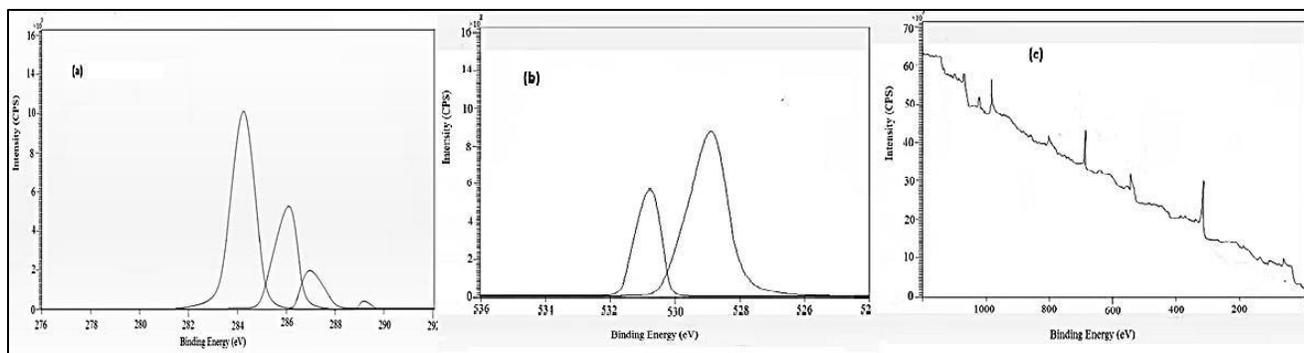


Figure 6: XPS spectra of NTSC before treatment of Chromium solution (a) C1s spectra, (b) O1s spectra and (c) survey scan

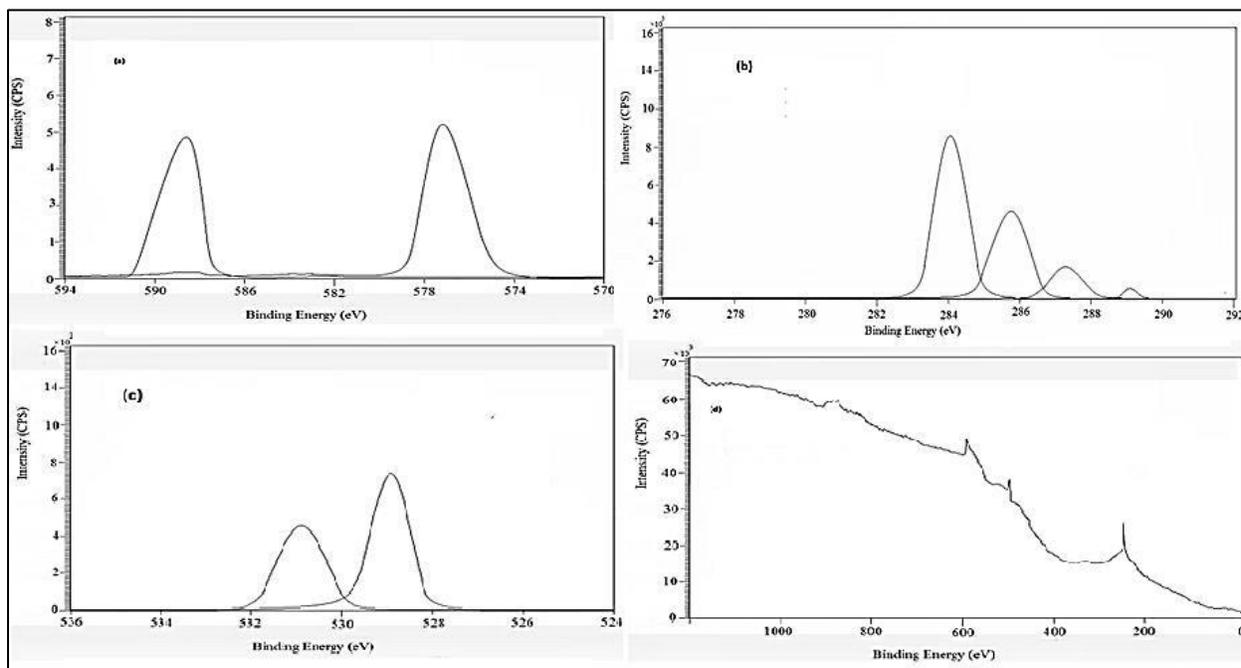


Figure 7: XPS spectra of NTSC after treatment of Chromium solution (a) Cr spectra, (b) C1s spectra (c) O1s spectra and (d) survey scan

