

# Preparation and Characterization of Activated Carbon from the Fruit of *Cordia Sebestena* as a Novel Adsorbent for Dye Removal

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**Abstract** - Low cost adsorbents derived from wastes have demonstrated outstanding capabilities for the removal of dyes from wastewater. In the present study, fruit of *Cordia Sebestena*, a gardening plant material was used for the preparation of Activated Carbon. Activated carbons from the fruit of *Cordia Sebestena* were prepared by physical and chemical processes such as impregnation of raw material with Conc. $H_2SO_4$ , KOH,  $ZnCl_2$ ,  $H_3PO_4$  solution, direct pyrolysis, dolomite process, chemical activation with  $H_2SO_4 + H_2O_2$  solution respectively followed by activation at  $800^\circ C$ . The physico-chemical characteristics such as moisture content, volatile matter, pH, conductivity, bulk density, specific gravity, porosity, methylene blue number, iodine number and SEM were investigated to study the adsorptive capacity. Among the prepared activated carbons, CSAC with  $H_3PO_4$  solution followed by activation at  $800^\circ C$  possess high surface area and more porosity and was chosen as best adsorbent for the removal of dyes from textile industry effluent.

**Keywords** : *Cordia Sebestena*, Activated Carbon, Adsorption,  $H_3PO_4$  impregnation, Dye removal.

## I. INTRODUCTION

Adsorption with activated carbon is a useful treatment method to remove pollutants from water and wastewater. Activated carbon can be manufactured from all carbonaceous materials and prepared to have high porosity and very large surface area available for adsorption. Activated carbons can be synthesized by two methods, chemical and physical activation<sup>1</sup>. In chemical activation<sup>2</sup>, the raw material is impregnated with a strong dehydrating agent and then followed by pyrolysis at high temperature to prepare activated carbon. Physical activation method consists of carbonization of the raw material in an inert atmosphere and gasification of the resulting char in the presence of steam, carbon dioxide or air. However, commercial activated carbons are expensive and it is important to find out new low cost materials available for use as adsorbents<sup>3</sup>. Hence, in this paper we made an attempt to use activated carbon developed from the fruit of gardening plant material, *Cordia Sebestena* as an adsorbent for the removal of dyes from textile industry wastewater.

*Cordia Sebestena* is widely planted throughout the tropics and subtropics as an ornamental plant in gardens because of its flowers. It has dark green, oval shaped leaves, and grows oval shaped fruits. It is commonly known as the Geiger tree. *Cordia Sebestena* tolerates drought but not frost. The fruit of this plant does not have any economical importance and

usually it is not used for edible purpose. Furthermore, it has also been proved to be a good and low-cost precursor material for the development of activated carbon. However, no literature has reported for the adsorption of dyes onto activated carbon prepared from the fruit of *Cordia Sebestena*(CS).

## II. EXPERIMENTAL PROCEDURE

*Cordia Sebestena* fruit was used as precursor for the preparation of activated carbon. The fruits were collected, dried in sunlight for 10 days and stored to prepare the activated carbons by various processes. The activated carbons were powdered, characterized using physicochemical methods and used for adsorption studies<sup>4</sup>.

### A. Carbonization procedures

The activated carbon were prepared by the following methods and listed in Table 1.

#### 1. Carbonization with $H_2SO_4$

The dried material was treated with excess conc.  $H_2SO_4$ . Charring occurred along with evolution of heat. The mixture was left in air oven at  $140 - 160^\circ C$  for a period of 24 hours. Then the product was washed with plenty of water, dried at  $110^\circ C$  and activated at  $800^\circ C$  for 10 min.

#### 2. Carbonization with KOH

The dried material is soaked with 10 % KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution decanted off and air dried. Then the material carbonized in muffle furnace at  $400^\circ C$  for 30 minutes. The carbon was powdered and activated in a muffle furnace at  $800^\circ C$  for a period of 10 minutes. After the activation, the carbon was washed sufficiently with 4N HCl to remove the residual KOH. Then the material was washed with plenty of water, dried and stored.

