

# Low Cost Biosorbent for the Removal of Chromium (VI) from Polluted Waters

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**Abstract:** An efficient and inexpensive activated carbon sorbent has been derived from the stems of *Carissa Carandas* (NCCC) for the removal of chromium (VI) from contaminated waters by using batch adsorption method. pH, contact time, adsorbent dosage initial concentration, particle size and temperature effected the percentage removal of chromium from solution. To study the mechanism of adsorption process, the adsorption isotherms have been applied. The adsorption is found to be physisorption. Kinetic studies for the adsorption process have been carried out. 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. The effect of interfering ions has also been studied. The developed methodologies have been put to test with respect to contaminated waters from industrial effluents and natural waters from lakes and found to be remarkably successful.

**Keywords:** *Batch adsorption technique; inexpensive adsorbent; Surface characterization; Adsorption isotherms; kinetic study, Applications.*

## I. INTRODUCTION

Increasing water pollution by heavy metals as major pollutants in marine, ground and industrial waters is the major concern for their treatment in polluted waters. The presence of heavy metals in the environment is a burning problem because of their toxic nature and other adverse effects on receiving waters. Chromium, copper, zinc, manganese, iron, mercury, lead and cobalt are the heavy metals to mention and their presence beyond the permissible limits can cause various chronic disorders in human beings. Chromium ions in water mainly hexavalent chromium originates from industries such as electroplating, metal finishing and tanning. As defined by US (EPA) Environment protection Agency chromium is the most toxic pollutant metal from all other polluted toxic metals. Chromium exists in environment mainly in two oxidation states, namely +3 and +6. The Chromium (III) on hydrolysis produces mononuclear species  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})_2^+$ ,  $\text{Cr}(\text{OH})_4^-$ ,  $\text{Cr}(\text{OH})_3$ , polynuclear species  $\text{Cr}(\text{OH})_2$  and neutral species  $\text{Cr}(\text{OH})_4$ . Whereas Chromium (VI) on hydrolysis produces neutral and anionic species. Chromium exists in the form  $\text{CrO}_4^{2-}$  at pH greater than 6.5. Therefore the removal of chromium ions from polluted waters is highly important as both the trivalent and hexavalent oxidation states are toxic and in which the former is less toxic than the latter because chromium (VI) compounds are highly soluble in water and have high mobility. The permissible maximum limit of chromium in water is 0.05ppm.

Many techniques are available for the removal of toxic heavy metal ions. Conventional methods such as ion exchange[1], Chemical reduction[2], Chemical precipitation[3], polymer based membrane separation[4,5],electrolysis and electroplating[6,7], solvent extraction[8], electro kinetic remediation[9] and non conventional methods based on biosorbent[10], activated carbons[11,12,13], coconut fiber[14], Eucalyptus bark [15], fly ash[16], bone charcoal [17,18], Neem saw dust [19] have been investigated to remove chromium (VI) from waste waters Nevertheless many of these approaches have one or other disadvantages. Therefore the need arises for a universally acceptable simple, economical, effective and eco-friendly method to remove the toxic metals.

In the present study, search has been carried out for active carbon derived from plant materials belonging to different classes of plant kingdom. Our investigations indicated that activated carbon of plant **Carissa carandas** (NCCC) is a low cost and effective material for the maximum removal of chromium (VI) from polluted waters and recovery of the adsorbent is also good. So this work is mainly concentrated to study in-depth the sorption characteristics of the above said active carbon towards chromium (VI) with respect to various physicochemical parameters such as contact time, pH, carbon dosage, initial concentration of chromium, particle size, temperature and the presence of foreign ions. The mechanism of sorption is probed in order to establish for the observed sorption phenomenon by making

morphological studies adopting techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and photoelectron Spectrometer (XPS).

The adsorption process has been analyzed by applying adsorption isotherms and kinetics of adsorption also studied. Further the applicability of the adopted methodologies has been tested for industrial effluents and natural lake waters.

## II. EXPERIMENTAL PROCEDURE

### 1. Plant description

The active carbon prepared from stems of **Carissa carandas** (NCCC) plant were used for chromium (VI) removal from waters.



Fig.1: Carissa carandas plant

The **Carissa carandas** plant (Fig.1), locally known as karonda or vakkay or kale (in Telugu), belongs to the Apocynaceae family in plant kingdom. Carissa carandas is a species of flowering shrub in the dogbane family. It produces berry-sized fruits that are commonly used as a condiment in Indian pickles and spices. It is a hardy, drought-tolerant plant that thrives well in a wide range of soils. It grows naturally in the Himalayas at elevations of 300 to 1800 meters from sea level in the Siwalik Hills, the Western Ghats and in Nepal and Afghanistan and flourishes well in regions with high temperatures. In India it is grown on a limited scale in Rajasthan, Gujarat, Bihar, West Bengal and Uttar Pradesh and also grows in the Sri Lanka lowland rain forests.

### 2. Preparation of NCCC (activated Carbons)

Stems of Carissa carandas (Apocynaceae) plant was collected and cut in to small pieces and air dried. It is washed with double-distilled water and treated with 0.1N HNO<sub>3</sub>. It is electrically heated at 500<sup>0</sup>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<sup>0</sup>C. The activated carbon was sieved to an average diameter of about 0.01119mm for adsorption experiments.

### 3. Chromium (VI) solution:

All the chemicals used in the present work were of Analytical Reagent grade and purchased from Merck. India Pvt. Ltd. (Bengaluru, India). A stock solution of chromium (VI) was prepared by dissolving appropriate amount of Potassium Dichromate in double-distilled water. This solution was diluted to obtain standard solution containing 5ppm chromium (VI) ions. 0.25% of 1,5 Diphenyl Carbazide in 50% of acetone and 6N Sulphuric acid was used.

### 4. Adsorption Experimental procedure:

Adsorption studies were carried out by batch method using a test solution of 50mg/lit of chromium (VI) ions. From this 50mg/lit chromium ion solution, 100ml of solution was pipetted out into a 250ml iodine flask at room temperature 30±1<sup>0</sup>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 pH meter using a combined glass electrode. The solution was shaken in an orbital electronic shaker at 120rpm. 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 mins. 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 in acidic solution as a complexing agent. The absorbance of purple violet colour solution is read at 540nm.

### 5. Chromium ion analysis:

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

$$\% \text{ Removal } (\%R) = \frac{(C_i - C_e)}{C_i} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_e)}{m} V$$

Where C<sub>i</sub> = Initial concentration of the chromium (VI) solution in mg/lit

C<sub>e</sub> = 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 for the experiments carried out by varying physicochemical parameters such that contact time, pH, carbon dosage, initial concentration of chromium, particle size, temperature and the presence of foreign ions.