XPS reference binding energy (eV) value for N1s and C1s binding energies for aliphatic species are studied. 576, 577 peaks corresponding to chromium (III) and 579 peak is of chromium (VI). Chromium is present in two different oxidation states; it can show catalytic activity for oxidation reactions. No intense peak of chromium was identified in the activated carbon of NTAC before treatment. Reduction in intensity of C1s and O1s spectra and increase in the chromium intensity was observed in spectra of chromium treated sample. The reduced chromium ions were adsorbed to the surface because of smaller repulsion effect between Carbon surface and chromium (III). It can be there is a significant change in chromium content in treated sample and it was conformation of adsorption of chromium.

### Factors Effecting the Percentage Removal of Chromium

#### pH:

Adsorption of heavy metals by the sorbent is affected by the change of pH. The effect of pH on the adsorption of chromium (VI) is attributed to interaction between the ions in solution and complex formed at the adsorbent surface. The fact is that as the pH is varying chromium (VI) forms different species in aqueous solutions. The study was carried out under optimum conditions of extraction, the effect of pH on the percentage removal of chromium is studied between the pH range from 1 to 10 and the results are presented in Figure 8.

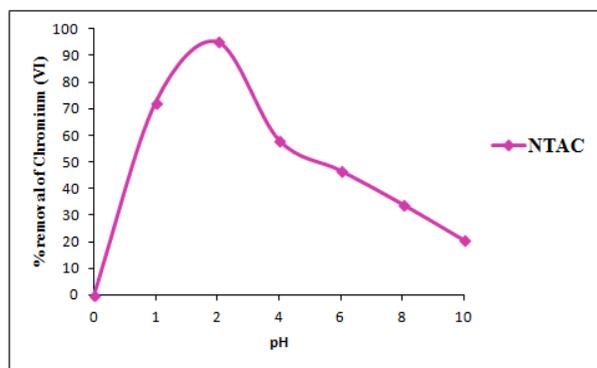


Figure 8: % Removal of chromium (VI) as a function of pH

As seen from Figure 9 that NTAC is active in acidic range especially at low pH range [51]. The maximum adsorption of chromium (VI) concentration on the adsorbent was at pH - 2.0 and negligible at pH-10. Chromium (VI) can exist in several stable forms such as  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$  and the relative abundance of particular complex depends on the concentration of chromium (VI) ion and pH of solution. Because of adsorption of excess  $\text{H}^+$  on the surface, the sorbent is positively charged at low pH. This prevailing positive nature on the liquid sorbent interface causes thrust for anions like dichromate ions exist mostly as an anion leading to a columbic attraction between the sorbent and the sorbate on the interface. So the adsorption of the chromium (VI) ions on the NTAC surface is supposed to be favoured [52]. As the pH of solution increases the sorbent undergoes deprotonation and the sorption capacity decreases. Therefore all further studies were carried out at pH 2.

#### Adsorbent dosage:

In order to know the effect of sorbent dosage on the removal of chromium (VI) ions from waste waters, the study was carried out by varying the concentration of the sorbent from 0.5 to 5.0 g/lit. A graph is drawn between the percentage removal of chromium and adsorbent dosage and is presented in Figure 9.