#### 3. Carbonization with $ZnCl_2$

The dried material was impregnated with 10% boiling solution of  $ZnCl_2$  for 2 hours and left for 24 hours. Then excess solution was decanted off and air dried. The dried material was carbonized at  $400^\circ C$  for 30 min. in muffle furnace, powdered and activated at  $800^\circ C$  for 10 min. After

the activation, the carbon was washed with 4N HCl to remove the cations. Then it was washed with plenty of water to remove the acid, dried and powdered.

#### 4. Carbonization with $H_3PO_4$

The dried material was impregnated with 35% boiling solution of  $H_3PO_4$  for 2 hours and left for 24 hours, then excess solution was decanted off and air dried. The dried material was carbonized at 550°C for 1½ hrs in muffle furnace, powdered and activated at 800°C for 10 min. The resulting carbon was washed with plenty of water to remove the acid, dried and powdered.

#### 5. Carbonization with sulphate salts

The precursor material was soaked in 10% solution of sodium sulphate for a period of 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400°C, powdered well and finally activated at 800°C for a period of 10 minutes.

#### 6. Direct pyrolysis

The precursor material was subjected to carbonization at 400°C, powdered well and finally activated at a temperature of 800°C for a period of 10 minutes. After the activation, the material was repeatedly washed with plenty of distilled water.

#### 7. Dolomite process

The dried material to be carbonized was taken over a calcium carbonate bed and the upper layer of precursor also covered with a layer of calcium carbonate. The whole material was carbonized at 400°C, powdered well and activated at 800°C. After the activation, the material was

repeatedly washed with excess water to remove calcium carbonate and dried at 110°C.

#### 8. Chemical activation with $H_2SO_4 + H_2O_2$

In this method, one part of the material and 1.5 parts of  $H_2SO_4$  were mixed with 0.4 parts of  $H_2O_2$  and kept in muffle furnace at 120°C for 12 hours. At the end of this period, the product was washed with large volume of distilled water to remove free acid, dried at 110°C and finally activated at 800°C.

#### B. Characterization of the carbons

Physico-chemical characteristics of the activated carbon samples were studied as per the standard testing methods [5,6,7] and were listed in Table 1. Fourier Transform Infrared (FT-IR) measurements were carried out using NICOLET AVATOR FT-IR model over the range 4000 – 400 $cm^{-1}$ . The Morphological characteristics of the samples were studied using FEI-Quanta 200 Scanning Electron Microscope (SEM).

### III. RESULTS AND DISCUSSION

The pH value of the carbon of CS2 to CS8 were basic in nature. Most of the commercial activated carbon are basic in nature [8]. The pH value of the carbon CS1 prepared by acid process was acidic. This may be due to the introduction of acidic groups onto the activated carbon surface.

Conductivity values of all carbons found with moderate conductivity. However, the conductivity of CS3, CS6, & CS7 was very low. It indicates the absence of more exchangeable sites.

TABLE 1 PHYSICO-CHEMICAL CHARACTERISTICS OF CORDIA SEBESTENA ACTIVATED CARBON

S.No	Properties	Carbon	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8
1	pH		6.9	9.7	7.5	7.2	9.4	9.1	10.7	8.3
2	Conductivity, mS $cm^{-2}$		0.266	0.534	0.128	0.586	0.225	0.139	0.067	0.298
3	Moisture content, %		6.8	10.6	10.8	5.4	8.6	7.8	2.6	9.6
4	Ash, %		28	24.75	24.24	17.82	18.81	14.85	18.25	19.60
5	Volatile matter, %		23.6	15.48	21.2	18.90	10.28	19.23	19.10	16.23
6	Matter soluble in water, %		0.48	0.50	0.50	0.51	0.48	0.40	0.60	0.60
7	Matter soluble in 0.25 M HCl, %		4.5	5.5	3.5	5	5.5	5	8	6.5
8	Bulk density, g $mL^{-1}$		0.56	0.59	0.65	0.53	0.46	0.40	0.50	0.38
9	Specific Gravity		1.53	1.49	1.64	1.46	0.55	0.69	0.59	0.50
10	Porosity, %		63.39	60.40	60.36	63.69	16.36	42.02	15.25	24.00
11	Surface area (BET), $m^2 g^{-1}$		166.96	99.40	300.54	391.36	104.64	303.85	241.2	286.51
12	Methylene Blue Value, mg $g^{-1}$		116	167	110	202	160	73	78	149
13	Iodine Number, mg $g^{-1}$		241.11	126.9	368.01	418.77	129.7	393.39	266.49	304.56
15	Fixed Carbon, %		41.6	49.17	43.76	57.88	62.31	58.12	60.05	54.57
16	Yield, %		39.3	52.3	48.4	53.5	47.7	51.5	49.2	50.6