### Characteristics of the Nitric acid activated Carbons:

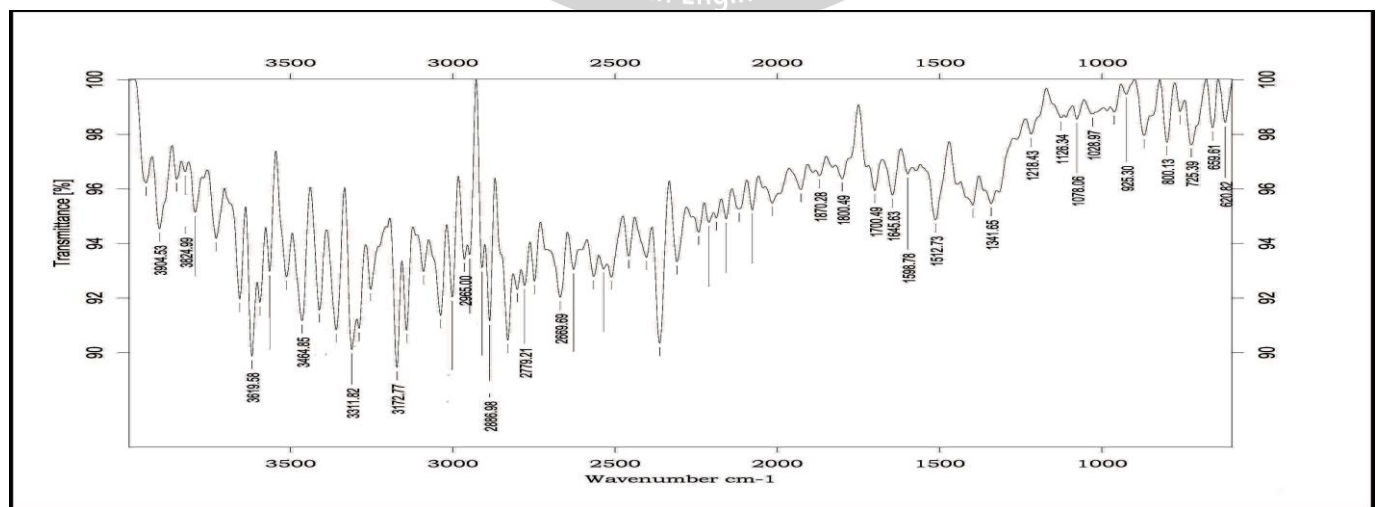
Physicochemical characteristics of NCCC were studied by using standard methods and the results are presented in table-1. The pH for the activated carbon adsorbent was determined using the Elico pH meter, model LI-120, and the pH<sub>ZPC</sub> was determined using the pH equilibrium method [20,21,22]. Particle size was determined using American

Standard Test Method (ASTM) sieves[23]. Iodine number[24,25], decolorizing power[26,27] 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[28,29]. The BET surface area[20,30,31] 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 [32, 33,34]

**Table 1: Physicochemical characteristics of NCCC**

S.No:	Parameter	Value	
1	Apparent density,(g/ml)	0.226	
2	Moisture content, (%)	5.210	
3	Loss on Ignition (LOI), (%)	79.80	
4	Ash content, (%)	5.899	
5	Water soluble matter, (%)	0.69	
6	Acid soluble matter, (%)	0.557	
7	Decolorizing power,(mg/g)	284.33	
8	pH	2.13	
9	pH <sub>ZPC</sub>	6.203	
10	Iodine number,(mg/g)	556.33	
11	Particle size(μ)	45	
12	BET Analysis - Surface area, m <sup>2</sup> /g	Before	208
		After	189.7
13	Surface functional groups (meq/g)-Boehm Titration		
I	Carboxyl	1.015	
II	Lactonic	0.983	
III	Phenolic	1.1153	
IV	Carbonyl	1.219	
V	Total basic groups	6.486	

**FTIR analysis**



**Fig.2: FTIR spectra of NCCC before chromium (VI) adsorption**

Fourier Transform Infrared spectroscopy (FTIR) is used to examine the surface functional groups on NCCC. The spectra were measured from 4000cm<sup>-1</sup> to 500cm<sup>-1</sup> on a BRUKER VERTEX 80/80v FT-IR spectrometer. Whose optical resolution is <0.06 cm<sup>-1</sup>, with automatic and vacuum compatible beam splitter changer (BMS-c) option. Anhydrous KBr pellet was used.

**Scanning electron microscopy (SEM)**

The analysis of the microstructure morphology and chemical composition characterizations were carried out by using Scanning electron microscopy (SEM). The micrographs of NCCC were recorded using LEO 1420 VP Compact variable pressure Digital SEM, manufactured by Leo Electron Microscopy Ltd. (Beam voltage 500 to 2000V, Magnifications 250 to 65,000 X, Resolution 3nm at 1000V).

**Energy Dispersive Spectroscopy (EDS)**

The elemental analysis to identify the elements and their relative proportions (atomic %) of a sample is carried out by using Energy-dispersive X-ray spectroscopy. The elemental analysis was recorded for NCCC BRUKER EDX Two-dimensional VANTEC-500 detector.

**Photoelectron Spectrometer (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 chemical information of the surface of the material being studied. XP Spectrometers to study the chemical analysis of NCCC, ESCA LAB 250Xi X-ray Photoelectron Spectrometer is used.