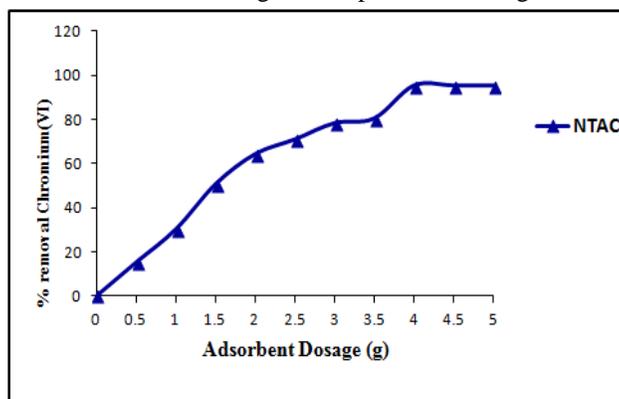


Figure 9: % Removal of chromium (VI) as a function of adsorbent dose

It is seen from the graph, up to 4.0 gm of sorbent dosage, the removal of chromium increases with increase in sorbent dosage and then onwards a saturation point has been reached i.e., no further removal of chromium (VI) ions with increase of sorbent dosage. This is observed due to the overlapping of active sites at higher dosage as well as decrease in the effective surface area resulting in the conglomeration of exchanger particles. The result can be explained as initially the bio-sorption sites remain unsaturated for the period of adsorption process and the number of bio-sorption sites increases with increase of bio-sorbent dosage. Further when the bio-sorbent ratio is small, the active sites available for metal ion binding on the surface of NTAC are less, so the adsorption effectiveness is low. With increase of adsorbent quantity, more active sites available to bind chromium (VI) ions, thus it results an increase in the adsorption efficiency until saturation.

#### Thermodynamic parameters:

The influence of temperature on chromium ion sorption has been studied at optimum conditions using Arrhenius equation between 303 to 323 K. The surface coverage ( $\theta$ ) and sticking probability  $S^*$  are related as

$$S^* = (1 - \theta) \exp(-E_a/RT)$$

$\Theta = (1 - C_e/C_o)$  and  $s^*$  is a function of adsorbate/adsorbent system and is a measure of the potential of an adsorbate to remain on the adsorbent indefinitely [53]. The intercept  $\ln s^*$  and slope  $E_a/R$  are obtained by plotting a linear graph between  $\ln(1 - \theta)$  and  $1/T$  (Figure 10).  $E_a$  is the activation energy (kJ/mole),  $R$  gas constant ( $\text{mol}^{-1}\text{k}^{-1}$ ) and  $T$  is the absolute temperature (K).  $E_a$  value in the present study is 8.4 (kJ/mole) which indicates the present phenomenon is physisorption which involves weak interactions between sorbate and sorbent.

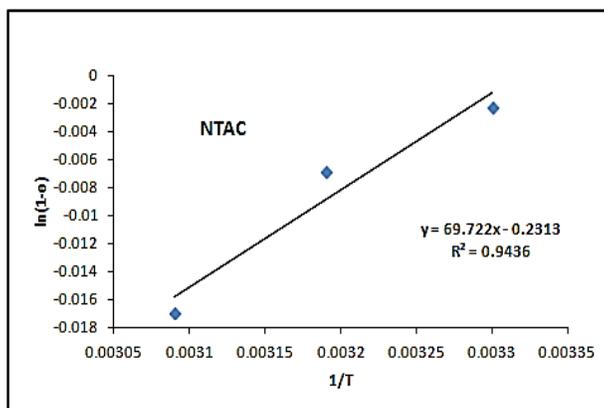


Figure 10: Variation of  $\ln(1 - \Theta)$  with  $1/T$

Thermodynamic parameters of the adsorption process such as change in free energy ( $\Delta G$ ) (kJ/mole), change in enthalpy ( $\Delta H$ ) (kJ/mole) and change in entropy ( $\Delta S$ ) (J/K/mole) were determined at different temperatures by using the equations [54-56].

$$\Delta G = -RT \ln K_d, \ln K_d = \Delta S/R - \Delta H/RT$$

$$K_d = q_e/C_e \text{ and } \Delta G = \Delta H - T\Delta S$$

Where,  $K_d$  is the distribution coefficient for the adsorption  $q_e$  is the amount of chromium ion adsorbed on the activated carbon adsorbent per litre of solution at equilibrium,  $C_e$  is the equilibrium concentration of chromium ion solution,  $T$  is the absolute temperature in Kelvin,  $R$  is the gas constant.  $\Delta G$  is the change in free energy,  $\Delta H$  is the change in enthalpy,  $\Delta S$  is the change in entropy. The values of  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of a plot between  $\ln K_d$  and  $1/T$  and  $\Delta G$  values were obtained from the equation  $\Delta G = \Delta H - T\Delta S$  [57,58] and tabulated in Table 3 (Figure 11).

