Amputation of Rash Dyes from Agricultural Waste Activated Carbon

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Abstract

Application of activated carbons developed from cashew nut and rose apple carbon from the agricultural waste product has been investigated for the removal of reactive green and reactive procion orange dyes from aqueous solution and waste water. Batch adsorption experiments are carried out for the removal of dyes (reactive green and reactive procion orange) from aqueous solution by using cashew nut (CNC) and rose apple carbon (RAC). The important parameters are studied like initial concentrations of dyes, contact time, dose of carbon, temperature variation and pH on removal of the dyes. The removal of dyes increased from 82 to 74 % for by decreasing the initial concentration 40 to 65 ppm for RG and 73to 62% by decreasing the initial concentration 60 to 85 ppm. The data are fitted into Langmuir and Freundlich adsorption isotherm models and their constants are determined. The characterization of the physio chemically modified carbons are carried out by SEM, EDX, XRD analysis, UV-VISIBLE and FT-IR analysis of before and after adsorption of dyes on the carbon surface area   morphology studied.

Keyword: Cashew nut, rose apple carbon, reactive procion orange, reactive green dye, adsorption isotherms, characterization.

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Introduction

Dyes and pigments are widely applied in the textiles, paper, plastics, leather, food and cosmetic industries to coloring products. Organic dyes appear in many industrial effluents. The wastewater contains a large amount of dissolved dyestuffs and other products, such as dispersing agents, dye bath carrier, salts, emulsifiers, levelling agents and heavy metal. The colored dye effluents are generally considered to be highly toxic to the aquatic system. Some dyes are reported to cause skin irritation, dermatitis, allergy and cancer for humans. Still, many researchers had investigated the adsorption capacity of less expensive materials such as red mud [1], natural zeolite [2] ,wood based biosorbents [3],marine alga padina [4] or bone char[5],peat[6], sugar beet pulp[7]etc., on removal dyes and heavy mates from adsorption method. Still adsorption is an efficient process which can use various biological materials, mineral oxides, activated carbon and even waste water materials. Reactive green HE4BD (RG) dye is a low reactivity, more substantively, high exhaustion and high fixation. Excellent build-up in high as well as liquor ratio. Excellent reproductability, batch to batch, high tinctorial value and hence are economical good general fastness properties. Due to suitability of dyeing at high temperature 80-85^{0}c., dye wastewater is usually treated by physical and chemical methods of sonochemical degradation, photochemical degradation, electrochemical degradation, coagulation and flocculation, membrane separation, activated carbon adsorption, oxidation or ozonation[8-9], and ion exchange[10] etc., However, in developing countries, these methods are still too expensive to be used widely. Developing economical

adsorbents to treat dyes wastewater has attracted towards a great interest in recent years. Recently, the application of low-cost adsorbents for the dyes and metal ions removal has been reviewed. Among these, the adsorption method, in using commercial activated carbons (CAC) as adsorbent has been proved to be simple, more efficient and economically feasible technique for removal of dyes from wastewater. Adsorption capacity, varies of carbons for the removal of dyes are found to be the order as follows

<div align="center">

CAC >RAC >CNC
</div>

Activated carbon is the most widely used adsorbent with a great success due to its large surface area, micro porous structure and higher adsorption capacity. However, its use is limited because of its cost. This has led in search for cheaper substitutes than CAC. Investigators have studied the feasibility of using low cost substances such as waste apricot, coconut shell, dairy sludge, bamboo grass treated with concentrated sulfuric acid, peat, bamboo, jack fruit peels, pistachio nut shells and date stone and palm tree waste as adsorbents for the removal of dyes and heavy metals from waste water.
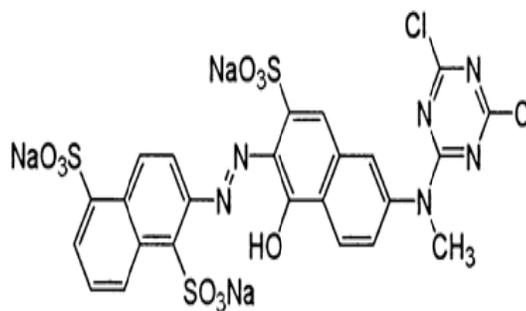
Materials and Methods

Adsorb ate (Dye solution preparation)

The dye Reactive Green HE4BD [C.I name = Reactive green, chemical formula weight = 1418.94, λmax-632nm] and Reactive procion orange [C.I. name = Reactive orange, λmax-482nm] supplied by S.D fine Chemicals, Mumbai, India is used as such without further purification. An accurately weighed quantity of dye is dissolved in double distilled water to prepare the stock solutions.
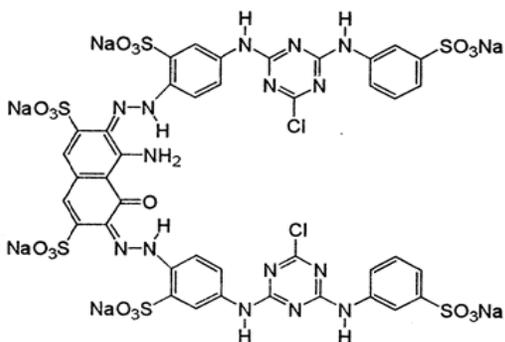
Reactive green dye (HE4BD**).**   **Reactive procion orange.**
Molecular Formula: $C_{40}H_{23}C_{l2}N_{15}Na_6O_{19}S_6$ **MolecularFormula:**$C_{24}H_{13}C_{l2}N_6Na_3O_{10}S_3$

Adsorbent

Cashew Nut Carbon (CNC) and Rose Apple Carbon (RAC) are used as an adsorbent in our study. It was obtained from Agricultural waste, washed up using tap water and finally with double distilled water to remove the suspended impurities, dust and soil and then dried in oven. About 500g of above powdered carbons (Cashew nut and Rose apple) are mixed with 100ml of concentrated Sulphuric acid separatively and kept   at room temperature for 24hrs. Then, it is dried in a hot air oven at 80˚C. The dried material is washed with distilled water to remove the excess of acid that can be checked with EBT indicator when solution becomes blue color which is free from acid. Charcoal was dried at 110˚C for 12 hours to remove moisture and kept in air tightened bottle.

Characterization of adsorbent

The surface functional groups of carbon CNC and RAC are detected by Fourier Transform Infrared (FTIR) spectroscope (Shimadzu-FTIR-180) using the KBr pellet method. UV-Visible spectrum was detected by wavelength of the dye solution (Shimadzu-UV 1800). The Scanning electron microscopy (SEM) (VEGA 3 TESCAN) analysis is carried out for the CNC and RAC before and after adsorption of dyes on RG& RPO. The EDX spectrum studies used for the elemental presence with the percentage of composition for activated carbons and after adsorption of the activated carbon by using Bruker instrumentation. The XRD analysis shows that linear porous nature and its size, characterized using X-ray phase analysis powdered technique. XRD measurement at 25^0C (XPERT-PRO).