**III. RESULTS AND DISCUSSIONS**

**FT-IR Analysis:**

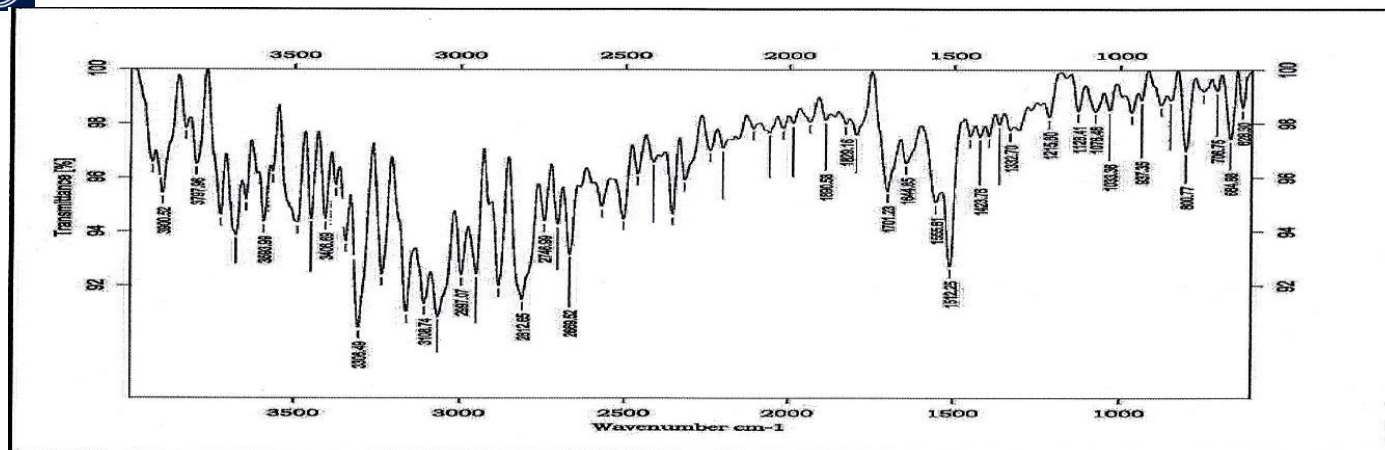


Fig.3: FTIR spectra of NCCC after Chromium (VI) adsorption

Fourier transforms infrared (FT-IR) spectroscopy give confirmation regarding the presence of specific functional groups on the surface of carbon materials. The FTIR spectra of NCCC before and after adsorption of chromium (VI) are presented in fig 2 and 3 and the results are presented in table -2. By observing the figures it is confirmed the occurrence of chromium (VI) adsorption on the active carbon NCCC as there was some changes in vibrational frequencies and decrease in the percentage of the transmittance in the FTIR spectra of the solid surface in the range 4000cm<sup>-1</sup> to 500cm<sup>-1</sup>. The FTIR spectra show the adsorption band at 3824cm<sup>-1</sup> and 3311cm<sup>-1</sup> corresponding to the stretching vibration of O-H and N-H respectively. The Adsorption bands at 1700cm<sup>-1</sup> (carboxylic) and 1645cm<sup>-1</sup> (carboxylate) are responsible functional groups for metal ion sorption [35]. Strong peaks at 2965cm<sup>-1</sup> and 2886 cm<sup>-1</sup> corresponding to stretching vibrations( symmetric and asymmetric) of aliphatic C-H,[36,37,38,39] bending vibrations of methylene and methyl peaks due to inplane bending vibration of C-H of methylene group[40,41,42], peaks due to C-O stretching in alcohols, phenols, lactones, ethers, esters, acids, epoxides[40,41,43-49], peaks due to out of plane deformation vibration of C-H groups in aromatic structures[50,51,52] have been observed. The adsorption process is understood to be of physisorption but not chemisorption due to the absence of C-Cr peak.

Table 2: Bands assigned to the surface functional groups of NCCC before and after absorption.

3	1870.28, 1800.49 1700.49 1645.63	1890.58, 1829.16, 1701.23 1644.85	-C=O in Carbonyl, Carboxyl groups and Lactones
4	1598.78, 1512.73, 1434.25, 1341.65	1555.61, 1512.25, 1423.76, 1332.70	-C=C- in Aromatic rings,-C=O in highly conjugated Carbonyl groups and -C-H Deformations in Alkanes.
5	1218.43 1126.34, 1078.06 1028.97	1215.60, 1128.41, 1076.46, 1033.36	-C-O- in Alcohols, Phenols, Ethers, Esters, Acids, Epoxides, Lactones and Carboxylic anhydrides.
6	925.30, 800.13, 725.39, 659.61, 620.82	871.86, 800.77, 706.75, 664.86, 628.30	-C-C- deformations and out of plane -C-H Deformations in Aromatic rings.

#### SEM Analysis:

SEM has been studied to know the surface characteristics of the adsorbent, NCCC 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 fig-4. From the above studies it is informed that a well developed surface area was observed in a randomly distributed pore size in all micrographs.

S.No:	Wave number (cm <sup>-1</sup> )		Bond Stretching
	NCCC (before)	NCCC (after)	
1	3824.99, 3619.58, 3464.85, 3311.82, 3172.77	3797.69, 3593.99, 3406.69, 3306.49, 3108.74	-O-H in Alcohols, Acids Phenols and -N-H in Amines and Amides
2	2965.00, 2886.98, 2779.21, 2669.69	2997.07, 2812.65, 2746.99, 2669.52	-C-H in -CH <sub>3</sub> and -CH <sub>2</sub>

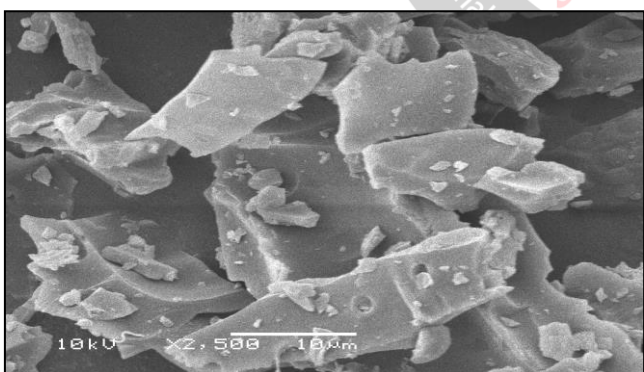
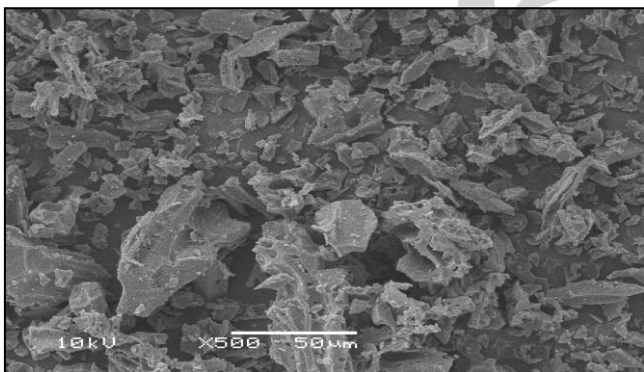
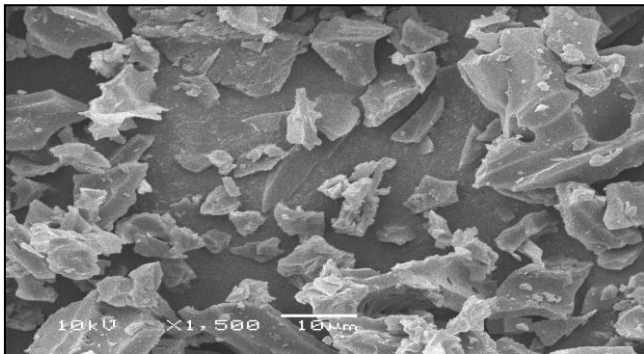
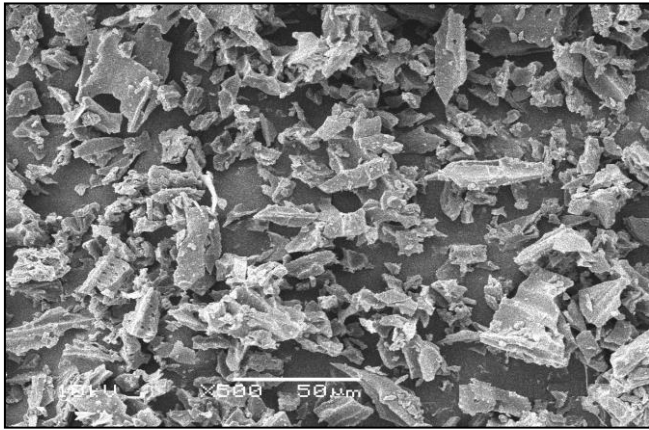


Fig.4: SEM analysis of NCCC before (left) and after (right) adsorption at X5000 and X6000 magnifications

**EDX Elemental Analysis:**

To study the chemical composition of the activated carbon the Energy-dispersive X-ray spectroscopy (EDX) studies were carried out for the activated carbon, NCCC. Fig 5 and 6 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 5 and 6, we observe an extra peak at 5.2 in fig 6 representing chromium after the adsorption which concludes there is chromium adsorption. The analysis results were shown in table 3.