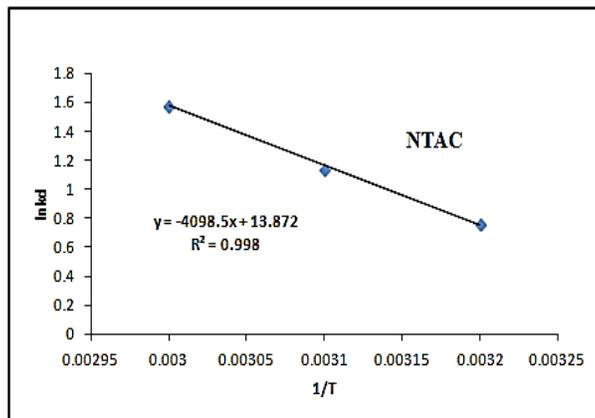


Figure 11: Effect of temperature on % removal of Chromium (VI) ion onto NTAC

It is observed that with increase in temperature from 303 to 323K (30 to 50°C), the efficiency of removal of chromium ion by the sorbent increases. As seen from the table that the negative values of  $\Delta G$  indicates that the adsorption is spontaneous and the negative values of free energy change increase with increasing temperature [59]. This may be ascribed to activation of more sites on the surface of NTAC with a rise in temperature. The adsorption is classified as physisorption when the free energy change ( $\Delta G$ ) lies between -20 and 0 KJ /mole, while in chemical adsorption the values of free energy change ranges from -80 to -400 KJ/mole.  $\Delta G$  for chromium (VI) adsorption onto NTAC was in the range of (-0.87 to -3.184) KJ /mole and so the adsorption was predominantly physisorption. The positive value of  $\Delta S$  shows that there is an increased disorder and randomness at the solid solution interface

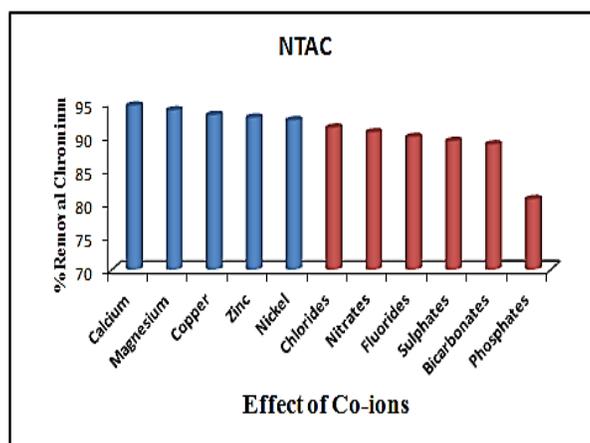
during the adsorption of chromium ions onto NTAC [60]. The positive value of  $\Delta H$  indicates that the adsorption is physisorption and endothermic [61].

**Table 3: Thermodynamic parameters of chromium ion adsorption on NTAC**

Parameter Temperature(K)	$\Delta H(\text{kJ/mol})$	$\Delta S(\text{J/mol/K})$	$\Delta G(\text{kJ/mol})$			$R^2$
			303	313	323	
NTAC	34.07	115.33	-0.87	-2.023	-3.177	0.998

### Co-ions interference:

The effect of the interfering common co-ions is studied on the % removal of chromium ions by NTAC was studied with tenfold excess of concentration of co-ions. Cations present in water such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{+2}$ ,  $\text{K}^+$  and anions such as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{HCO}_3^-$  under optimum conditions. The results obtained were presented in Figure 12.



**Figure 12: Effect of co-ions on (% removal of chromium ion onto NTAC)**

It was observed from the graph, cations had insignificant effect on the sorption of chromium (VI) on NTAC. This can be understood by the fact that the overall surface charge on the sorbent surface becomes positively charged which will inhibit the approach of positively charged metal cations as a result of repulsive force [52]. Anions had reduced the removal of chromium (VI) ions efficiency under the given experimental conditions. The effect of ions  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$  on the removal of chromium (VI) by NTAC is less when compared to  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{PO}_4^{3-}$ .  $\text{SO}_4^{2-}$  has significant effect on the adsorption of chromium and it could be attributed to higher negative charge compared to that of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$  ions. The positive charge on the active sites of active carbon is reduced by the alkalinity of the bicarbonate ion there by the affinity of chromium (VI) ions towards the absorbent surface is decreased and this results decrease in the removal of chromium ions. The effect of interference of  $\text{PO}_4^{3-}$  ion on the removal of chromium ions is maximum because of its high negative charge compared to the other anions. The  $\text{PO}_4^{3-}$  ion needs three close surface groups for being adsorbed. So it can significantly interfere with chromium ions and hence decrease in the percentage of removal chromium (VI) ions from water in presence of tenfold excess of common ions. The factors effecting the removal of chromium other than pH, sorbent dosage and temperature are:

1. Initial concentration of chromium ion,
2. Contact time and
3. Particle size is studied.

The following results have been observed:

1. The percentage removal of chromium decreases with increases in initial concentration.
2. The percentage removal of chromium increases with increases with increasing contact time and attained equilibrium at 90 min.
3. The percentage removal of chromium ions decreases with increase in particle size and maximum removal of chromium has been observed at  $45 \mu$  particle size.

