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CHARACTERIZATION STUDIES OF ACTIVATED CARBON FROM LOW COST AGRICULTURAL WASTE: *LEUCAENA LEUCOCEPHALA* SEED SHELL

A. Babu Rajendran[1,*], G. Manivannan[2], K. Jothivenkatachalam[3] and S. Karthikeyan[4]

[1]Department of Chemistry, Govt. Hr. Sec. School, Kannivadi, Tirupur- 639202, (TN) India.
[2]Department of Chemistry, Erode Arts and Science College, Erode- 638009, (TN) India.
[3]Department of Chemistry, Anna University, BIT Campus, Tiruchirappalli- 620024, (TN) India.
[4]Department of Chemistry, Chikkanna Govt. Arts College, Tirupur- 641602, (TN) India.
[*]E-mail: skmush@rediffmail.com

ABSTRACT

Agricultural Solid waste was used for the recovery of valuable materials like *Leucaena leucocephala* seed shell find a significant role in the adsorption. Activated carbon samples are prepared by different activation process and SEM, XRD, FTIR analysis. Owing to the high active surface properties of the activated carbons are due to the functional groups present in it and Surface morphology also plays a vital role in the sorption properties. The carbon samples were analysed for their Physico-Chemical characteristics. The results show that an activated carbon with high adsorptive properties can be conveniently prepared from *Leucaena leucocephala* seed shell waste impregnation with H_3PO_4 solution process followed by activation at 800 ^oC yields with more porosity and high surface area. Suitability of the effective adsorbent was analysed for the various dye solutions.

Keywords: *Leucaena leucocephala* seed shell, Adsorption, Activated carbon, Carbonisation process, Surface area.

INTRODUCTION

Nowadays pollution of water due to the discharge of dyeing industry effluent is a major concern. Dyeing industrial wastewater unfavorably alters the environment due to its high toxicity and non-biodegradable nature. Several techniques such as electrochemical coagulation, Reverse osmosis, nano filtration, adsorption using activated materials etc., are used for the removal of dye from wastewater. Dyeing industry effluent was treated by adsorption technique to be an efficient and economic process. In recent years, many naturally occurring waste materials have been investigated to evaluate their suitability and ability to be used as an adsorbent. Recently some agricultural wastes and forestry products have been developed as adsorbents. The cost of these biomaterials is very low when compared to the commercially available activated carbon and also renewable sources of raw materials for the production of activated carbon. Activated carbon prepared from different materials like agricultural wastes[1], sago waste[2], moringa oleifera fruit shell waste[3], albizia amara pod shell[4], jatropha curcas stem[5], oil palm waste[6], coconut shell waste[7], tropical wood[8], saw dust[9], pinus pinaster bark[10], corncob[11], eucalyptus bark[12], pistachio shells[13], babool wood[14], etc., Which have been used for the preparation of activated carbon. Basically there are two different processes for the preparation of activated carbon namely physical and chemical activation[15]. Physical activation involves carbonization of precursor followed by activation of the resulting char in presence of activating agents such as CO_2 or steam. Chemical activation on the other hand, involves the carbonization of precursor in presence of chemical agents[16]. In the chemical impregnation methods, first impregnation of precursor with the selected chemical followed by carbonization and activation. In case of acid process, charring of the material done with acid like H_2SO_4 followed by activation. The purpose of carbonization and charring is to remove the volatile matter and increase the carbon content. Chemical

activation has more advantages[17] over physical activation with respect to higher yield, more surface area and better development of porous structure, oxygenated surface complexes in carbon. In the present investigation, activated carbon is prepared from *Leucaena leucocephala* seed shell waste by various physical and chemical activation processes.

EXPERIMENTAL

Leucaena leucocephala seed shell is used as precursor for the preparation of activated Carbon. The seed shell was broken into small size, washed with distilled water, dried in sunlight for 3 days, and used for the preparation of activated carbons by suitable physical and chemical processes. The carbonized material was finely powdered, characterized using Physico-Chemical methods and used for adsorption studies.