Adsorption Experiments

Batch mode adsorption studies are carried out by adding certain amount of adsorbent (dose) and 50ml of dye solutions of certain concentrations, contact time and temperatures in a thermostat water bath shaker at 200 rpm. The samples are withdrawn from the shaker at predetermined time intervals and solutions are separated from the adsorbent by centrifugation at 400 rpm in 5min. To determine the residual dye concentration, the adsorbance of the supernatant solution is measured before and after treatment with double beam spectrophotometer (VISISCAN 167 Spectrophotometer). The initial dye concentrations in the test solution and the contact time are changed to investigate their effect on the adsorption kinetics. The pH of the dye solution is adjusted by using NaOH or HCl solution. The adsorption studies are carried out at different temperatures (308, 318 and 328K). This is used to determine the effect of temperature on the thermodynamic parameters. The percentage removal and the amount of adsorption in batch experiments are calculated as follows:

Percentage removal (%)   = $(C_i-C_e)/C_i\times100$ Eq. (A.1)

Amount adsorbed   (q)   = $(C_i - C_e) V/m$ Eq. (A.2)

Where,

C_i -is the initial concentration (mg/L), C_e - is the equilibrium concentration (mg/L),

V -is the volume of solution (mL), M -is the mass of adsorbent (g), Q -is the amount adsorbed (mg/g).

Adsorption Isotherms

The applicability of adsorption isotherms has been important for the water and waste water treatment by adsorption technique. These isotherms are estimated to the adsorption capacity of various carbons with respect to CAC. The analysis of the isotherm data by fitting them into different isotherm models is an important step to find out the suitable model that can be used for purpose [11]. In this work, the isotherm models of Langmuir [12], Freundlich [13] are used to describe the relationship between the amount of dye adsorbed q_e and its equilibrium concentration C_e.

Freundlich isotherm

We can draw a graph of log X/m vs. C_e

$X/m = q_e = KC_e 1/n$ Eq. (A.3)

X -is the amount adsorbed in ppm (X=C_0-C_e), m -is the mass of adsorbent (g/L), C_e -is the equilibrium concentration in ppm, K -is the Freundlich constant (to measure the adsorption capacity), 1/n to measure the adsorption intensity. The log X/m vs. log Ce graph should be linear in all cases. Values of 1/n for the dye substances indicate the adsorption mechanism with intra particle   diffusion was the rate determined step and suggested by Weber and Morris [14].

$$Q_t = Kp \, t_{1/2} + C$$

Eq. (A.4)

Q_t - is the amount adsorbed dye at a time t.

C - Intercept

Kp - intra particle diffusion rate constant (to measure the adsorption capacity)

1/n to measure the adsorption intensity.

The graph should be linear in all cases as shown in the Fig.A.1a and 1b. The values of 1/n for the dye substances indicate the adsorption mechanism with intra particle diffusion at a rate determined step is suggested by Weber and Morris [14]

Langumuir isotherm

$$C_e/q_e = (1/ab) + C_e/a \qquad\qquad \text{Eq. (A.5)}$$

q_e - is the amount adsorbed, C_e - is the equilibrium concentration, a and b are Langumuir constant,

a –measure the adsorption capacity for the monolayer coverage, b- is the energy of adsorption .

We can draw a plot of C_e/q_e vs. C_e will be straight line as shown in Fig.A.2a and 2b for RG and RPO respectively. The values of 1/ab are intercept and 1/a value is slope.

Results and Discussion:

i) Effect of concentration variation:

In order to study the effect of initial concentration of RG varying (40-65ppm) and RPO varying (60 - 85 ppm) and fixed amount of dose and contact time on the extent of the removal of dyes in terms of the percentage removal and amount adsorbed (mg/g) by using various carbons(CNC and RAC). The batch adsorption experiments are performed with the fixed dose of 20g/L and constant contact time (40 min.) and particle size 90 microns at 32 ± 1^0c. Initial concentration (C_o) of dyes (40 – 65 ppm for RG and 60 - 85 ppm for RPO) as shown in the Table-A.1. Equilibrium concentration (C_e) of dyes can be calculated with the help of calibration curve known as concentration of dyes without carbon and the absorbance should be noted by using the Fig.A.3a and 3b for effect of concentration respectively RG and RPO. The amounts of dyes were found to increase exponentially at an increasing initial concentration of dyes. The concentration of dyes increases the percentage removal of adsorption decreases; this is due to lack of available active sites on the surface, which will enhance the formation of unilayer on the surface of carbon. Further formation of layer of dye molecule on the surface of carbon is highly hindered due to repulsive force between the adsorbate (dye molecule) and adsorbent (carbon) in the bulk of the solution. We have to optimize the initial concentration of dyes are fixed as 40 ppm for RG and 60 ppm for RPO. From this study, conclude agriculture wastes are used as low cost adsorbents, for the removal of dyes. These are used as an alternative to CAC for the purpose of economic and social point of view for the removal of dyes in organic pollutants (pesticides, insecticides, organic acids) are general dyes removal in particular also.

Table-A.1. Effect of initial concentrations of RG and RP

	RG					RPO			
	CNC		RAC			CNC		RAC	
(ppm)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.	Conc. (ppm)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.
40	78.5	1.57	82	1.64	60	69.6	2.09	73	2.16
45	76	1.71	80.8	1.82	65	68.6	2.23	67.3	2.19
50	69.6	1.74	79.6	1.99	70	67.8	2.38	66.1	2.32
55	68.3	1.88	73.4	2.02	75	66.8	2.50	64.8	2.43
60	66.6	2.00	72	2.16	80	66.1	2.65	63.3	2.54
65	64	2.08	67.3	2.19	85	64.9	2.80	62.3	2.65

Table-A.2 Effect of contact time for RG and RPO

	RG					RPO			
	CNC		RAC			CNC		RAC	
Cont. time (min.)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.	Cont. time (min.)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.
10	74.5	1.49	77	1.54	10	47	1.41	51.7	1.55
20	76	1.52	78	1.56	20	54	1.62	61.7	1.85
30	77.5	1.55	80	1.60	30	59.6	1.79	65.8	1.98
40	78	1.56	80.2	1.61	40	65.6	1.97	71.3	2.14
50	77	1.55	79.2	1.58	50	65	1.95	70.3	2.10
60	75	1.50	77.5	1.55	60	64.6	1.91	68	2.04

Table-A.3. Effect of adsorbent mass of RG and RPO

	RG					RPO			
	CNC		RAC			CNC		RAC	
Dose (g)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.	Dose (g)	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.
0.2	74	1.48	73	1.46	0.2	45	1.36	43.3	1.34
0.4	75.5	1.51	74.5	1.49	0.4	53	1.60	57.7	1.73
0.6	76	1.55	76	1.52	0.6	61.7	1.85	70.3	2.11
0.8	77	1.56	77.5	1.55	0.8	68.2	1.98	71.6	2.14
1.0	78.5	1.57	79.5	1.59	1.0	70.2	2.10	72.6	2.18
1.2	78.5	1.57	79.5	1.59	1.2	70.2	2.10	72.6	2.18

Table-A.4. Thermodynamics parameters for the adsorption of RG&RPO on the adsorbents of RAC& CNC.