### Desorption

NTAC which adsorbed at maximum concentration of chromium (VI) was used for desorption studies at optimum conditions. Desorption of chromium (VI) ions was studied by using HCl strength varying from 0.02 to 0.2 M. The NTAC carrying 11.9 mg Cr (VI) /g was placed in the desorption medium and stirred at 120 rpm at  $30 \pm 1^\circ\text{C}$ . The

final chromium (VI) ion concentration in the aqueous phase was determined spectrophotometrically. The desorption ratio was calculated from the amount of Chromium ion adsorbed on the activated carbon and the final Chromium ion concentration in the desorption medium using the equation.

$$(\%) = \frac{\text{Amount of Chromium ions desorbed}}{\text{Amount of Chromium ions absorbed}} \times 100$$

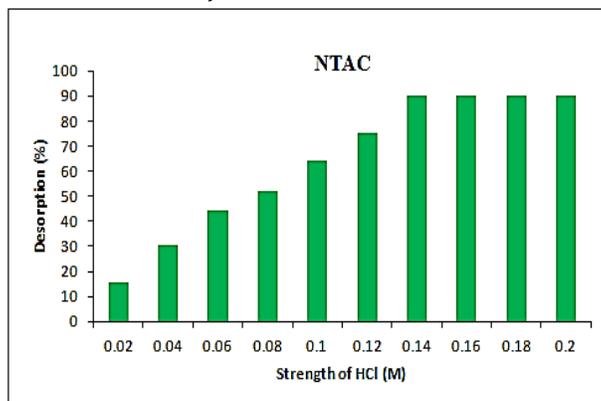


Figure 13: Desorption studies using various strength of HCl NTAC

The results are plotted in Figure 13. It is observed from the graph that 0.2 M HCl could desorb maximum and it is found to be of 90% from NTAC.

### Adsorption Isotherms

Four adsorption isotherm models were studied for the adsorption of chromium (VI) ions onto NTAC: Freundlich [62], Langmuir isotherms [63], Temkin [64] and Dubinin Radushkevich [65] isotherms. The aim of adsorption isotherms is to explain the relation between the remaining concentrations of the adsorbate and the adsorbed quantity on the sorbent surface. The four adsorption isotherms can be represented as:

1. Freundlich:  $\log(q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e$
2. Langmuir:  $C_e/q_e = (a_L/k_L)C_e + 1/k_L$
3. Temkin:  $q_e = B \ln C_e + B \ln A$  and
4. Dubinin Radushkevich:  $\ln q_e = -\beta \epsilon^2 + \ln q_m$ .