Carbonization procedures[18]

1. Carbonization with H_3PO_4

The material to be carbonized is impregnated with a boiling solution of 10% H_3PO_4 for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess solution was decanted off and air dried. Then the material was carbonized in muffle furnace carbonized at 120-130 °C. The dried material was powdered and activated in a muffle furnace at 800 °C for a period of 60 minutes. Then the material was washed with large volume of water to remove residual acid, dried and powdered.

2. Dolomite process

Sufficient quantity of dried material 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 followed by the thermal activation at 800 °C. After the activation, the material was repeatedly washed with excess water to remove calcium carbonate and dried at110°C.

3. Carbonization with sulphate salts

In this method 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.

4. Carbonization with Zinc chloride

The material to be carbonized is impregnated with a boiling solution of 10% zinc chloride for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess chloride solution decanted off and air dried. Then the material was carbonized in muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace kept at 800 °C for a period of 10 minutes. Then the material was washed with plenty of water until the chloride had disappeared from the washed water (tested by the $AgNO_3$ method) to remove residual acid, dried and powdered.

Table-1: List of Activated Carbons prepared from *Leucaena leucocephala* seed shell waste and their Preparation Methods

S. No.	Activated Carbon	Preparation Method
1	LSAC1	H_3PO_4 impregnation
2	LSAC2	Na_2SO_4 impregnation
3	LSAC3	H_2SO_4 Process
4	LSAC4	$ZnCl_2$ impregnation
5	LSAC5	Dolomite process

5. Acid process

The dried material was soaked well with excess of sulphuric acid solution for a period of 24 hours.

Charring of the material take place immediately, followed by evolution of heat and fumes. At the end of 24 hours the excess of sulphuric acid were decanted off and air dried. Then the reaction subsided, the mixture was left in the muffle furnace carbonized at 140-160 °C. At the end of this period, the product was washed with large volume of water to remove free acid, dried at 110 °C and finally activated at 800 °C. Table -1 shows List of Activated Carbons prepared from *Leucaena leucocephala* seed shell waste and their Preparation Methods.

Characterization of the Activated Carbon

Physio-chemical characteristics of the activated carbon samples were studied as per the standard testing methods.[19-21] *Leucaena leucocephala* seed shell activated carbon and their values were given in the Table-2.

Surface area and Pore size distribution Analysis

The N_2 adsorption- desorption isotherms of activated carbon were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta chrome corporation) in order to determine the surface area and pore volume. The surface area calculated using the BET equation. In addition, the t-plot method applied to calculate the micropore volume and external surface area (Mesoporous Surface area). The total pore volume of adsorbate (N_2) at relative pressure of 0.99. All the surface area calculated from the nitrogen adsorption isotherms by assuming the area of nitrogen molecule was 0.162 nm^2.

FTIR spectra and SEM

The electronic structure of carbon samples were examined using FTIR 1725x (Perkin-Elmer) Spectrometer. The measurements were carried out over the range of 4000-400 cm^{-1}. Carbon samples (0.33 wt%) were stirred with dry KBr (Merk, spectroscopy grade) and then pressed to form appropriate tablets. The Morphological characteristics of the carbon samples were studied using Scanning Electron Microscope (SEM) (Make: Philips SIRON with EDX facility at IISc Bangalore).

RESULTS AND DISCUSSION

General Properties

The characteristics of the activated carbon prepared from *Leucaena leucocephala* seed shell waste in various methods were listed in Table 2. The pH values of the carbon prepared by acid processes (LSAC1, LSAC3 and LSAC4) were acidic. This may be due to the introduction of acidic groups on to the activated carbon surface. Except the above said three carbons, the remaining two carbons were basic in nature. Mostly the commercial activated carbons are basic in nature[22] due to the presence of residual salts present in the carbon. Conductivity values do not show much difference. This is because of the cations in anionic carbons and anions in basic carbons may be responsible for the conductance. Although moisture content has no effect on adsorption power, it dilutes the carbon and adds the weight of carbon during treatment process.[18].