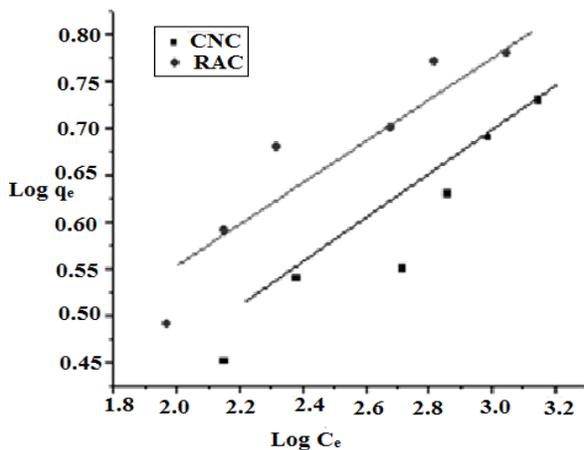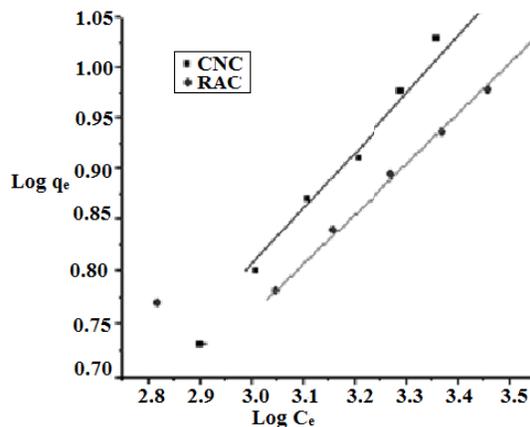| Adsorbent	R^2	ΔH^o kJ/mol k	ΔS^o	$-\Delta G^o$ KJ/mol		
				308K	318K	328K
RAC	0.999	24.53	0.651	172.72	175.98	179.3
CNC	0.995	23.45	0.633	169.67	172.83	175.4

Fig- A.1a   Freundlich isotherm for RG

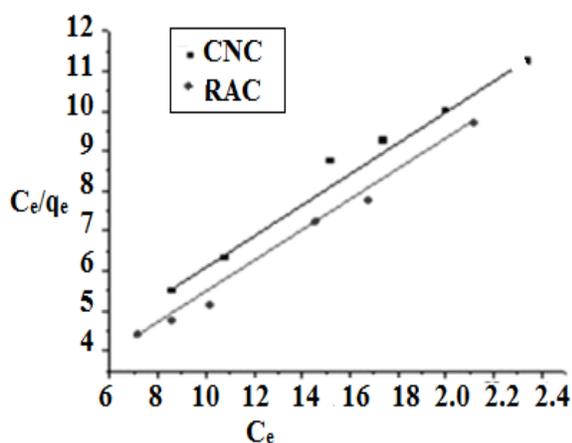**Fig- A.1b   Freundlich isotherm for RPO**
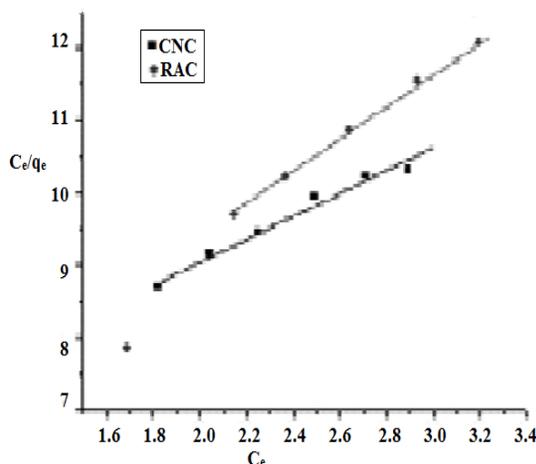

Fig- A.2a Langmuir isotherm for RG

Fig- A. 2b Langmuir isotherm for RPO

ii) Effect of contact time:

In order to study the kinetics and dynamics for adsorption of dyes using various carbons by the fixed amount of initial concentration and dose by varying the contact time (10 to 60 min.) Particle size 90 microns at 32 ± 1^0C and its solution pH. The stop watch is started simultaneously at the beginning of the experiment. The bottles are withdrawn from the followed shaker and the different time (10 to 60 mints). Initially, the percentage removal increases with the increase in contact time to obtain maximum adsorption at 40 minutes and after that to attain stagnated. When time goes on increasing adsorption efficiency decrease due to desorption for effect of contact time respectively RG and RPO dyes as shown in the Fig.A.4a and 4b. The effect is considered which amount of adsorption efficiency present in the carbon as shown in the Table-A.2.

iii) Effect of adsorbent mass

The adsorption experiment, the percentage removal and amount adsorbed surface of carbon are obtained with different dose of adsorbent (0.2-1.2mg) with fixed amount of initial concentration of dyes (40ppm for CNC) and (60ppm for RAC) as shown in the Fig.A.5a and 5b for RG and RPO dyes

