Adsorption of Reactive Green and Reactive Red Dyes from the Aqueous Solution using Activated Carbons

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Abstract: ***Application of carbon developed from ground nut shell (GNC) and baby corn carbon (BCC) an agricultural waste product has been investigated for the removal of reactive green and reactive red dyes from aqua solution and waste water. Batch adsorption experiments were carried out for the removal of dyes RG and RR (reactive green and reactive red) from aqua solution on to GNC and BCC effect of important parameters initial concentrations of dyes, contact time, and dose variation was studied on removal of the dye. The removal increased from 93.75-94.91 % by decreasing the initial concentration 100 to 20mg/L. Equilibrium data were fitted to Langmuir and Freundlich isotherm constants were determined. The characterization of the physio chemically modified carbons was carried out. SEM and XRD analysis. UV-Visible and FT-IR analysis of before and after adsorption of dyes on the carbon surface area for morphological studies.***

Keywords: Ground nut carbon, Baby corn carbon, reactive red, reactive green dye, adsorption isotherm.

1. Introduction

Dyes and pigments are widely applied in the textiles, paper, plastics, leather, food and cosmetic industries to color products. Organic dyes appear in many industrial effluents. The wastewater contains large amount of dissolved dyestuffs and other products, such as dispersing agents, dye bath carrier, salts, emulsifiers, leveling agents and heavy metals. 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 in humans. Synthetic dyes are extensively used in textile industry but about 20-40% of these dyes remain in the effluents [1-3]. Various techniques such as chemical precipitation , coagulation , biochemical degradation , solvent extraction, sonochemical degradation, photo catalytic degradation , micellar enhanced ultra filtration , electrochemical degradation , ozone oxidation, ion exchange and adsorption [4-7] etc., are used to remove dyes from waste water. Recently, the application of low-cost adsorbents for the dyes and metal ions removal has been reviewed. Among these, the adsorption method, using GNC and BCC activated carbons as adsorbent has been proved to be simple, more efficient and economically feasible technique for removal of dyes from waste water.

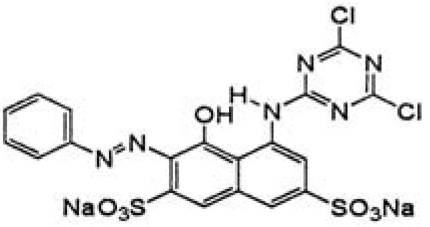
2. Experimental Method

2.1 Adsorbent

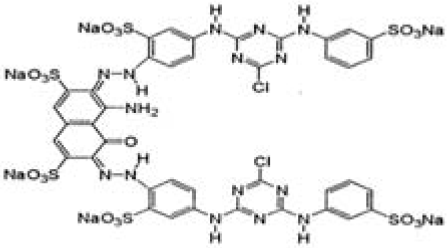
Groundnut shell and Baby corn carbon was used as an adsorbents in this study. These carbons obtained from agricultural waste, washed with double distilled water to remove the suspended impurities, dust and soil and then dried in an air oven. About 500 g of carbonized powder groundnut and baby corn carbon was mixed with 100ml of con. Sulfuric acid separately and kept at room temperature for 24 hrs. Then it was dried in a hot air oven at 80˚C. The dried material was washed with distilled water to remove excess of acid by checking with EBT indicator when solution becomes blue color which is free from acid. Activated Charcoal was dried at 120˚C for 12 hrs to remove moisture and kept in air tightened bottle.

2.2. Dye Solution Preparation

The dye Reactive Red [C.I name = Reactive Red 2, molecular weight = 615.33, λmax-482 nm] and Reactive Green HE4BD [C.I. name = Reactive green 19, molecular weight =418.94, λmax-544nm] was used as such without further purification.Anaccurately weighed quantity of dye was dissolved in double distilled water to prepare the stock solutions.



Reactive red dye.
M. F: $C_{19}H_{10}C_{12}N_6Na_2O_7S_2$



Reactive green dye (HE4BD)
M.F: $C_{40}H_{23}C_{12}N_{15}Na_6O_{19}S_6$

2.3. Adsorption Experiments and Isotherm

2.3.1. Freundlich isotherm

We can draw a graph of log q_e vs. Log C_e

$X/m = q_e = KC_e^{1/n}$ Eq (1)

X -is the amount adsorbed in ppm ($X = C_i - C_e$), 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 c_e graph should be linear as shown in Fig-1 for Freundlich isotherm model of RG and RR dyes. 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.