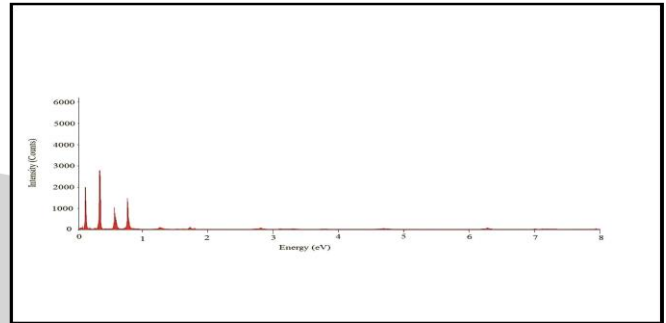


Fig.5:EDX spectra of NCCC before adsorption

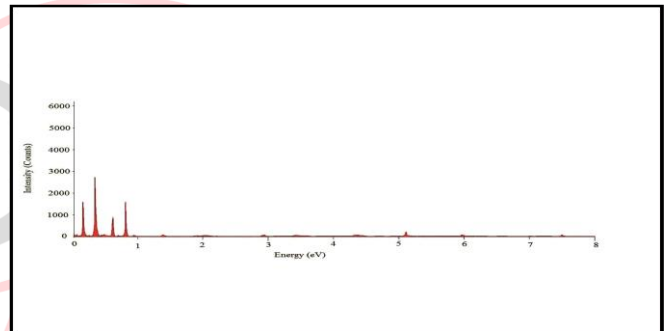


Fig. 6: EDX spectra of NCCC after absorption

Table 3: Elemental analysis of NCCC before and after absorption of Chromium (VI)

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)	73.5	8.8	17.7	---	100	69.9	7.4	19.6	3.1	100

At%	72.8	9.2	18.0	---	100	69.1	7.6	20.1	3.2	100
(Atomic percentages)										

**Photoelectron Spectrometer (XPS):**

XPS is a useful analytical technique to study elemental analysis and was studied to investigate the chemical composition of surfaces of NCCC before and after chromium (VI) ion treatment. The X-ray spectra of the activated carbon NCCC before treatment exhibited the peaks between 285 -290; 390-400; 528-535 (ev) indicates the presence of C, N, and O elements on the surface of the sample. The XPS survey scan spectra of NCCC are presented in fig-7. The high intensity peak at the 579 region in addition to the above said peaks indicates the presence of chromium (VI) when the sample is treated with chromium (VI) ions. XPS binding energy (eV) value for N 1s and C 1s for aliphatic species are presented in table-4.

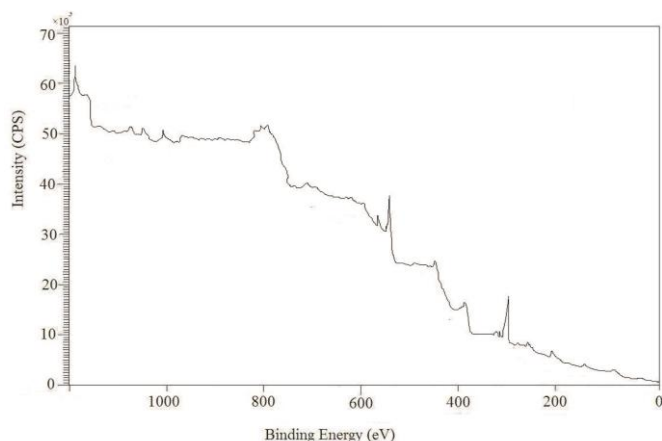


Fig.7: XPS Survey Scan spectra of NCCC

**Table 4: XPS reference table with N 1s and C 1s binding energies**

C-H	284.3
C-C	285
C-N	285.7
C=N/C≡N	286.5-286.7
C-O	286.2-286.7
C=O	287.6-287.9
CO NH <sub>2</sub> (amide)	287.9-288.3
COOH	289.3-290.5
COOR	289.4
N=C	397.8-399.0
N≡C	398.0
N=C=C	398.8
NH <sub>2</sub>	399.0-399.3
NHC=O	400.3-400.7
NH <sub>2</sub> /NH <sub>3</sub>	400.6-401.9

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 5.0g/lit. A graph is

drawn between the percentage removal of chromium and adsorbent dosage and is presented in fig -8.

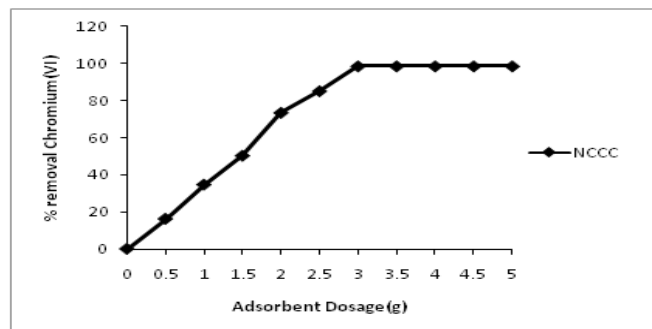


Fig. 8: Removal of chromium (VI) as a function of adsorbent dose

It is seen from the graph, up to 3.0 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. 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 NCCC 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.

**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 fig-9.

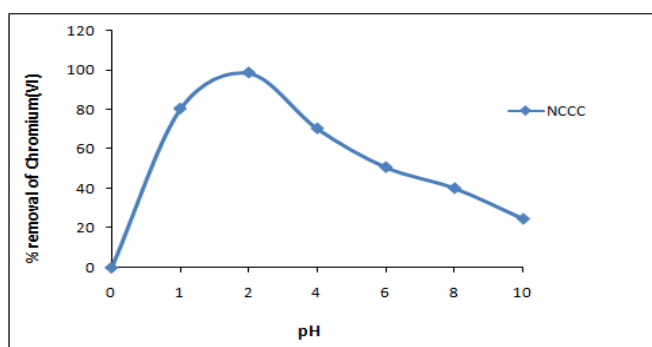


Fig. 9: Removal of chromium (VI) as a function of pH

As seen from fig-9 that NCCC is active in acidic range especially at low pH range. The maximum adsorption of

chromium (VI) on the adsorbent was at pH - 2.0 and negligible at pH-10. Chromium (VI) can exist 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 NCCC surface is supposed to be favored. 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.

#### Contact time:

The effect of contact time of the chromium (VI) ion with adsorbent on removal of chromium (VI) ion was studied at optimum conditions with varying contact time from 0 to 100 min. For every 10 min interval an aliquot of the solution was withdrawn and the removal of chromium (VI) was established by analyzing chromium (VI) spectrophotometrically. A plot is drawn between the % removal of chromium (VI) ion and contact time (min) and is presented in Fig.10.