respectively. The percentage removal increases with the increasing amount of dose due to increasing available active site surface of carbon. The effect of adsorbent mass considered which amount of adsorption efficiency present in the carbon for using the respective dyes as shown in the Table-A.3. From the studies reveals that 20g/l optimum the amount of dose of adsorbent.
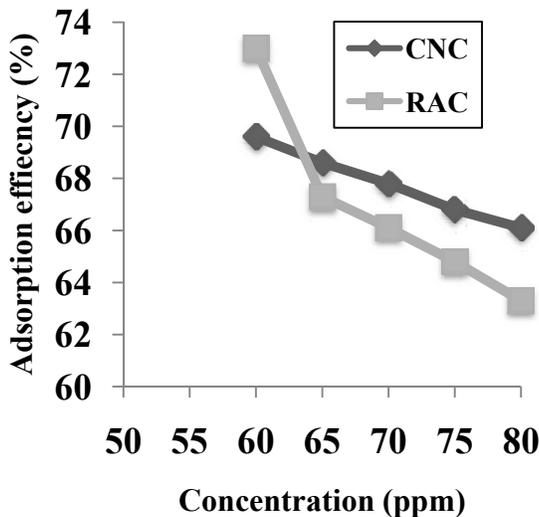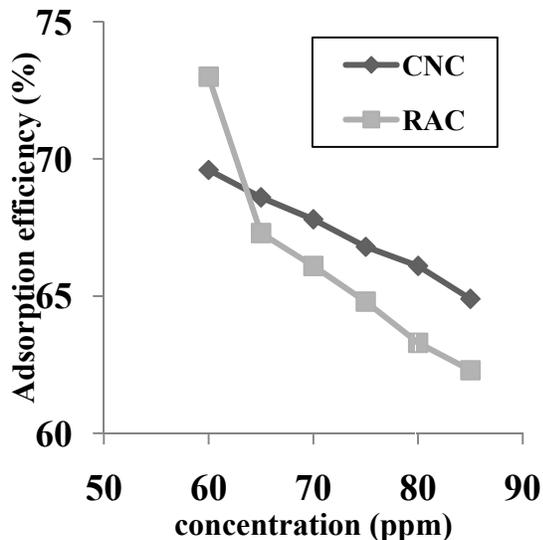
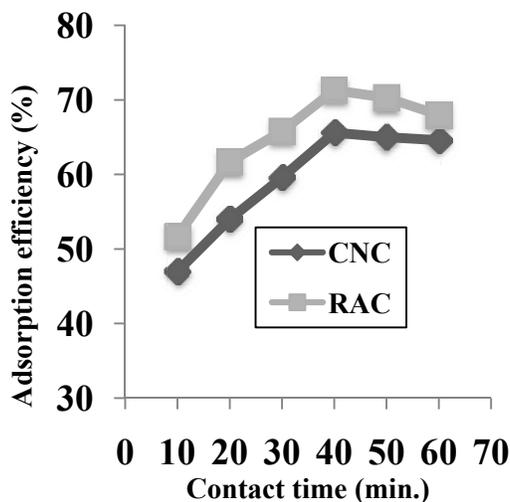**Fig- A.3a   Effect of initial concentrations of RG   Fig- A.3b   Effect of initial concentrations of RPO**
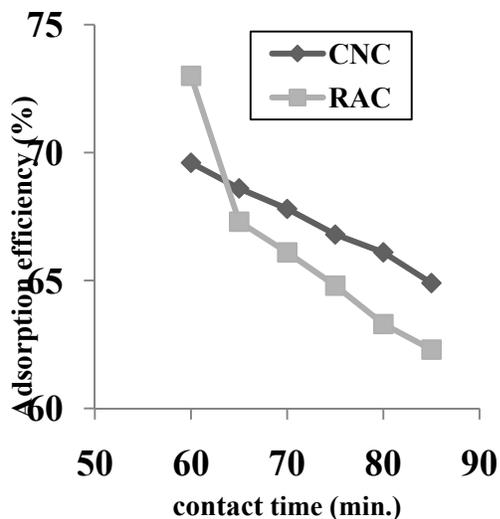
Fig-A.4a Effect of contact time variation of RG   Fig-A.4b Effect of contact time variation of RPO

iv) Effect of pH

The value of pH is affected at the zero point charge (ZPC) of the solid surface of the carbon pH_{ZPC} is found to be at pH of 3 for the sulphuric acid treatment of adsorbents becomes positive charge, meanwhile the surface of adsorbents of carbon will become negatively charged the solution pH greater than pH_{ZPC} by the removal of dyes decreased with increased pH of the solution as shown in Fig.A.6a and

6b for RG and RPO dyes respectively, because surface of carbon negatively charged. This is an enhanced columbic equilibrium between surface and dye anions.

v) Effect of temperature with a thermodynamic parameter

Adsorption studies are carried out at four different temperatures (35, 40 and 45^{0}C). The thermodynamic parameters are determined as:

$$Log (Q_e/ C_e) = (\Delta S^0/2.303R) + (-\Delta H^0/2.303RT) \qquad \text{Eq. (A.6)}$$

Where Q_e - is the maximum RG and RPO adsorbed unit mass of RAC and CNC (mg/g).
C_e - equilibrium concentration (mg/lit), R - is the universal gas constant (8.314 Jmol/K), T - is the absolute solution temperature, K: S^0 is the change in standard entropy (KJ/mol K) and , H^0 is the change in standard enthalpy (KJ/mol). Experimental data considered for calculation of thermodynamic parameters (ΔG^0, ΔS^0 and ΔH^0) are in the linear range of equilibrium adsorption isotherm [15]. Gibbs free energy (ΔG^0) can then be calculated using the relation below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{Eq.(A.7)}$$

where ΔG^0 is the change in standard free energy (KJ/mol). With an increase in temperature adsorption capacity there by indicating the adsorption as an endothermic process [15]. The value of thermodynamic parameters for the RAC and CNC are given the Table.A.4. Positive value suggests an increasing randomness at the adsorbent/solution interface which occurs in the internal structure of the adsorption. The positive value of H^o indicates that the adsorption process is an endothermic process. Change in enthalpy is obtained at a value of 24.53KJ/mol by indicating slightly predominantly chemisorptions process.The activation energy (Ea) is found to be indicating chemisorptions process due to the slightly higher value. The negative value of G^o indicates that adsorption processes are spontaneous at all the solution temperature. Similar result was reported in the literature for adsorption of basic dye using acid treated Kenaf fiber char [16] and the adsorption of malachite green dye into carbon derived from palm flower waste [17].

vi) Kinetics studies:

Pseudo-first-order model

The effect of contact time on the adsorption of RG on carbon of CNC and RAC. The pseudo-first order kinetic model also known as the Lagergren [18] kinetic equation is widely employed for understanding the kinetic behavior of the system. It is given by the equation,

$$dq_t /dt = k_1 (q_e - q_t) \qquad \text{Eq (A.8)}$$

Where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg g^{-1}), k_1 is the pseudo-first order rate constant (min^{-1}). The values of k_1 and q_e calculated from Fig-A.7a and 7b from the slope and intercept of plots of $1/q_t$ vs. $1/t$ respectively RG and RPO dyes. The pseudo-first-order kinetic model and the rate controlling step are determined by intra-particle diffusion model [19] the rate constant of pseudo-first-order kinetic model. Values of k_1 and q_e can be obtained from the slope and intercept of the plot ln (q_e-q_t) versus t.
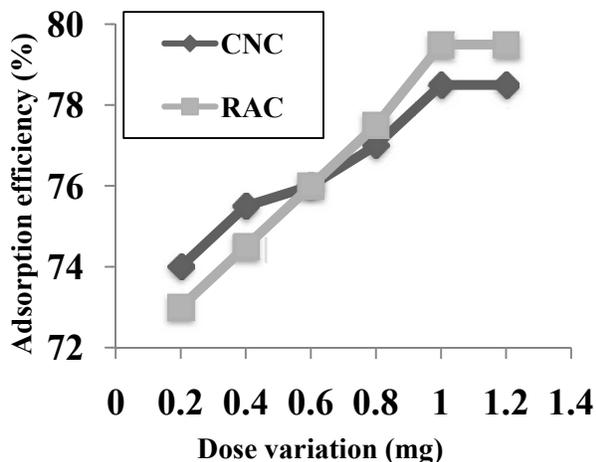
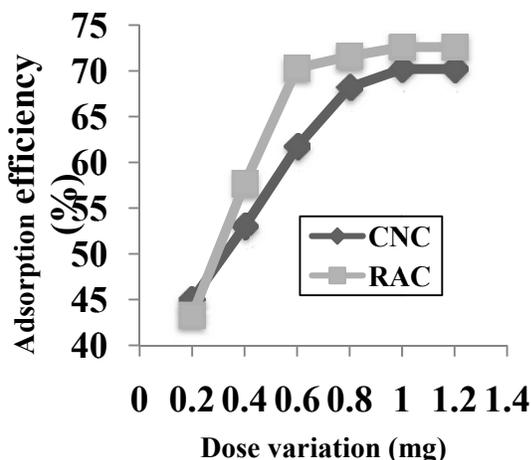**Fig- A.5a Effect of Dose variation of RG**
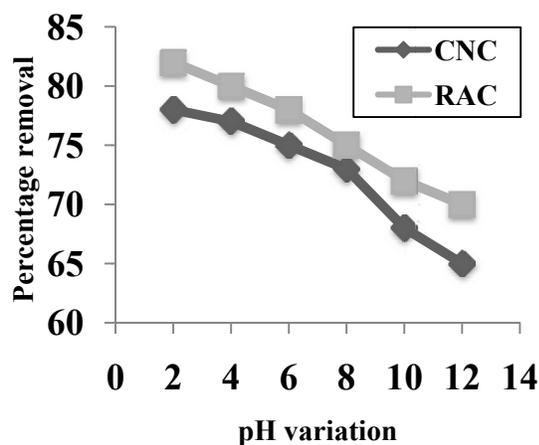