$q_t = K_p t^{1/2} + C$ Eq (2)

q_t- is the amount adsorbed dye at a time t. C – Intercept, K - Intra particle diffusion rate constant

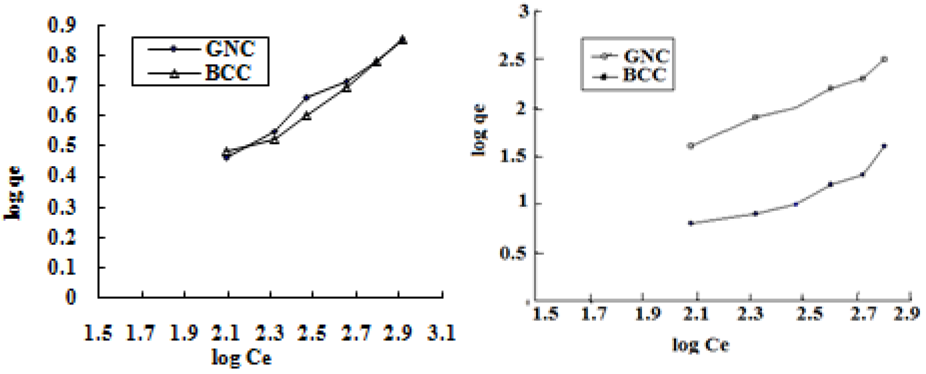


Figure 1: Freundlich isotherm for RG &RR

2.3.2. Langmuir isotherm

We can draw a graph of log C_e/q_e vs. C_e

$C_e/q_e = (1/ab) + C_e/a$ Eq (3)

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

a - measure the adsorption capacity for the monolayer coverage, b - Energy of adsorption

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

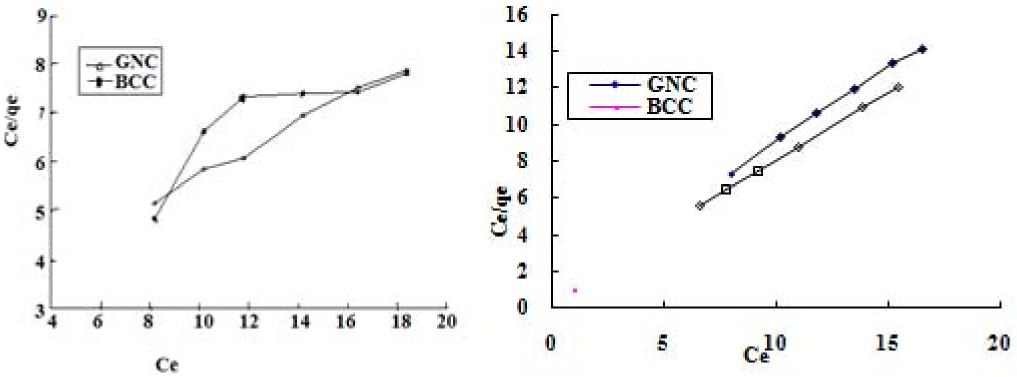


Figure 2: Langmuir isotherm for RG & RR 3. Result and discussion

3. Effect of Concentration

In order to study the effect of initial concentration of RG and RR varying (40 - 65 ppm and 30-40 ppm respectively) 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 (GNC and BCC). The amount of dyes was found to increase exponentially with increasing initial concentration of dyes. The concentration of dyes increases the percentage removal of adsorption decreases as shown in the Fig-3.This is due to lack of available active site on the surface, which will enhance the formation of uni-layer 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. The effect of initial concentrations of RG and RR dyes as given in the Table- 1. Adsorption capacity of various carbons for the removal of dyes are found to be order as follows CAC >BCC >GNC