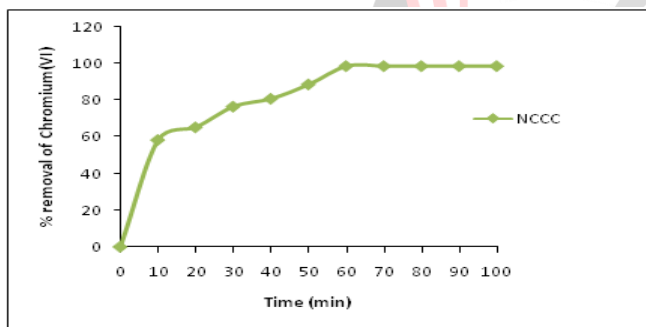


Fig. 10: Removal of chromium (VI) as a function of contact time (min)

From the figure it is seen that with increase in contact time the percentage removal of chromium (VI) increases and attains equilibrium at 60 min. After this period the percentage removal remains constant that is an equilibrium state has been reached. At the equilibrium state the rate of sorption of chromium (VI) is equal to the rate of desorption on the intersurface. This indicates that the optimum time required for maximum removal of chromium (VI) is 60 min. The rate of adsorption is found to be more initially but as the time passes on it decreases and reaches a steady state after certain time. This can be explained that initially in the sorbent surface many active sites are available for adsorption of chromium (VI) ions to occur and with time they are progressively used up, and hence the rate of adsorption is decreased. A saturation state has been reached after certain time as there are no active sites on the surface of sorbent for the adsorption to take place and therefore there will not be any further adsorption. The decrease in the

removal rate indicates the possible monolayer of chromium (VI) ions on the outer surface and pores of the adsorbent leading to pore diffusion onto inner surface of adsorbent particles.

#### Initial concentration

The removal of chromium by the sorbent with initial concentration of chromium ion in solution has been studied and the initial concentration was varied from 10 to 100 mg/lit. The variation of the % removal of chromium (VI) ion with concentration of it in solution is shown in Fig.11.

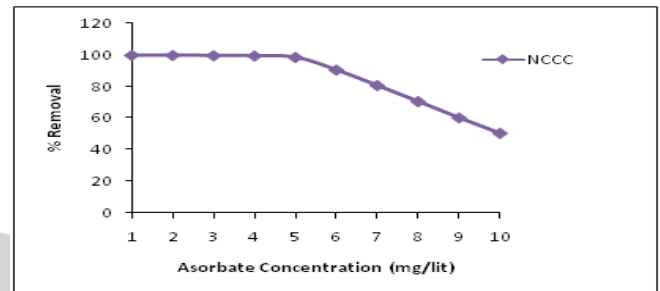


Fig.11: Removal of chromium (VI) as a function of concentration of chromium ion Solution

As the concentration of chromium (VI) ions in solution increases, the % adsorption of chromium (VI) ions decrease due to the number of active adsorption sites are not enough to accommodate the chromium (VI) ions as concentration is increased, because insufficient number of active sites available for adsorption as the concentration of chromium(VI) is increased. At low concentration of chromium (VI) ions in solution, the availability of active sites on the adsorbent surface is more to interact sufficiently and be removed from the solution. As the initial concentration of chromium (VI) ions increases in solution from 10 to 100 mg/lit, the percentage removal of chromium ion decreased from 99.7 to 50.4% for NCCC.

#### Particle Size:

The percentage removal of chromium was effected by the size of the particle and the studies were carried out with the change in particle size from 45 to 150 $\mu$  mesh at optimum conditions. A plot is drawn between the % removal of chromium ion and particle size and is presented in fig.12.

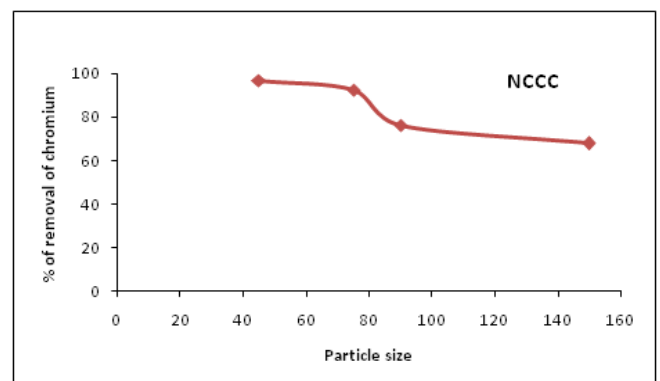


Fig.12: Removal of chromium (VI) as a function of particle size

It is seen from the graph that the % removal of chromium ion is inversely related to the particle size of the activated carbon adsorbent that is as the particle size decreases the adsorption of chromium ion increases and vice versa. The reason is that more will be surface area and more will be number of sites available on the surface as the size of the particle decreases and hence adsorption will be more with increase in size of the particles there will be insufficient number of active site available and the percentage removal of chromium (VI) ion decreases. The maximum removal of chromium (VI) ions is achieved with a particle size below 45 $\mu$ .

#### Co-ions on chromium (VI) adsorption:

The effect of the interfering common co-ions is studied on the % removal of chromium ions by NCCC was studied with tenfold excess of concentration of co-ions. Commonly found cations in water such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, K<sup>+</sup> and anions such as PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> under optimum conditions. The results obtained were presented in Fig.13.

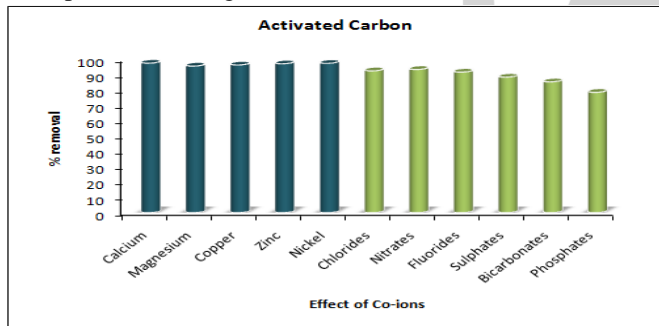


Fig. 13: Effect of co-ions on (% removal) of chromium ion onto NCCC

It was observed from the graph cations on the sorption of chromium (VI) by NCCC had insignificant effect. This can be understood by the fact that the overall surface charge on the sorbent surface becomes positively charged which will inhabit the approach of positively charged metal cations as a result of repulsive force [53]. Anions had reduced the removal efficiency under the given experimental conditions. The effect of ions Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> on the removal of chromium (VI) by NCCC is less when compared to SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>. SO<sub>4</sub><sup>2-</sup> has significant effect on the adsorption of chromium and it could be attributed to higher negative charge compared to that of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> 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 adsorbent surface is decreased and this results decrease in the removal of chromium ions. The effect of interference of PO<sub>4</sub><sup>3-</sup> ion on the removal of chromium ions is maximum because of its high negative charge compared to the other anions. The PO<sub>4</sub><sup>3-</sup> 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.

#### Temperature:

The effect of temperature on the % removal of chromium was studied at different temperatures 303, 313 and 323K, at optimum conditions of extraction. The results obtained were plotted as lnK<sub>d</sub> Vs 1/T as shown in Fig.14. Thermodynamic parameters 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) of the adsorption were determined at the above said temperatures by using the following equations.

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

$$\Delta G = -RT \ln K_d$$

$$\ln K_d = \Delta S/R - \Delta H/RT \text{ and}$$

$$K_d = q_e/C_e$$

Where K<sub>d</sub> is the distribution coefficient for the adsorption, q<sub>e</sub> is the amount of chromium ion adsorbed on the activated carbon

adsorbent per litre of solution at equilibrium,

C<sub>e</sub> 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 lnK<sub>d</sub> and 1/T and  $\Delta G$  values were obtained from the equation  $\Delta G = \Delta H - T\Delta S$  and are presented in table-5.