Fig- A.5b Effect of Dose variation of RPO
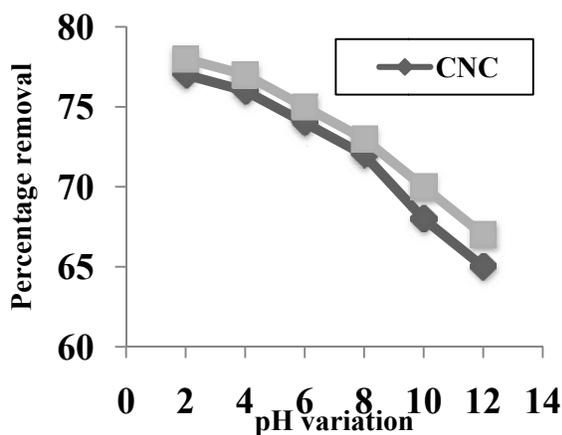

Fig –A.6a Effect of pH for RG
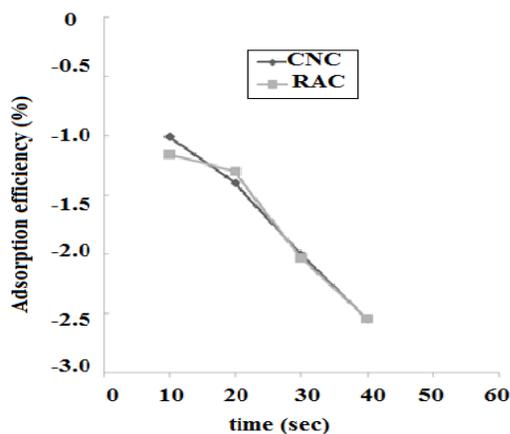

Fig- A.6b Effect of pH for RPO

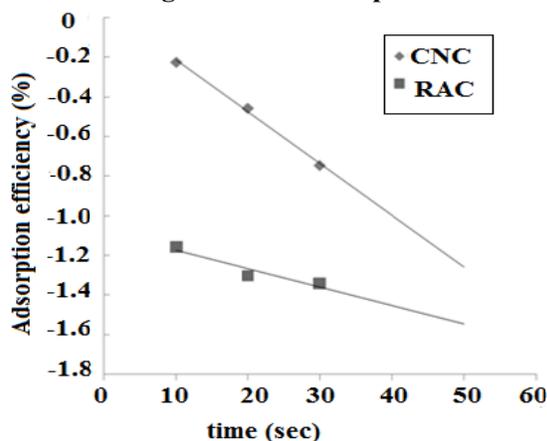**Fig- A.7a Kinetic pseudo first order reaction of RG**

Fig- A.7b Kinetic pseudo first order reaction of RPO

Spectra details

i) UV-Visible spectra

These spectra used in the λ_{max} value for the dye solution. UV-Visible spectra for RG and RPO as shown in Fig.A.8a and 8b respectively. The range of RPO is 482 nm and RG is 632 nm obtained for this spectrum.

ii) FTIR Spectroscopy

FTIR technique is an interesting application for studying the interaction between an adsorbate and the active groups on the surface of adsorbent [20] .FTIR spectra of before and after adsorption of activated carbon (CNC) is given below Fig.9 respectively.

A strong bands at 1035.77, 1157.29 cm^{-1} S=O stretching, 1338.6 cm^{-1} at C-O stretching, 2274.07 cm^{-1} at Si-H stretch, 2453 cm^{-1} at broad N-H stretch these additional peaks are observed due to the presence of dye on the surface of activated carbon (CNC). This shows that IR is the analytical technique to identify the adsorption when it takes place. The Similarly IR data observed in another kind of carbon (RAC) for the following additional peaks are observed.1028, 1288.45, 1328.95, 1680, 2276, 2536.39 shown in Fig-10.
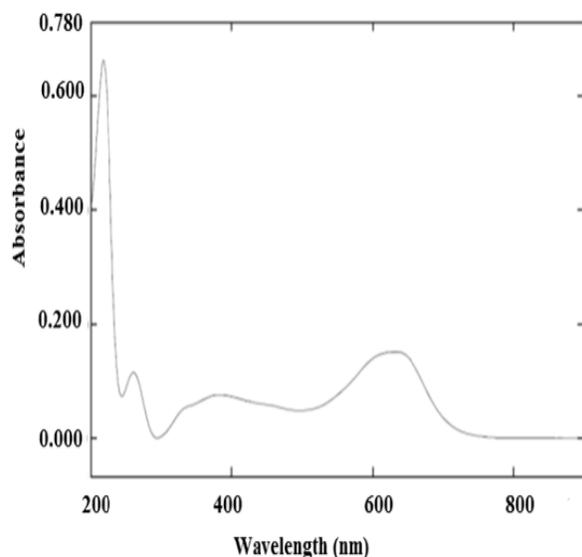
Fig-A.8a UV-Visible spectrum of RG   **Fig-A.8b UV-Visible spectrum of RPO**
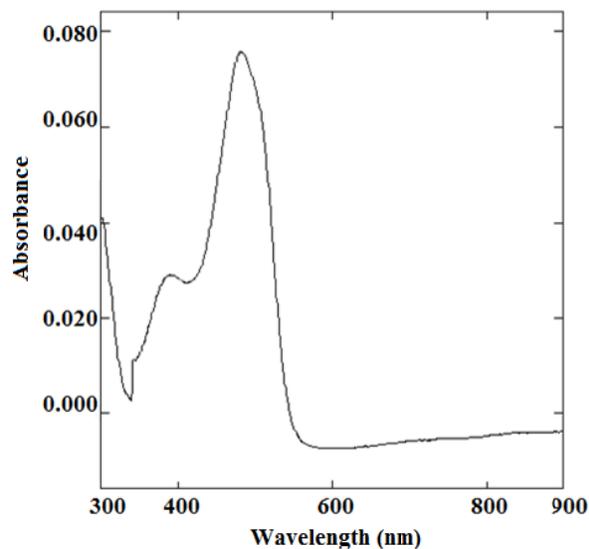
iii) Scanning electronic microscope (SEM):