Table 1: Effect of initial concentrations of RG and RR

Conc. (ppm)	*RG*				*Conc. (ppm)*	*RR*			
	GNC		*BCC*			*GNC*		*BCC*	
	Ads. Eff. (%)	*Amt. Ads.*	*Ads. Eff. (%)*	*Amt. Adsorb.*		*Ads. Eff. (%)*	*Amt. Ads.*	*Ads. Eff. %*	*Amt. Ads.*
40	79.5	1.59	80.5	1.61	30	73.3	1.09	78	1.17
45	77.3	1.74	75.1	1.69	32	68.1	1.10	75.6	1.21
50	76.4	1.94	73	1.84	34	65.3	1.11	72.9	1.23
55	74.1	2.04	72.9	2.01	36	62.5	1.12	69.4	1.25
60	72.6	2.18	72.8	2.19	38	60	1.14	63.6	1.26
65	71.6	2.33	72	2.34	40	58.7	1.18	61.5	1.28

3.1 Effect of Contact Time

In order to study the kinetics and dynamics for adsorption of dyes using GNC and BCC carbons by the fixed amount of initial concentration (40 ppm for RG and 30 ppm for RR) and dose (20g/l) by varying the contact time (10 to 60 min.). Initially the percentage removal increases with increase in contact time to obtain maximum adsorption at 40 minutes after that to attain stagnated. When time goes on increasing adsorption efficiency decreases due to desorption as shown in the Fig.4 for effect of contact time respectively RG and RR dyes. The effect considered which amount of adsorption efficiency present in the carbon as shown in the Table-2.

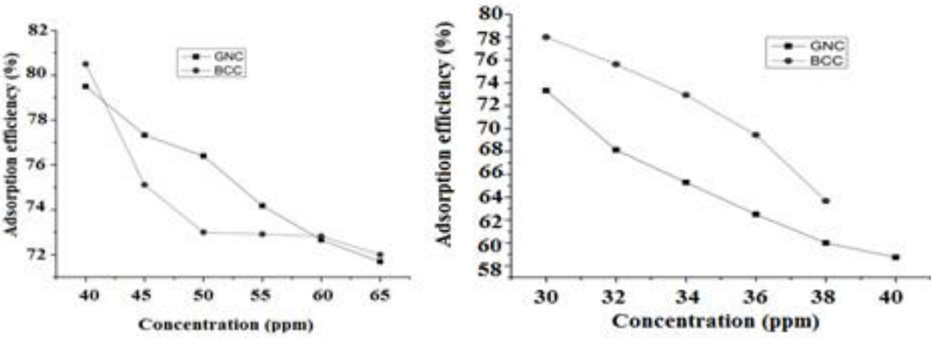


Figure 3: Effect of initial concentration for RG & RR

Table 2: Effect of contact time for RG and RR

Time (Min.)	RG				Time (Min.)	RR			
	GNC		BCC			GNC		BCC	
	Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.		Ads. Eff. (%)	Amt. Ads.	Ads. Eff. (%)	Amt. Ads.
10	71.2	1.42	74	1.48	10	66	0.99	65.3	0.98
20	73.5	1.47	76	1.52	20	67.3	1.01	68	1.02
30	75.5	1.51	77.2	1.54	30	69.3	1.04	72.6	1.09
40	78.5	1.57	79	1.58	40	70.7	1.06	75.6	1.14
50	78.5	1.57	79	1.58	50	70.7	1.06	75.6	1.14
60	78.5	1.57	79	1.58	60	70.7	1.06	75.6	1.14