Considering moisture content of the carbon, it has no effect on its adsorptive power, it dilutes the carbon and necessitates the use of additional weight to carbon during treatment process [9]. Carbon derived by  $ZnCl_2$  impregnation,  $H_2O_2 + H_2SO_4$  process, KOH impregnation have high moisture content of 10.8%, 9.6 % and 10.6% respectively. CS7 has low moisture content of 2.6% comparing to other carbon. Moisture content of other carbons are similar to the commercial activated carbon and are comparable with the results of earlier researchers [10, 11].

Ash content provides the amount of inorganic constituents present in a carbon. CS2 has more ash content, which may be incorporated by the activating agents. CS4 & CS6 shows less ash content, which supports the above said assumption. Less ash content increases the fixed carbon percentage.

Naturally occurring plants have more volatile organic compounds and high percentage of volatile matter. High value of volatile matter reduces the quantity of fixed carbon. From the data, it was clear that all carbons have a good percentage of fixed carbon. Due to high volatile matter, the percentage of fixed carbon was found low in CS1.

Solubility studies of carbon in water and acid were performed to evaluate the amount of impurities present in carbon prepared by different carbonization process. The presence of impurities in carbon may affect the expected quality of the treated water during treatment. From the data it was clear that all the carbon possesses moderate level of impurities. It indicates that all the carbon have very low level of water soluble matter and acid soluble matter.

Bulk density indicates the fibre content of the precursor. Bulk density of all activated carbons do not show much variations indicating that it depends on the nature of the precursor and effect of activating agent is less.

Adsorptive properties are directly related to the porosity of activated carbon, as the highly porous carbon can adsorb large amount of organic compounds. Thus porosity is related to the bulk density and specific gravity of activated carbon. CS4 has higher porosity than the other carbons.

Iodine number can be correlated with the ability of a carbon to adsorb low molecular weight substances. As iodine molecule is relatively small and so provides a measure of surface area or capacity to adsorb small adsorbates. Iodine number for commercial adsorbent ranges from 300 to 1200 mg/g [12]. Iodine number of CS4 carbon is 418.77mg/g, which is comparable with the commercial carbon.

Methylene blue number is an indication of ability of a carbon to adsorb high molecular weight substances like dye

molecule. CS4 shows methylene blue number of 202, indicates that the carbon is good for dye adsorption. Higher yields are desirable in activated carbon production and it helps to reduce production costs. High yield was obtained in the  $H_3PO_4$  process followed by KOH impregnation process.

By comparing the data obtained from characterization studies, CS4 is suitable for preparing the activated carbon of high porosity.

#### *A. Scanning electron microscope analysis*

SEM micrographs of activated carbon particles (Fig. 2a to 2h) showed pores and rough surfaces on carbon sample, which indicated that porous network. CS4 showed the morphology of highly porous activated carbon.

#### *B. FTIR spectra analysis*

In order to gain better insight into the surface functional groups available on the surface of the adsorbents, their FTIR spectra were recorded and they were shown in figs. 1a to 1h. The summary of the peaks and their assignments were given in Table 3. The peak observed around  $3400cm^{-1}$  on the surface of the all activated carbons indicates the presence of O-H stretching vibration in the carbons [13]. The peak around 2923.56 was assigned to C-H stretching of aliphatic compounds [13] were noticed in CS2, CS4, CS6 and CS7. The peaks around 1400, a finger print of C-O stretching were noticed in CS1, CS2, CS5, CS6 and CS7 and peaks at 1000 which are finger print of OH bending of alcohol and carboxylic acids were noticed for all carbon samples. Presence of -CH deformation were noticed in CS1, CS2, CS5 and CS7 carbons around  $870cm^{-1}$ . The peak around  $600-700cm^{-1}$  may be attributed to the C-C stretching vibrations were noticed in CS1, CS6, CS3 and CS2.