SEM analysis is carried out for carbon RAC and CNC to study their surface textures. The SEM analysis was done at 1000 X magnification. In addition, the surface functional groups of carbon were detected by FT-IR. SEM was carried out for free carbon and after adsorption of carbon in finding their changes in respective characteristics. The SEM photographs of adsorbents before and after adsorption are shown Fig-A.11a, and 11b, 12a and 12b respectively. From these pictures, it is clear that there was significant difference in the appearance of the adsorbent surfaces. The white clumps on the adsorbent surface represent the adsorbate [21].
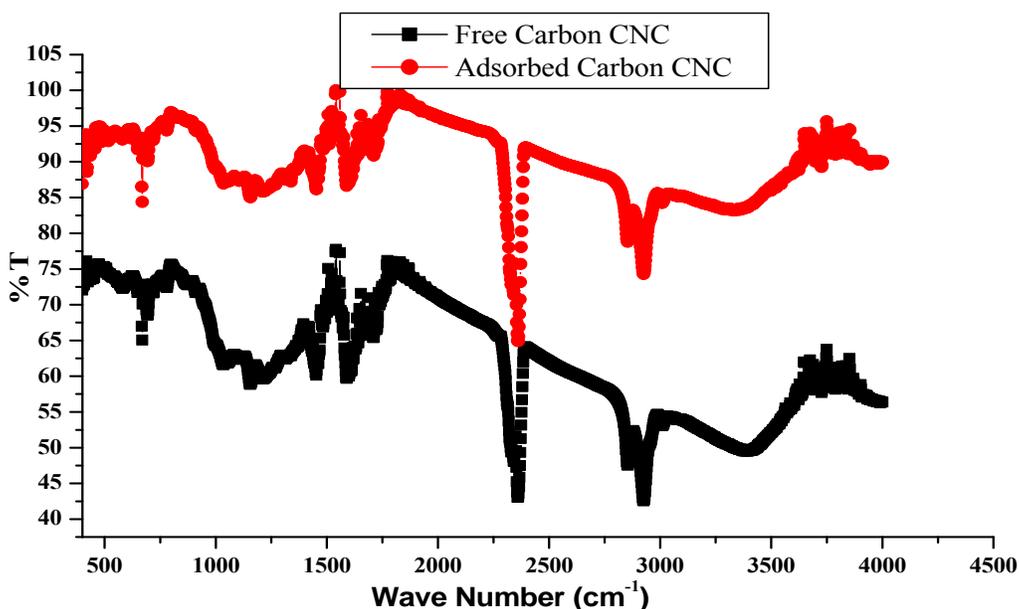
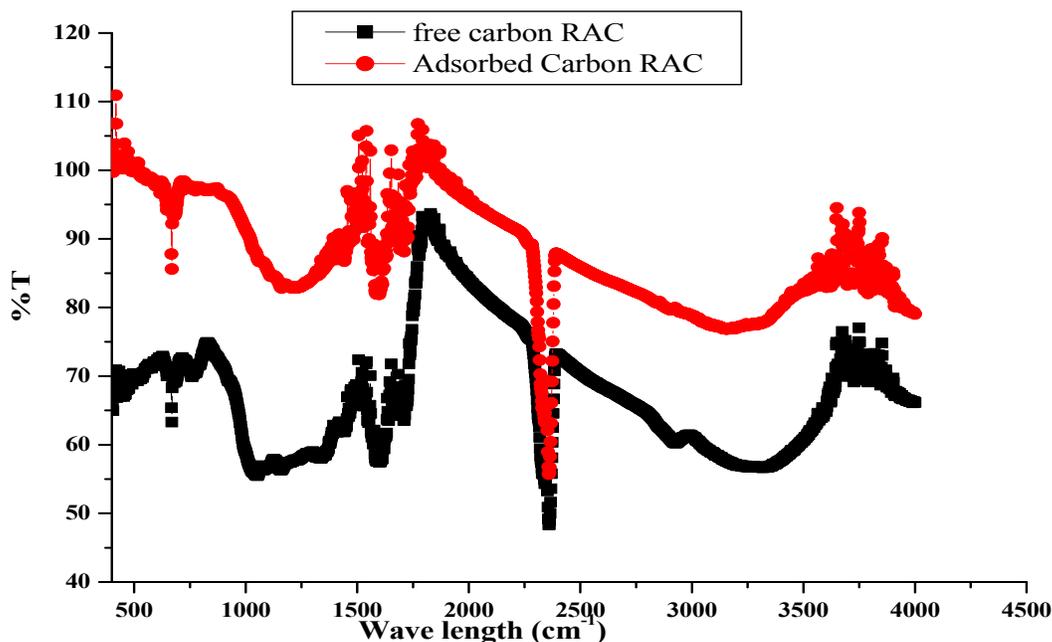**Fig.9 FTIR Spectrum of before and after adsorbstion of CNC carbon from RR dye**

Fig-10 FTIR Spectrum of before and after adsorption of RAC carbon from RPO dye

iv) XRD spectrum:

The XRD spectra shows that the major components of RAC and CNC are carbon (graphite), SiO_2 combined with Al_2O_3 trace amount of Fe_2O_3 and CaO, TiO. XRD chemical and structural changes are monitored in morphology modification resulting in large differences in carbon affinity for dye