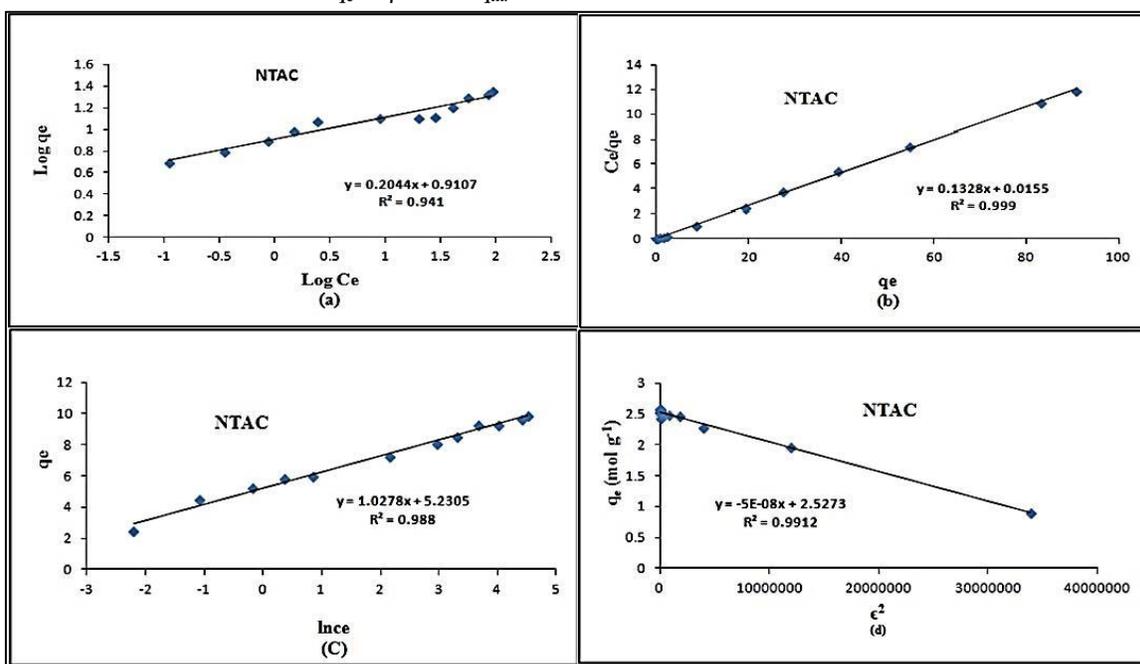


Figure 14: Adsorption isotherms: (a) The Freundlich, (b) Langmuir, (c) Temkin and (d) Dubinin-Radushkevich adsorption isotherms

Linear graphs are observed for all the four isotherms when we plot  $\log q_e$  versus  $\log C_e$  for Freundlich,  $C_e/q_e$  versus  $C_e$  for Langmuir,  $q_e$  versus  $\ln C_e$  for Temkin,  $\ln q_e$  versus  $\varepsilon^2$  for Dubinin Radushkevich and they are presented in Figure 14 (a-d). From graph 14(a) the Freundlich constants  $n$  and  $k_f$  are calculated from slope and intercept of linear plot, and  $a_L/k_L$  and  $1/k_L$  are calculated from the slope and intercept of linear graph 14(b) of Langmuir isotherm. The important characteristics of Langmuir isotherm are expressed in terms of dimensionless constant separation factor  $R_L$  expressed as  $R_L = 1 / (1 + a_L C_i)$ , where  $C_i$  is the initial chromium (VI) ion concentration. The correlation coefficient  $R^2$  values close to unity for above two linear isotherms indicate their applicability and confirmed the heterogeneous surface of the adsorbent and the monolayer coverage of chromium (VI) ion on the active carbon surface. The equilibrium parameter ( $R_L$ ) indicates the isotherm shape and nature of the adsorption process as shown in Table 4.

**Table 4: Characteristics of Langmuir adsorption isotherms**

S.No	Separation factor $R_L$	Types of Isotherm
1	$R_L > 1$	Unfavorable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favorable
4	$R_L > 0$	Irreversible

The dimensionless equilibrium factor ( $R_L=0.0023$ ) value indicates the favorability of the Langmuir isotherm. The applicability of Temkin isotherm is known from the linear graph of 17(c). The  $R^2$  value for this isotherm is 0.988 and the Temkin constants  $A$  and  $B$  are calculated from intercept and slope of the plot (14-c). In Dubinin Radushkevich isotherm  $\beta$  is a constant related to sorption energy,  $E = 1/\sqrt{2\beta}$ ,  $\varepsilon$  is the Polanyi potential which is related to equilibrium concentration,  $\varepsilon = RT \ln(1+1/C_e)$ , where  $R$  is gas constant,  $T$  is absolute temperature. In this isotherm the  $R^2$  value is 0.991 and  $\beta$  and  $\ln q_m$  are calculated from slope and intercept of the graph 14(d). The Dubinin Radushkevich mean free energy  $E$  is found to be 3.16 kJ/mole for activated carbon adsorbent NTAC. The value of  $E$  (<8 kJ/mole) infer that the present sorption system is possibly governed by physical forces [66]. The values of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherms constants along with their correlation coefficient values are present in Table 5. Based on the correlation values, the validity of isotherm models is in the following order Langmuir > Dubinin-Radushkevich > Temkin > Freundlich.