#### *C. Dye adsorption characteristics*

Acid, Reactive and Direct dyes have anionic character, whereas Basic dyes are cationic in nature. In this study, Acid orange 7, Basic red 29, Reactive orange 16, and Direct Green 6 were selected for the analysis of adsorption characteristics of CS4 at room temperature. The amount of basic red 29 (cationic dye) adsorption is very high. All the anionic dyes [acid, reactive and direct dyes] show lesser adsorption. Amount of acid orange 7 adsorption is slightly higher than reactive orange 16 and Direct Green 6. This may be due to its smaller molecular size. Reactive orange 16 and Direct Green 6 are high molecular weight dyes; hence, they occupy more area in the activated carbon. This leads to the lowest amount of adsorption on the carbon surface.

TABLE 2 PEAK ASSIGNMENTS OF FUNCTIONAL GROUP OF ALL SAMPLES

Peak positions/Samples								Possible assignments	References
CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8		
-	-	3555.13	-	-	-	3639.02	3639.98	O-H stretching	[14]
3430.74	3420.14	3443.28	3422.06	3436.53	3431.71	3430.74	-		
-	-	3378.67	-	-	-	-	-		
-	-	3280.32	-	-	-	-	-		
-	-	3205.11	-	-	-	-	-		
-	2923.56	2723.96	2922.59	-	2923.56	2924.52	-	C-H stretching & C=O str of carboxylic acids	[15,19]
-	-	-	-	-	-	2514.72	2519.54		
-	-	-	-	-	-	-	2356.59		[14,16]
						1797.33		C=O str of carbonyl group	[7,18]
-	-	-	-	-	-	-	-	C-O str and OH bending of alcohol and carboxylic acids	[13,18]
1426.1	1408.75	-	-	1425.14	1417.42	1427.07	-		
1119.48	-	-	-	-	-	-	1245.79		
1029.8	1026.91	1038.48	1045.23	1029.8	1029.8	1040.41	1015.34		
872.631	867.81	-	-	871.667	-	874.56	-	-CH def	-
615.181	699.069	686.534	-	-	606.503	-	-	C-C stretching	[20]
-	-	-	-	-	-	710.64	700.034	C-C stretching	[20]
-	-	575.865	532.257	-	-	-	581.433	Out of plane C-H bending mode	[21]
-	-	468.617	404.978	-	446.44	-	448.369	Inplane aromatic ring deformation vibration	[22]