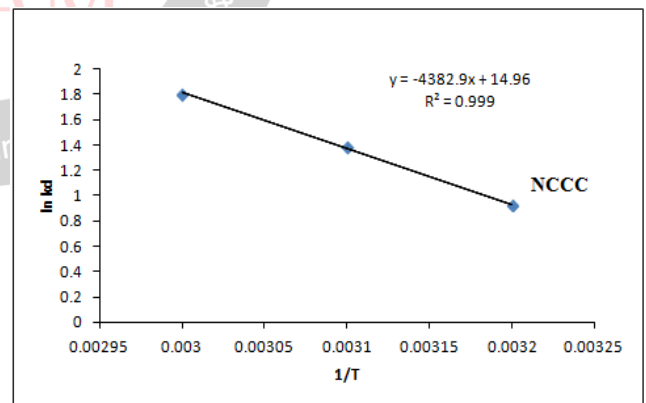


Fig. 14: Effect of temperature on (% removal) of chromium ion onto NCCC

It is seen from table-5 that  $\Delta G$  has negative values indicating that the adsorption process is spontaneous. It is also observed that negative values of free energy change, increases with increase in temperature. This may be ascribed to activation of more sites on the surface of NCCC with a raise in temperature or that the energy of adsorption sites as an exponential distribution band at higher temperature enabling the energy barrier of adsorption to be



overcome. When the free energy change  $\Delta G$  ranges between -20 and 0 KJ/mol, adsorption is classified as physical adsorption, while in chemical adsorption values of free energy change range from -8 to -400KJ/mol. The  $\Delta G$  for chromium (VI) adsorption on to NCCC was in the range of (-1.25 to -3.73) KJ/mol and so the adsorption was predominantly physical adsorption or physisorption. The positive value of  $\Delta S$  (124.38) J/molK indicates there is an increased randomness at the solid solution interface during the adsorption of chromium (VI) ions onto NCCC. It is also known from the table-5 that the adsorption is an endothermic process.

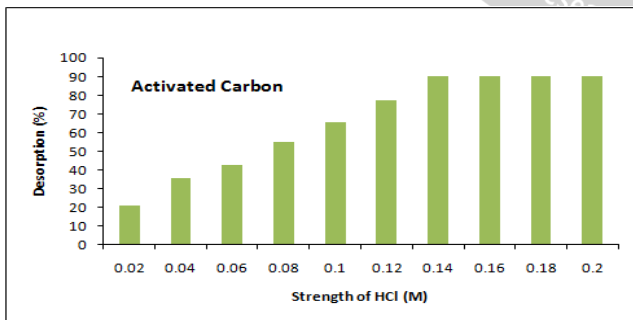
**Table 5: Thermodynamic parameters of chromium ion adsorption on NCCC.**

Parameter	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)	$\Delta G$ (kJ/mol)			$R^2$
			303	313	323	
Temperature(K)						
NCCC	36.44	124.38	-1.25	-2.4	-3.73	0.999

**Desorption:**

NCCC 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 acid strength varying from 0.02 to 0.2 M. The NCCC carrying 16.43mg Cr (VI) /g was placed in the desorption medium and stirred at 120 rpm at 30±1oC. The final chromium (VI) ion concentration in the aqueous phase was determined spectrophotometrically, the desorption ratio was calculated from the amount of metal ion adsorbed on the carbon and the final metal ion concentration in the desorption medium using the equation.

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



**Fig -15: Desorption studies using various strength of HCl NCCC**

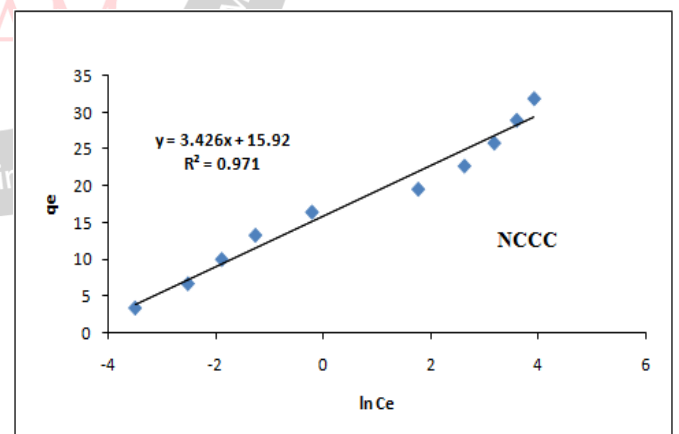
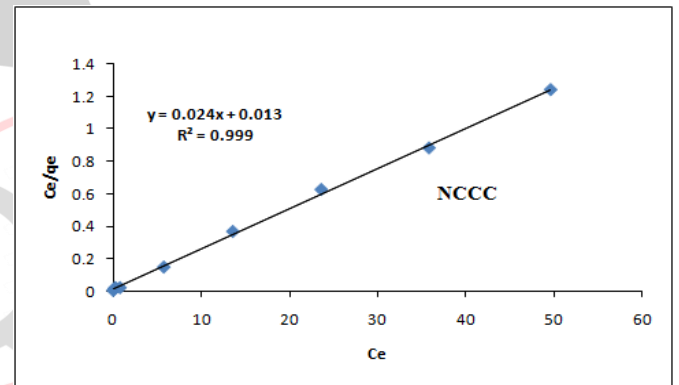
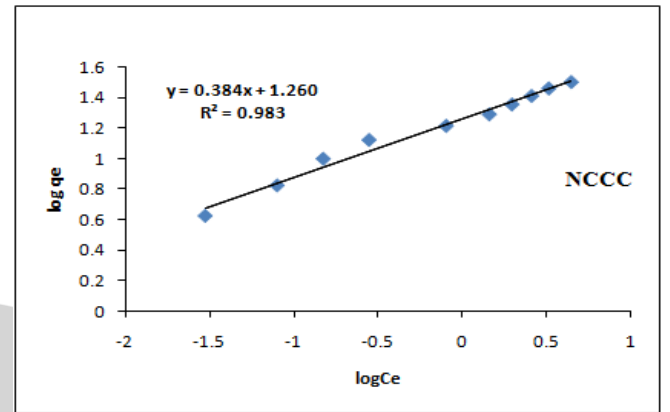
The results are plotted in fig-15. It is observed from the graph that 0.2M HCl could desorb a maximum of 92.5% from NCCC.

**Adsorption Isotherms**

Four adsorption isotherm models were studied for the adsorption of chromium (VI) ions onto NCCC: Freundlich [54], Langmuir [55], Temkin [56] and Dubinin-

Radushkevich [57] 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 Freundlich:  $\log(q_e) = \log k_f + (\frac{1}{n}) \log C_e$ , Langmuir:  $C_e/q_e = (a_L/k_L)C_e + 1/k_L$ , Temkin:  $q_e = B \ln C_e + B \ln A$  and Dubinin Radushkevich:  $\ln q_e = -\beta \epsilon^2 + \ln q_m$



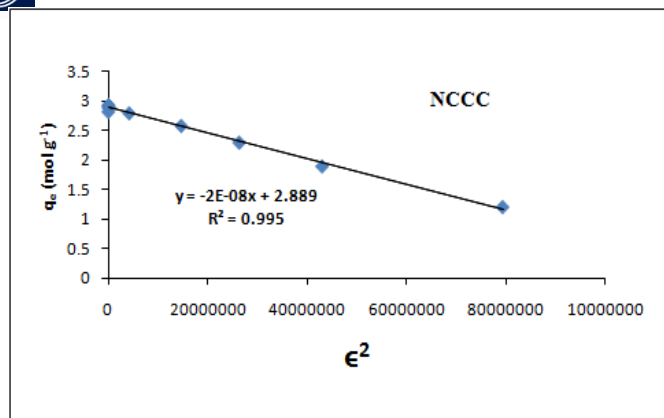


Fig-16: The Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherms.