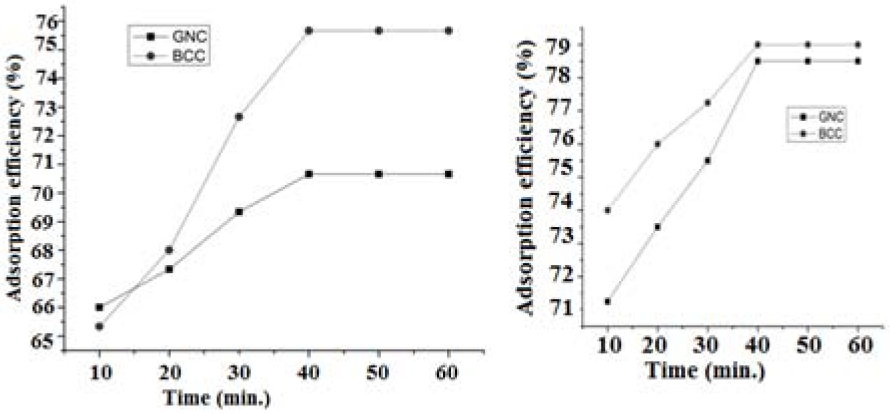


Figure 4: Effect of contact time for RG &RR

3.2 Effect of Adsorbent Mass

The percentage removal and amount adsorbed dyes on the surface of carbon where obtained with different dose of range (0.2g-1.2g) with fixed amount of initial concentration (40 ppm for RG and 30 ppm for RR) and contact time (40 Min.) as shown in the Fig-5 for RG and RR dyes respectively. The percentage removal of dyes increase with increase in the amount of dose due to increasing active site on the surface of carbon. From the study reveals that optimize the amount of dose of adsorbents (carbons) 20mg/L. The adsorption efficiency of RG and RR shown in the Table-3.

Table 3: Effect of dose variation for RG and RR

Dose (g)	RG				Dose (g)	RR			
	GNC		BCC			GNC		BCC	
	Ads. Eff. %	Amt. Ads.	Ads. Eff. %	Amt. Ads.		Ads. Eff. %	Amt. Ads.	Ads. Eff. %	Amt. Ads.
0.2	69	1.38	71.2	1.42	0.2	65.3	0.98	66	0.96
0.4	71	1.42	73.2	1.47	0.4	67.3	1.01	68.6	1.03
0.6	73	1.46	76.5	1.53	0.6	69.3	1.04	72.6	1.09
0.8	77	1.54	78.5	1.57	0.8	72	1.08	76.6	1.15
1.0	77	1.54	78.5	1.57	1.0	72	1.08	76.6	1.15
1.2	77	1.54	78.5	1.57	1.2	72	1.08	76.6	1.15

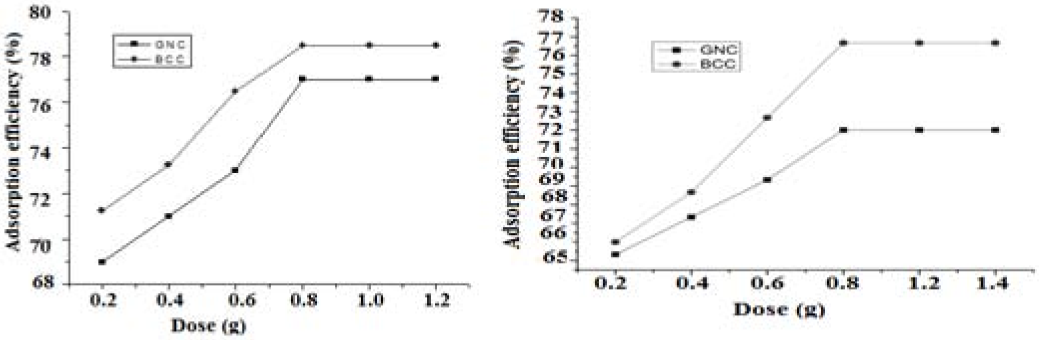


Figure 5: Effect of dose variation for RG &RR

4. Spectra Details

4.1 UV-Visible Spectrum

These spectra used in the λ_{max} value for the dye solution. The range of RG is 544 nm and RR is 482 nm is obtained for this spectrum. The shown in the figure-6 for RG and RR dyes respectively.