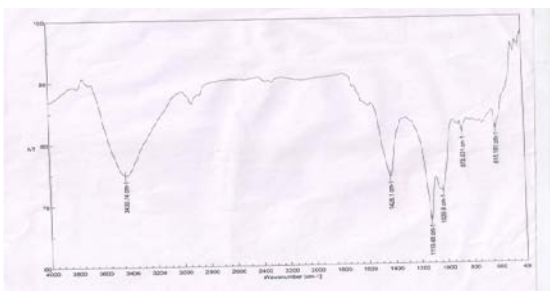


Fig.1a FTIR spectra of CS1

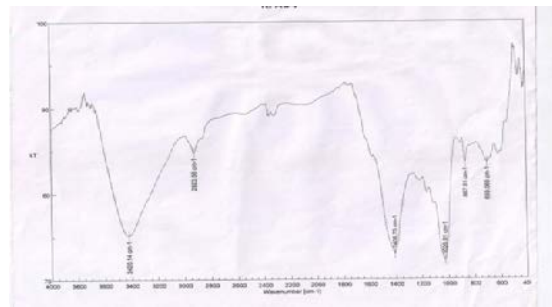


Fig.1b FTIR spectra of CS2



Fig.1c FTIR spectra of CS3

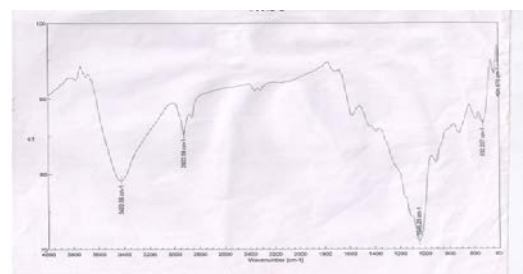


Fig.1d FTIR spectra of CS4

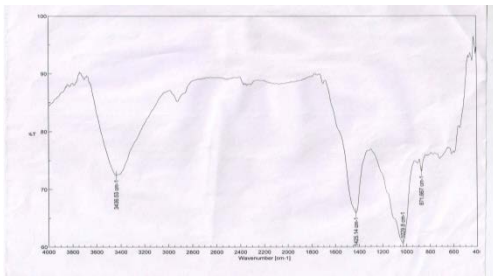


Fig.1e FTIR spectra of CS5

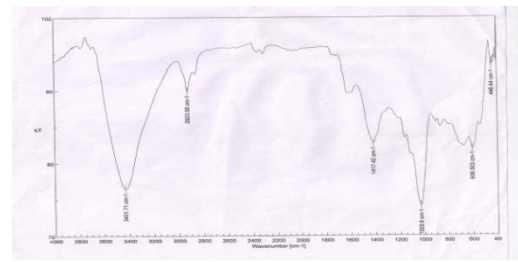


Fig.1f FTIR spectra of CS6

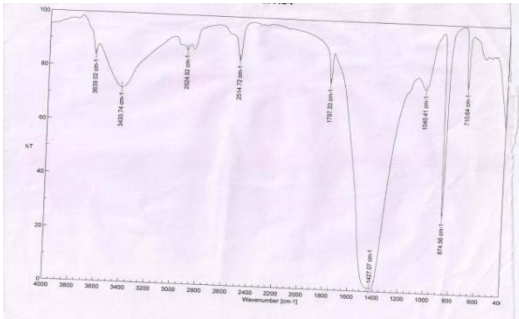


Fig.1g FTIR spectra of CS7

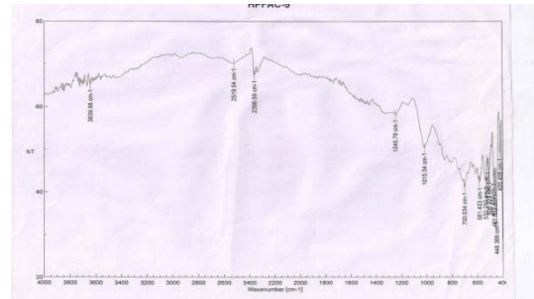


Fig.1h FTIR spectra of CS8

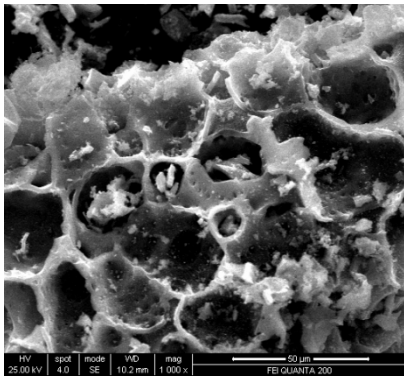


Fig.2a SEM image of CS1

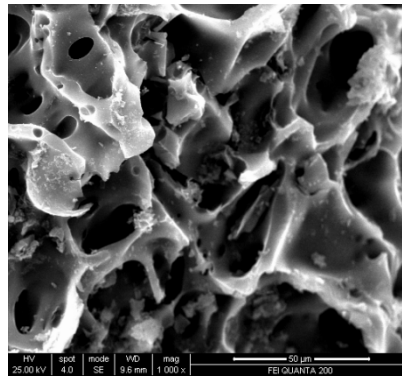