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  $\epsilon^2$  for Dubinin Radushkevich and they are presented in fig-16 (a-d). From graph 16(a) the Freundlich constants  $n$  and  $k_f$  are calculated from slope and intercept of linear plot and found to be 2.60416 and 3.5254 respectively. The correlation coefficient  $R^2$  value is 0.983.  $aL/kL$  and  $1/kL$  are calculated from the slope and intercept of linear graph 16(b) of Langmuir isotherm. The important characteristics of Langmuir isotherm are expressed in terms of dimensionless constant separation factor  $R_L$  is expressed as  $R_L = 1/(1 + aL C_i)$ , 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 conformed 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-6.

Table -6: 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 correlation coefficient ( $R^2=0.999$ ) value was higher for the activated carbon NCCC in the Langmuir isotherm than the Freundlich isotherm. The dimensionless equilibrium factor ( $R_L=0.01072$ ) value indicates the favorability of the Langmuir isotherm. The applicability of Temkin isotherm is known from the linear graph of 16(c). The  $R^2$  value for this isotherm is 0.971 and the Temkin constants  $A$  and  $B$  are calculated from intercept and slope of the plot. In Dubinin Radushkevich isotherm  $\beta$  is a constant related to sorption energy,  $E = 1/\sqrt{2\beta}$ ,  $\epsilon$  is the Polanyi potential which is related to equilibrium concentration,  $\epsilon = RT \ln(1+1/C_e)$ , where  $R$  is gas constant,  $T$  is absolute temperature. In this isotherm the  $R^2$  value is 0.995 and  $\beta$  and  $\ln q_m$  are calculated from slope and intercept of the graph 16(d). The Dubinin

Radushkevich mean free energy  $E$  is found to be 5.0 kJ/mole for activated carbon adsorbent NCCC.

The adsorption mechanism is physisorption since the value is less than 8kJ/mole. The values of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherms constants along with their correlation coefficient values are present in table-7

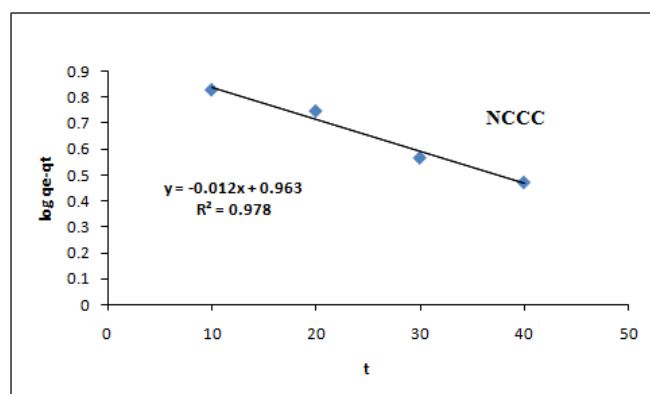
Table 7: Adsorption isothermal parameters of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich plots

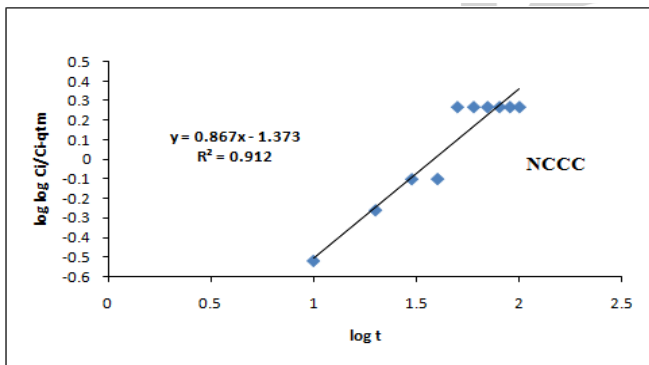
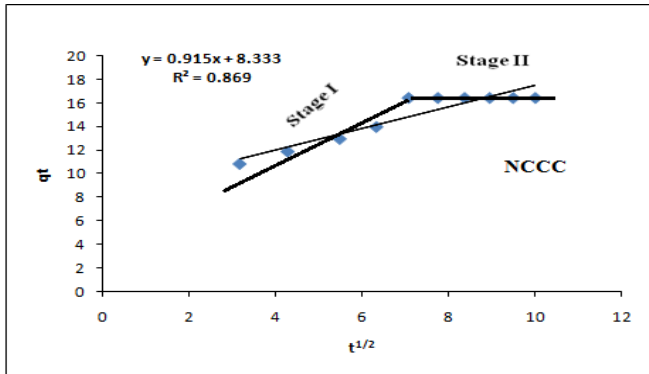
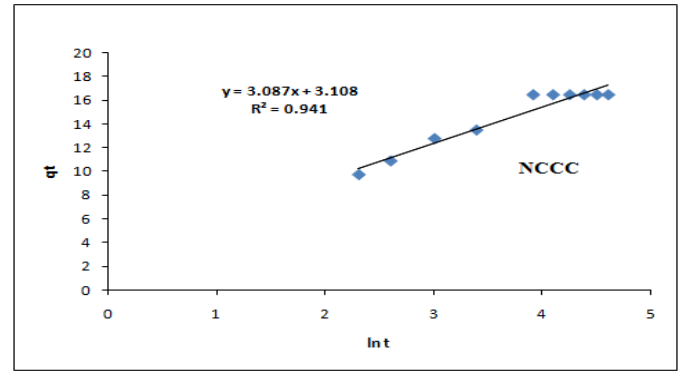
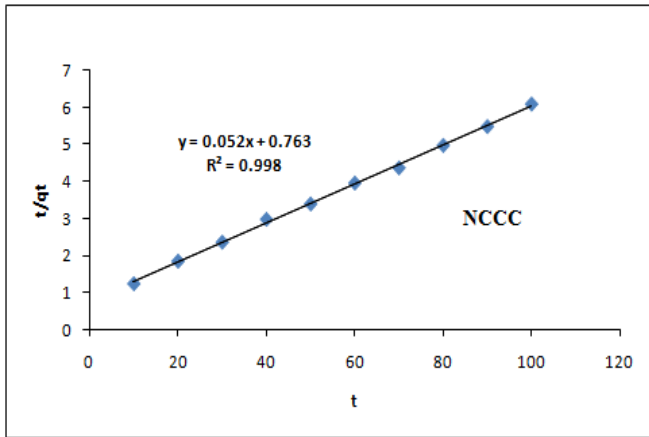
S.No:	Adsorption isotherms		Slope	Intercept	$R^2$
1	Freundlich Isotherm		0.384	1.266	0.983
2	Langmuir isotherm	$R_L=0.01072$	0.024	0.013	0.999
3	Temkin Isotherm	$B=3.426$ J/mol	3.426	15.92	0.971
4	Dubinin-Radushkevich isotherm	$E = -5.0$ kJ/mol	-2E-08	2.889	0.995

### Adsorption Kinetics

To study the rate and kinetics of adsorption of chromium (VI) ions onto the activated carbon sorbent, NCCC, some kinetic models were applied and discussed in the present work. The applied kinetic models are pseudo first-order model [58] which is represented as  $\log(q_e - q_t) = \log q_e - k_1 t / 2.303$ , pseudo second-order model [59] is  $t/q_t = 1/k_2 q_e^2 + (1/q_e) t$ , Weber and Morris intraparticle diffusion Model [60] equation is  $q_t = k_{ip} t^{1/2} + c$ , Bangham's pore diffusion model [61] equation is  $\log[\log(C_i/C_i - q_m)] = \log(k_p / 2.303 V) + \alpha \log(t)$  and Elovich equation<sup>62</sup> as  $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$ .