**Table 5: Adsorption isotherms parameters for chromium (VI) adsorption**

	Freundlich	Langmuir		Temkin		D-R	
$K_f$ ( $\text{mg g}^{-1}$ )	1.2267	$a_L$ ( $1 \text{ mg}^{-1}$ )	8.5677	$B$ ( $\text{J/mol}$ )	1.0278	$q_m$ ( $\text{mg g}^{-1}$ )	65102
$n$ ( $\text{g l}^{-1}$ )	1.098	$R_L$	0.0023	$A$ ( $1 \text{ g}^{-1}$ )	3.9169	$E$ ( $\text{kJ mol}^{-1}$ )	3.16
$R^2$	0.941	$R^2$	0.999	$R^2$	0.988	$R^2$	0.991

### Adsorption Kinetic Study

To study the rate and kinetics of adsorption of chromium (VI) ions onto the activated carbon sorbent, NTAC, some kinetic models were applied and discussed in the present work. The applied kinetic models are pseudo first-order model [67] which is represented as  $\log (q_e - q_t) = \log q_e - k_1 t / 2.303$ , pseudo second-order model [68] is  $t/q_t = 1/k_2 q_e^2 + (1/q_e) t$ , Weber and Morris intraparticle diffusion Model [69] equation is  $q_t = k_p t^{1/2} + c$ , Bangham's pore diffusion model [70] equation is  $\log [(C_i/C_i - q_t)m] = \log (k_o/2.303V) + \alpha \log(t)$  and Elovich equation [71] as  $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$ .

Linear plots 15. (a-e) are observed for the experimental results under study for all the above five kinetic models, when we plot  $\log (q_e - q_t)$  versus  $t$  for pseudo first-order model,  $(t/q_t)$  versus  $t$  pseudo second-order model,  $q_t$  versus  $t^{1/2}$  for Weber and Morris intraparticle diffusion Model,  $\log [\log (C_i/C_i - q_t)m]$  versus  $\log t$  for Bangham's pore diffusion model and  $q_t$  versus  $\ln t$  for Elovich equation. Figure 15c represents the applicability of Weber and Morris intra particle diffusion model for the adsorption of chromium (VI). Here  $k_t$  and  $C$  were calculated from the slope of the pot and  $C$  ( $\text{mg/g}$ ) is a constant, gives an idea about the thickness of the boundary layer. The boundary layer effect is more when  $C$  is having larger value. In the diagram the boundary layer diffusion is represented by the initial curved portion while intra particle diffusion is represented by linear portion. The total figure indicates the attainment of equilibrium in the chromium (VI) adsorption kinetics. It is seen from figure the linear portion of the curve did not pass through origin and indicates that the chromium ion adsorption mechanism was governed by both intra particle and surface diffusion. The values calculated from intercept and slope of the graphs (Figures 15a-15e) for different kinetic models under study are presented in Table 6.