Fig.2b SEM image of CS2

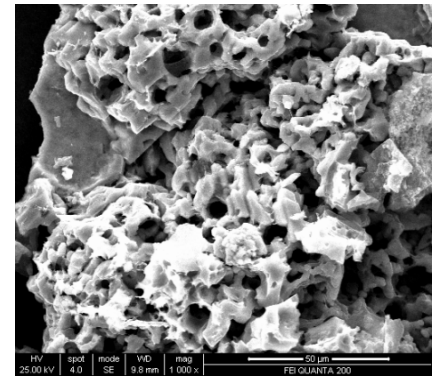


Fig.2c SEM image of CS3

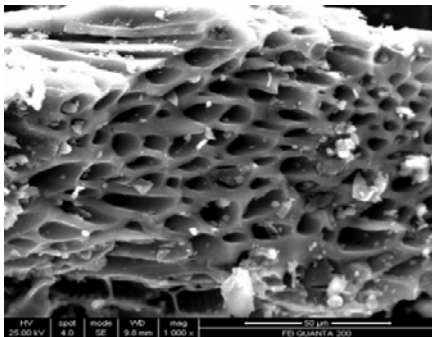


Fig.2d SEM image of CS4

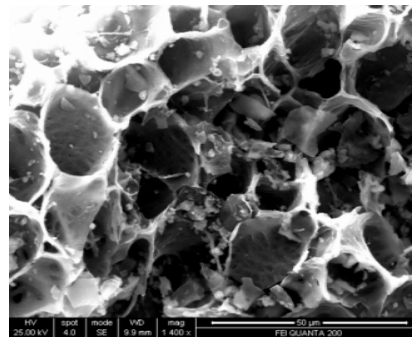


Fig.2e SEM image of CS5

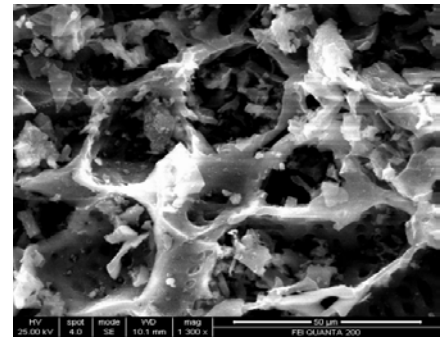


Fig.2f SEM image of CS6

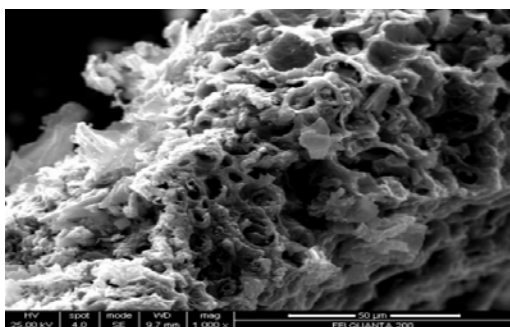


Fig.2g SEM image of CS7

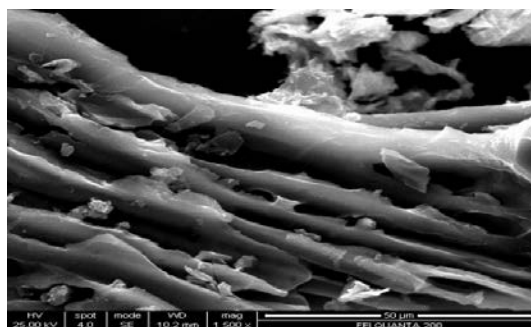


Fig.2h SEM image of CS8

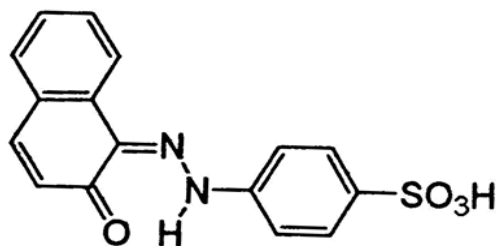


Fig.3a Acid Orange 7(C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S)  
(C.I.15510,M.W: 350.33,λ<sub>max</sub>:484nm)