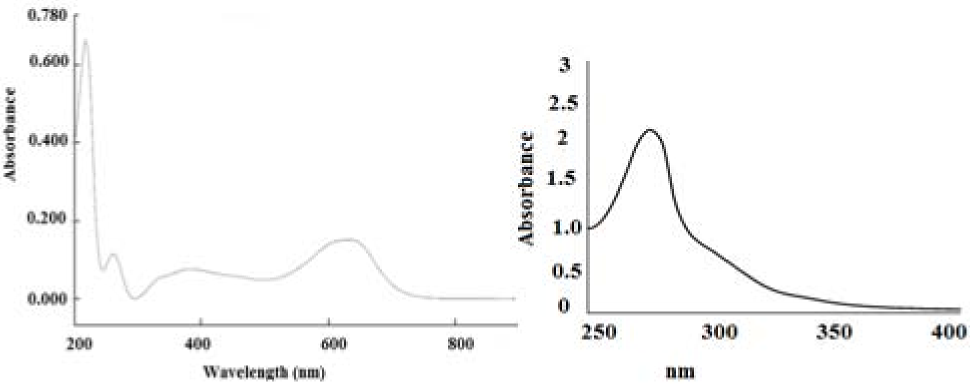


Figure 6: UV-Visible spectrum of RG and RR Dye

4.2. Fourier Transform Infrared spectroscope (FT-IR-shimadzu -180)

FTIR technique is an interesting application for studying the interaction between an adsorbate and the active groups on the surface of adsorbent [8]. FT-IR spectra of before and after adsorption of GNC carbon as shown in the Fig-7 respectively. A strong band at 1201 cm^{-1} for S=O stretching, 2276 cm^{-1} at Si-H stretch, 2341.58 cm^{-1} broad N-H stretch these additional peaks are observed due to the presence of dye on the surface of activated carbon (BCC). This shows that IR is the analytical technique to ensure the adsorption take place. The similar IR data observed in another kind of carbon (GNC) for the following additional peaks are observed at 1201 cm^{-1} broad N-H stretch, 2181, 2276, 2341.58, 2358.94 cm^{-1} for NH_3.

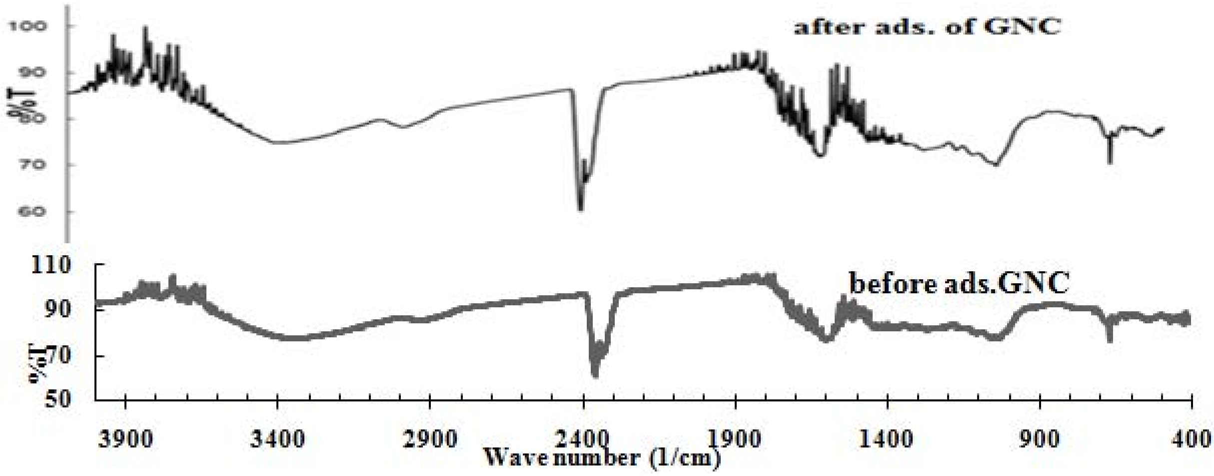


Figure 7: FTIR spectra for before and after adsorption of GNC

4.3. SEM (Scanning Electronic Microscopy)

SEM (VEGA 3 TESCAN) is widely used to study the morphological features and surface characteristics of the adsorbent materials [9]. In present study, SEM photographs of adsorbents for free carbon & after dye adsorbed carbon shown below in the Fig-8. From this analysis, it is clear that the appearance of surface is a microcrystalline structure [10].