Linear plots 17. (a-e) are observed 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  $t$  for pseudo second-order model,  $q_t$  versus  $t^{1/2}$  for Weber and Morris intraparticle diffusion Model,  $\log[\log(C_i/C_i - q_m)]$  versus  $\log t$  for Bangham's pore diffusion model and  $q_t$  versus  $\ln t$  for Elovich equation. The values calculated from intercept and slope of the graphs [fig-17 (a-e)] for different kinetic models under study are presented in table-8.





**Fig.17: Pseudo first-order, Pseudo second-order, Weber and Morris intra particle diffusion, Bangham's pore diffusion and Elovich model.**

The applicability of kinetic equations is compared from the correlation coefficients (R2) of these five kinetic models. 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 (R2=0.998) is best fit to the experimental data of the present studied adsorption system. Next best model is pseudo first-order model (R2=0.978) followed by Elovich (R2=0.941), Bangham's pore diffusion model (R2=0.912) and least is Weber and Morris intraparticle diffusion model (R2=0.869).

**Table 8: Kinetic parameters**

S.No:	Adsorption Kinetics	Slope	Intercept	R <sup>2</sup>
1	pseudo first-order	-0.012	0.963	0.978
2	pseudo second-order	0.053	0.669	0.998
3	Weber and Morris intraparticle diffusion	0.915	8.333	0.869
4	Bangham's pore diffusion	0.867	-1.373	0.912
5	Elovich model	3.087	3.108	0.941

**Comparison of NCCC with other carbon sorbents:**

Comparison of maximum adsorption capacity, qe of NCCC with those of some other adsorbents stated in literature is presented in table -9. A comparison with other adsorbents proves that NCCC may be considered as good adsorbent. The variances in qe could be ascribed to the properties and nature of each adsorbent such as structure and surface area of the adsorbent.

**Table-9: Comparison of maximum uptake capacity for various carbon sorbents**

S. No.	Adsorbent	pH	Ci (mg/l)	qe (mg/g)	Reference
1	Gooseberry seeds	2.0	20-100	9.201	63
2	Dolochar	1.5	10-50	0.572	64
3	Sugarcane bagasse	2.0	10-40	2.12	65
4	Coconut Tree saw dust	3.0	5-20	3.38	66
5	Bamboo (Oxytenanthera abyssinica)	2.0	25-150	0.384	67
6	Marine algae Graciliria edulis	1.0	10-60	0.429	68
7	Coconut Shell	3.0	80	1.150	69
8	Palmyra palm fruit seed	2.0	3-20	0.54	70
9	Marine algae Enteromorpha SP.	1.0	10-50	8.0	71
10	NCCC	2.0	10-100	16.4	Present work

**APPLICATION:** The adoptability of the methodologies of this present work has been put to test by applying them to diverse water samples collected from the effluents of Tannery, Chrome plating industries and also in natural lakes. The results are presented in table-10.

**Table-10: Extractability of Chromium in different industrial effluents and natural lake samples using activated carbon (NCCC)**

% of extraction of chromium in diverse samples is as shown in the table					
<b>Tannery Industry effluents</b>					
Samples from different placeses	S-1	S-2	S-3	S-4	S-5
Concentration(ppm)	(12.5ppm)	(21.5ppm)	(15.5ppm)	(20.5ppm)	(14.5ppm)
Sorbent (NCCC)	84.6%	88.3%	80.2%	82.1%	86.4%
<b>Chrome plating Industry effluents</b>					
Samples from different placeses	S-1	S-2	S-3	S-4	S-5
Concentration(ppm)	(20ppm)	(20.5ppm)	(15.8ppm)	(21.0ppm)	(21.5ppm)
Sorbent (NCCC)	87.2%	81.9%	83.7%	84.5%	83.9%
<b>Natural Lake Samples</b>					
Samples from different placeses	S-1	S-2	S-3	S-4	S-5
Concentration(ppm)	(15ppm)	(20ppm)	(25ppm)	(21.0ppm)	(24ppm)
Sorbent (NCCC)	83.2%	83.8%	85.1%	86.5%	89.8%

It is found that the adsorbent, NCCC is used in the present work is successful in the removal of chromium ions at optimum conditions: pH, equilibration time, particle size, temperature and adsorbent dosage has discussed in the test.

From the table it is found that the % removal of chromium is found to vary from 80.2% to 89.8% in the collected samples and it may be concluded from the results presented in table that NCCC is a good sorbent in lowering the chromium content in water samples much below the permissible limits under optimum experimental conditions.

### III. CONCLUSIONS

An efficient and in expensive adsorbent (activated carbon adsorbent) has been developed for the removal of chromium ion from aqueous solutions in this study. The adsorption of chromium (VI) ions on to activated carbon prepared form stems of *Carissa carandas* (NCCC) plant was found to depend on pH values of solutions, adsorbent mass, contact time, temperature and initial chromium (VI) ion concentration. FTIR study indicated the participation of surface active sites on the adsorption of chromium ions. FTIR, SEM, EDX and XPS techniques confirmed adsorption of chromium (VI) ions on the adsorbent surface. Data of adsorption of chromium (VI) on NCCC were applied to adsorption isotherm models.

It is observed that the adsorption process satisfactorily fitted with Langmuir adsorption isotherm which has good

correlation coefficient value indicating monolayer adsorption. Freundlich, Temkin and Dubinin-Radushkevich isotherms indicated linear relationship and confirmed the heterogeneous surface of the adsorbent. The Dubinin-Radushkevich mean free energy,  $E = 5.0$  kJ/mol for the activated carbon adsorbent, NCCC indicates the phenomenon is physisorption. The thermo dynamic parameters proved that the adsorption process is spontaneous and endothermic. The kinetic studies of removal of chromium has been undertaken to identify the rate, and kinetics of adsorption process. In this adsorption process pseudo second order model has good correlation coefficient values indicating it is the best fit of all the kinetic models under study. Bangham's pore diffusion plays an important role in controlling the rate of reaction. The sorbent developed has been found to be effectively decreasing the chromium (VI) ions concentration in chromium solutions below the permissible limits and hence the adsorbent NCCC is a low cost, ecofriendly and effective sorbent and can be successfully applied to polluted water treatment technology in controlling the chromium (VI) ion concentration.

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