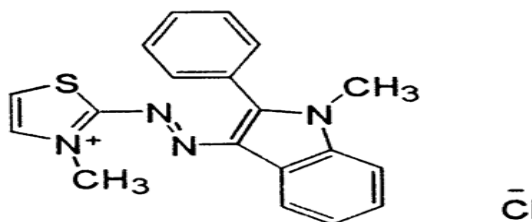


Fig.3b Basic Red 29(C<sub>19</sub>H<sub>17</sub>ClN<sub>4</sub>S)  
(C.I. 11460,M.W: 368.98,λ<sub>max</sub>:511nm)

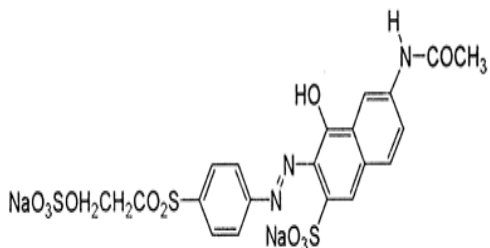


Fig.3c Reactive Orange 16(C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>11</sub>S<sub>3</sub>)  
(C.I. 17757,M.W: 617.54,λ<sub>max</sub>:494nm)

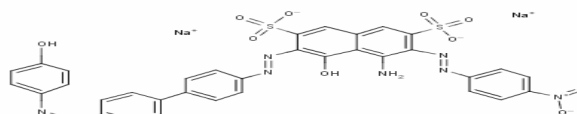


Fig.3d Direct Green 6(C<sub>34</sub>H<sub>22</sub>N<sub>8</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>2</sub>)  
(C.I.30295,M.W: 812.69,λ<sub>max</sub>:621nm)

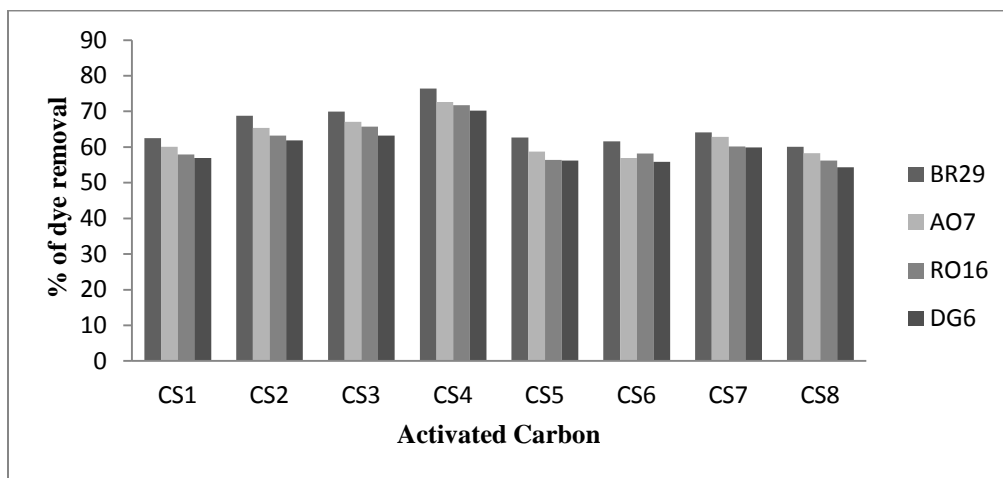


Fig.3 Percentage Of Various Dyes Adsorbed Onto Various Activated Carbon Prepared From **Cordia Sebestena**

#### IV. CONCLUSION

From the results of the present investigation, it was found that Cordia Sebestena fruit, a type of gardening plant material has been conveniently utilized and economically used to prepare the activated carbon. An extensive study was made with different activated carbons prepared by various processes reveal that CS4 is assumed as a better activated carbon. It was proved by characterisation studies from IR spectroscopy and SEM analysis. H<sub>3</sub>PO<sub>4</sub> activation process produces highly active carbon with high porosity. Porosity plays a major role in the selected adsorbent – adsorbate system. The adsorption capacities of various carbons for different categories of dyes (Acidic, Basic, Reactive and Direct) are tested. Basic dye is adsorbed more than the other dyes by the activated carbon obtained from H<sub>3</sub>PO<sub>4</sub> activation process. A detailed study on the kinetics and isotherms of the above said four dyes is under progress.

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