substances. Various pore size distributions and morphologies appeared due to leaching of the alkaline and Aluminium Oxides followed by the formation of new structure with carbon & dye modified XRD method. It shows that linear porous nature and its size, characterized by using X-ray phase analysis powdered technique. Surface area increases the affinity for the removal of dye due to presence of alkali & metal oxide (Al_2O_3) are present on the surface of carbon. XRD spectrum for before and after adsorption of carbon RAC and CNC show the Fig-A.13a, and 13b, 14a and 14b respectively.
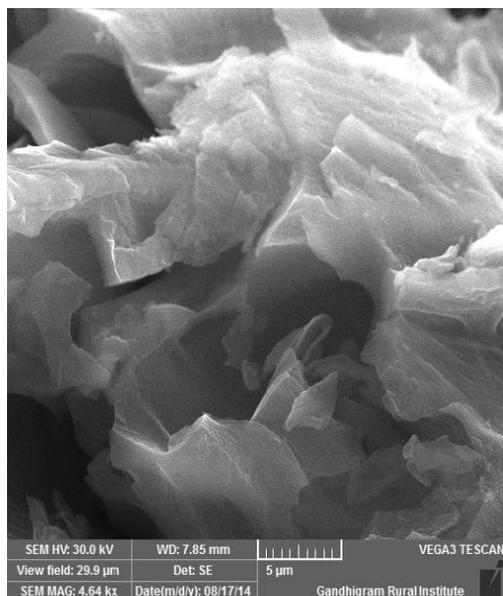
Fig-A.11a free carbon RAC
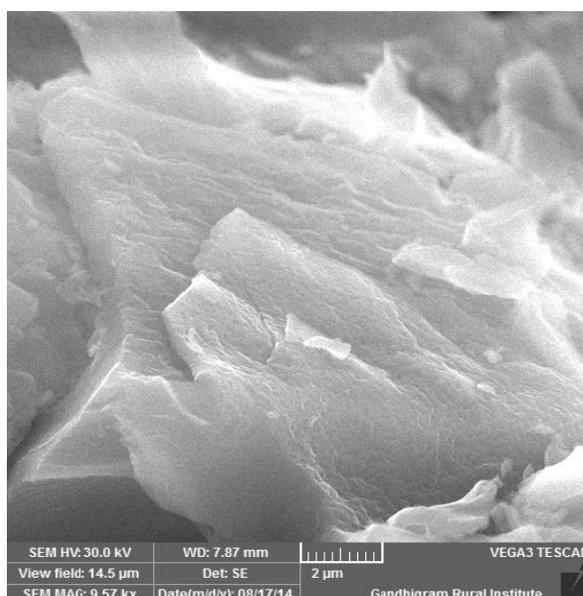
Fig-A.11b AC for RAC+ reactive green
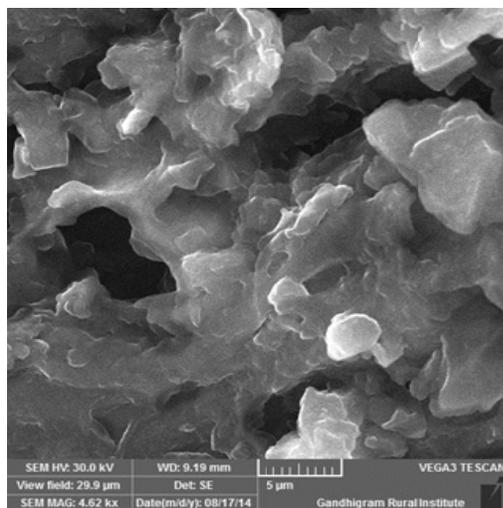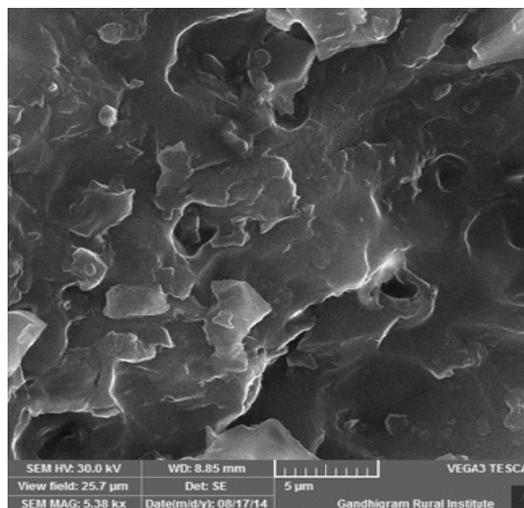

Fig-A.12a free carbon CNC

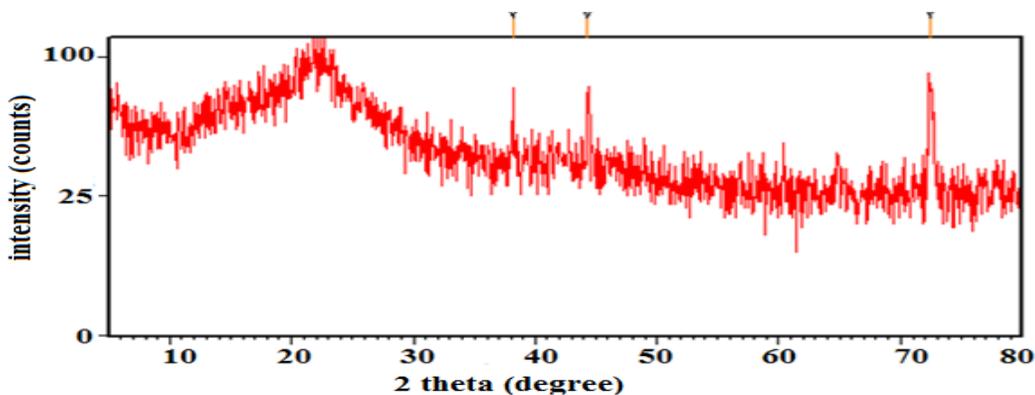**Fig-A.12b AC for CNC+ reactive procion orange**