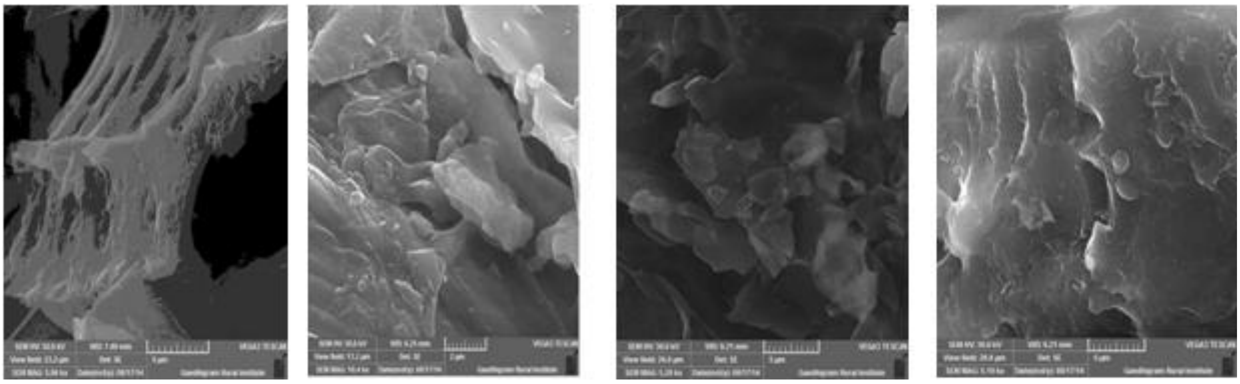


Figure 8: SEM photographs of adsorbents for free carbon & after adsorbed GNC&BCC

4.3.1 XRD

It shows that linear porous nature and its size, characterized using X-ray phase analysis powdered technique XRD measurement at 25˚C (XPERT-PRO).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. Shown on the XRD spectrum for before and after adsorption of carbon BCC& GNC in Fig-9 and 10.

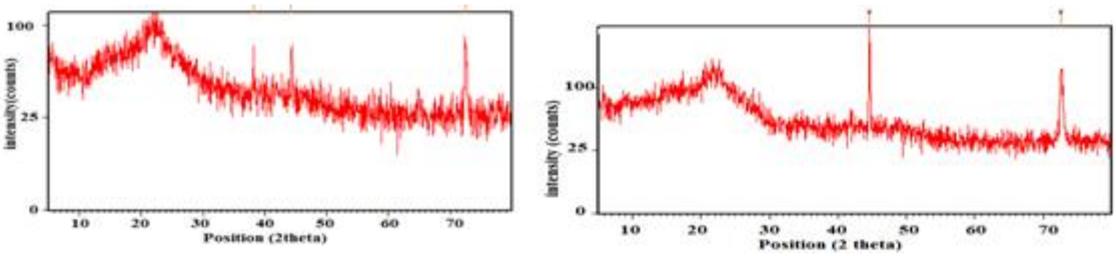


Figure 9: free & after adsorption BCC carbon

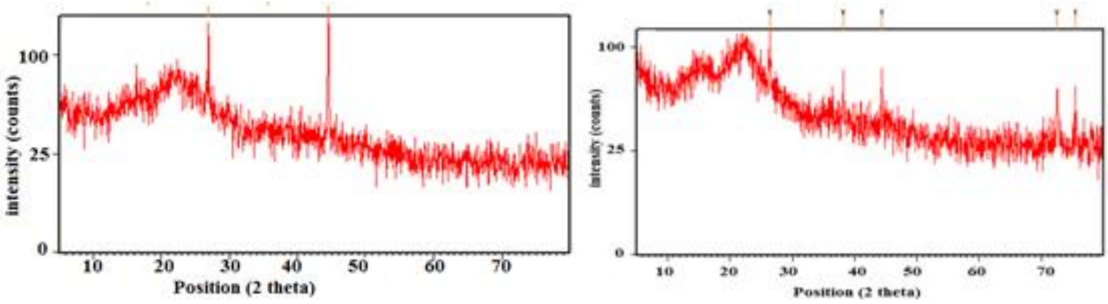


Figure 10: XRD for free & after adsorption GNC carbon

5. Conclusion

Carbon is used as an adsorbent and the removal of dye from an aqueous solution. Various indigenously prepared carbon with maximum monolayer adsorption capacity. The amount of adsorption dye increases with increasing time and dose of adsorbent & contact time decreases with increase in particle size of the carbon & concentration of dye. Isotherm models are agreed with our experimental part. This was attributed to the presence of excess positive charge on its surface. Adsorption kinetics followed the 1st order model indicating that chemisorptions were the rate controlling step in the adsorption of dye. Agricultural waste carbon are used for removal of dyes from the aqueous solution which is alternative the CAC. The adsorbent are due to availability, higher adsorption capacity and low cost nature.

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