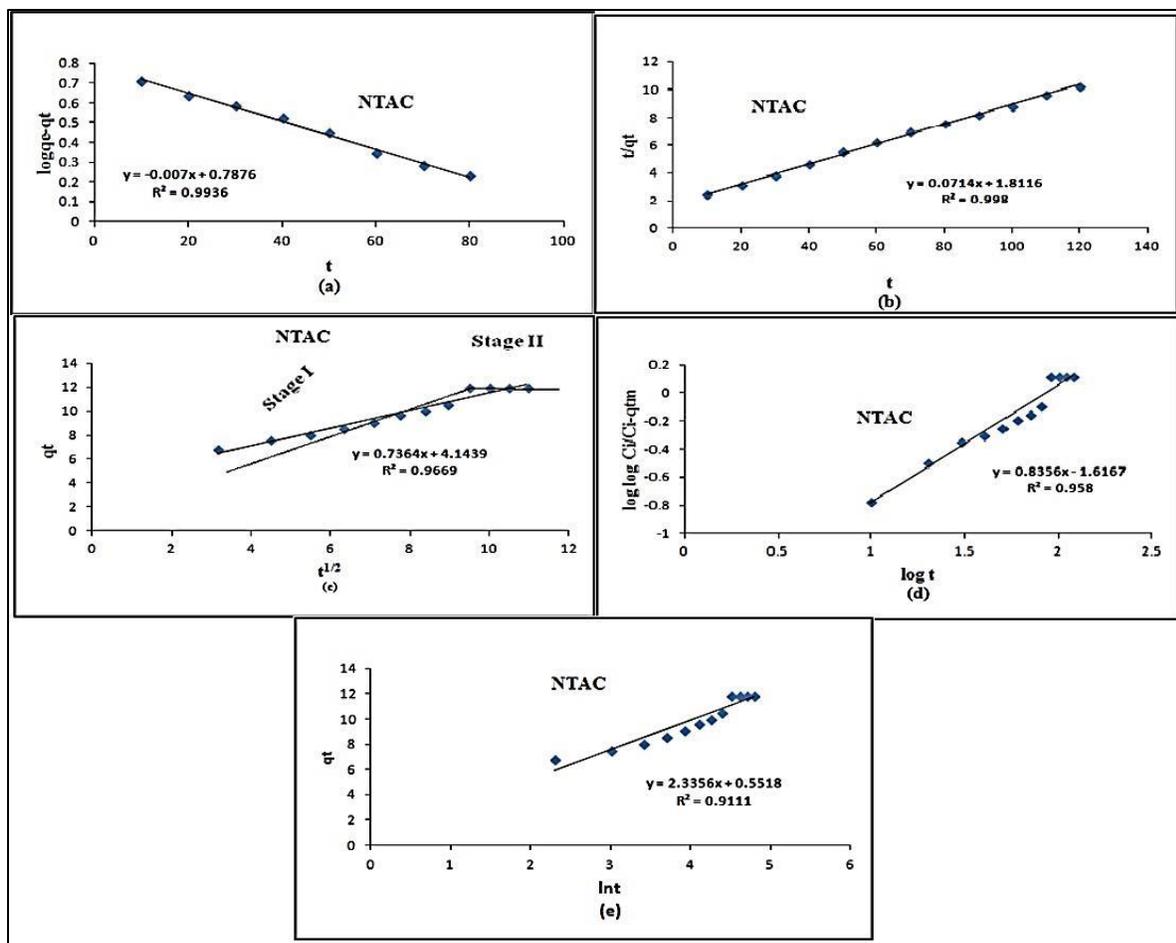


Figure 15: Kinetic models: (a) Pseudo first-order, (b) Pseudo second-order, (c) Weber and Morris intra particle diffusion, (d) Bangham's pore diffusion and (e) Elovich model

Table 6: Kinetic parameters

Pseudo first-order	Pseudo second-order	Weber and Morris	Pore diffusion	Elovich					
$q_e$	2.1982	$q_e$	14.0056	$q_e$	11.13	$q_e$	8.35	$q_e$	4.818
$K_1$	1.61	$K_2$	0.28	$K_{ip}$	0.736	$K_0$	23.11	$\beta$	0.4281
$R^2$	0.993	$R^2$	0.998	$R^2$	0.966	$R^2$	0.958	$R^2$	0.911

Units:  $q_e$ ( $\text{mg g}^{-1}$ ),  $k_1 \times 10^{-2}$ ( $\text{min}^{-1}$ ),  $K_2 \times 10^{-2}$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $K_{ip} \times 10^{-2}$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ),  $K_0$ ( $\text{mlg l}^{-1}$ )

The applicability of kinetic equations is compared from the correlation coefficients ( $R^2$ ) of these five kinetic models. Based on correlation coefficient values ( $R^2$ ), the applicability of the above five kinetic models to the present adsorption process is as follows. Pseudo second-order > pseudo first-order > Weber -Morris intraparticle diffusion > Bangham's pore diffusion > Elovich. The correlation coefficient value for pseudo second-order model is greater than that of other models and this indicates that the pseudo second-order model ( $R^2=0.998$ ) is best fit to the experimental data of the present studied adsorption system.

## CONCLUSION

An efficient and inexpensive adsorbent has been developed for the removal of chromium ion from aqueous solutions in this study. The results indicated that the maximum chromium ion adsorption takes place at the pH: 2.0, adsorbent dosage: 4.0 g/lit; equilibrium time: 90 min, Particle size: 45  $\mu$  and temperature:  $30 \pm 1^\circ\text{C}$ . It is observed that the adsorption process satisfactorily fitted with Langmuir adsorption isotherm which has good correlation coefficient value ( $R^2=0.999$ ) indicating monolayer adsorption. The Temkin heat of sorption,  $B=1.0278$  J/mol and the Dubinin-Radushkevich mean free energy,  $E=3.16$  kJ/mol for the activated carbon adsorbent NTAC are an indication of

'physisorption' process. In the kinetic studies of the adsorption of chromium ion on the adsorbent NTAC, the pseudo-second-order kinetic model with good correlation coefficient ( $R^2=0.998$ ) is best fit for the adsorption process. SEM, EDX data of the active carbon have shown a morphological change on the adsorbent surface before and after adsorption of chromium ion and FTIR studies have indicated the involvement of some surface functional groups in chromium ion adsorption. XPS report to investigate the chemical composition of surfaces of sample before and after chromium ion treatment shows a change.

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