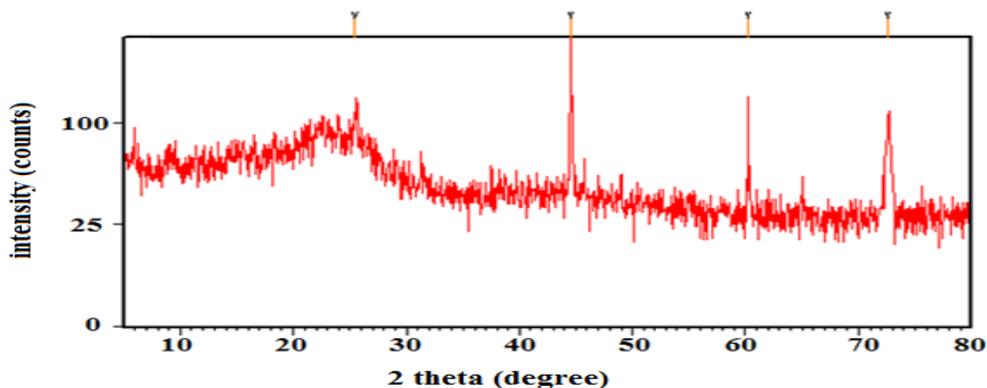**Fig-A.13a XRD for free carbon RAC**

:
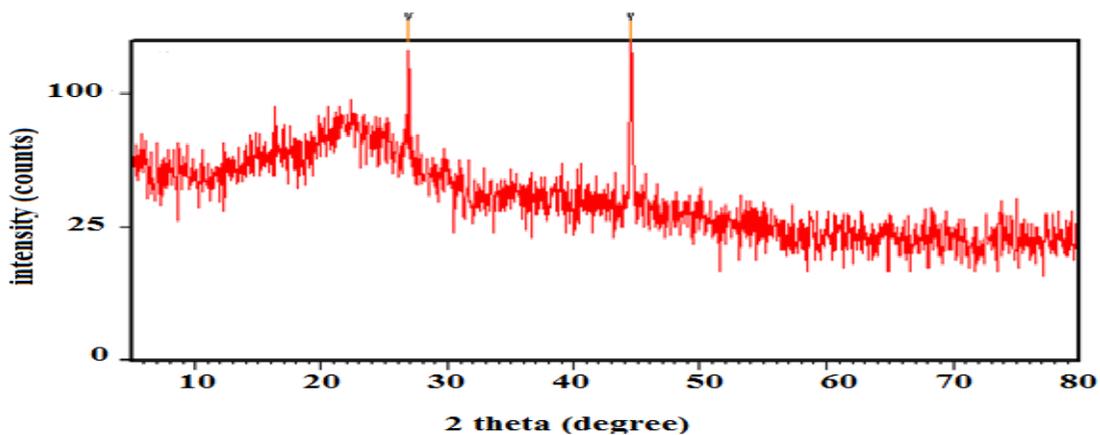**Fig –A.13b XRD for RAC + reactive red**
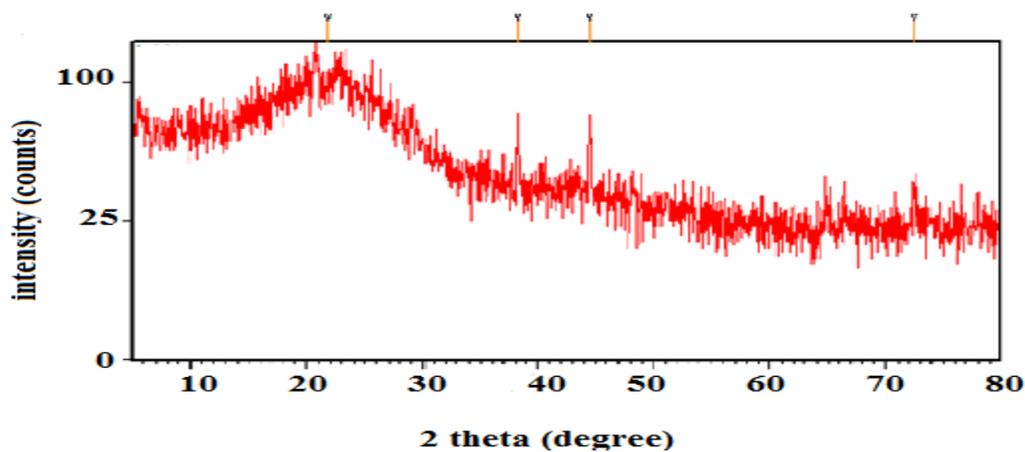

Fig-A.14a XRD for free carbon CNC

Fig-A.14b XRD for CNC + reactive red
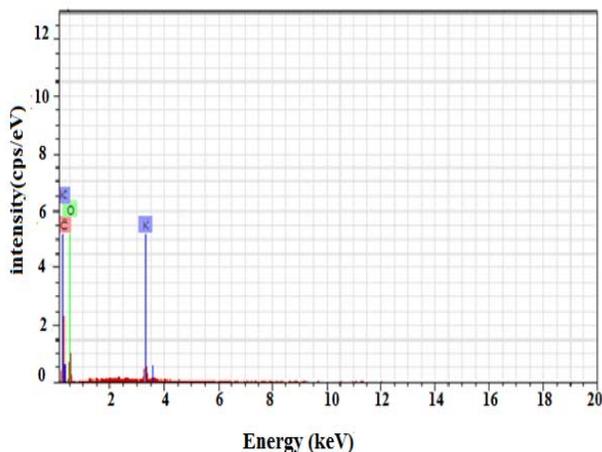

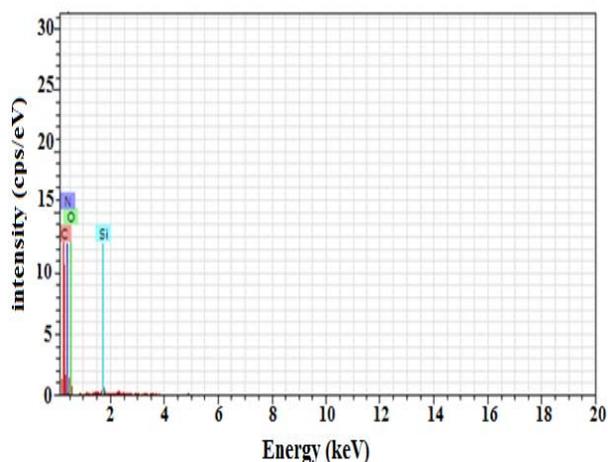**Fig –A.15a before adsorption of RAC**   **Fig –A.15b after adsorption of RAC**
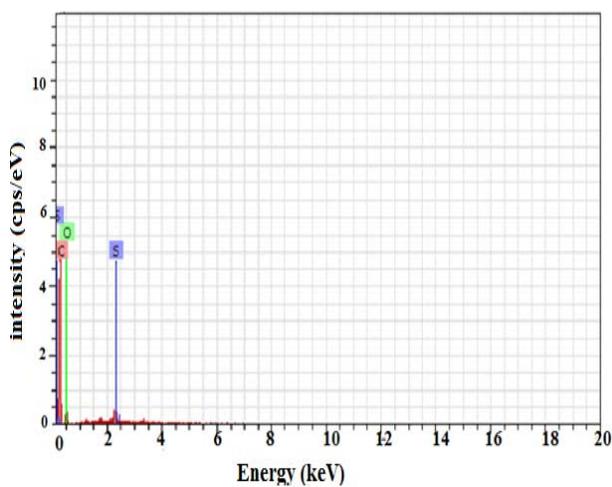

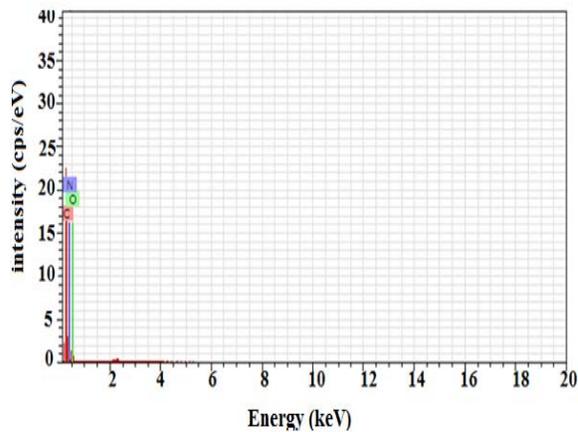**Fig –A.16a before adsorption of CNC**   **Fig –A.16b after adsorption of CNC**

v) EDX spectrum:

The EDX spectrum indicates the elements and their presence in percentage of composition for the activated carbon. EDX spectrum for before and after adsorption of carbon RAC and CNC are below the Fig-A.15a and 15b, 16a and 16b. The elements of carbon, oxygen, potassium and sulphur were present in the carbon RAC and CNC for before the adsorption. After the adsorption the carbon level increased so the dye containing carbon can be adsorbed by the carbon. Not only the carbon as well as nitrogen and silicon are adsorbed.

Conclusion

Activated carbons from agricultural by products/ wastes are used as adsorbent. Which are found to possess the essentially needed physico-chemical and textural properties of an   adsorbent and hence they can be used as adsorbent materials. The percentage removals of dyes are found to increase with the decrease in initial concentration of dyes, increase with the increase in contact time and dose of adsorbent. The process parameters are optimized. The relative adsorption capacities of the activated carbons have the maximum adsorption capacity, low cost adsorbents alternatives to CAC in water and waste water treatment, especially for the removal of pollutants in general and dye in particular. The adsorption data obeyed Freundlich and Langmuir adsorption isotherms indicate the formation of monolayer of dye molecules on the surface of the adsorbent. The result of the linear regression analysis of adsorption data revealed that the adsorption process is first order with intra particle diffusion as one of the rate determining step.

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