LSAC1 has high moisture content when compared to other carbon. The moisture is absorbed by any porous materials. The moisture content of all the carbons discussed are nearly normal and compared with the values given[16&23]. Ash content gives an idea of the amount of inorganic constituents associated with the carbon. Table-2 shows that all the five activated carbons have less ash content which increase fixed carbon value. Volatile matter is due to the presence of organic compounds present in the raw material. The data given in the Table-2 have a good percentage of fixed carbon. The amount of impurities present in carbon showed from matter soluble in acid which affect the water quality. But the present data shows that all the carbons contain low amount of impurities.

The adsorption power of an activated carbon is increased by mainly on porosity. Porosity is related to bulk density and specific gravity of the activated carbon. LSAC1 has higher surface area and porous carbon compared to other activated carbons.

Bulk density shows the fibre content of the adsorbent. From the above data shown that all the five carbons have almost equal bulk density. In general an adsorbent with bulk density need not be regenerated

frequently because it can hold more adsorbate per unit weight[24]. Iodine number is used to characterize activated carbon performance. It is a measure of activity level (higher value shows higher degree of activation).

Table -2: Physio-Chemical characteristics of *Leucaena leucocephala* seed shell waste activated carbon

S. No	Carbon Properties	LSAC1	LSAC2	LSAC3	LSAC4	LSAC5
1	pH	9.42	5.98	8.97	9.94	9.32
2	Moisture Content, %	7.4	2.4	4.98	2.4	2.4
3	Ash Content, %	13	9.9	7.99	19.4	14.28
4	Volatile matter, %	19.3	20.1	21.5	20.3	21.2
5	Conductivity, ms/cm	1.153	0.72	0.29	0.64	0.82
6	Specific Gravity, S	0.662	0.731	1.20	1.25	1.29
7	Bulk Density, g/cm^3	0.241	0.40	0.495	0.326	0.322
8	Porosity, %	62.73	43.1	58.36	73.66	74
9	Matter soluble in water, %	5.74	2.35	4.95	3.1	1.95
10	Matter soluble in Acid, %	14.2	8.92	6.7	14	11.3
11	Iodine Number, mg/g	484	219	152	216	225
12	Surface area, m^2/g	499.23	231	163	228	237.5
13	Fixed Carbon, %	58	65.5	64	52	57
14	Yield, %	59.5	36	47	49	52
15	Process	H_3PO_4	Na_2SO_4	H_2SO_4	$ZnCl_2$	$CaCO_3$

Scanning Electron Microscope (SEM)

SEM Microscopes Fig-1 of activated carbon showed cavities, pores and more rough surfaces on the carbon samples. The surface area of the adsorbent increased by these Granular pores with H_3PO_4 activation process. From the results of SEM, It was found that there are holes and cave type opening on the surface of the specimen that would have increased surface available for adsorption[25]. The surface area of LSAC1 carbon will be enhanced by the presence of more porosity which can hold more solute from the dye solution during the adsorption process.

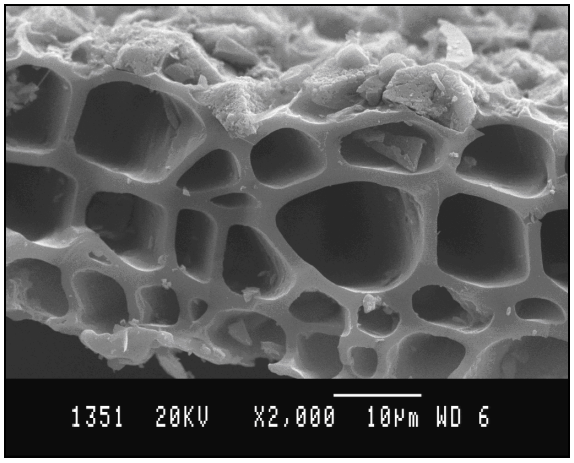
XRD

Fig-2 shows that the XRD pattern of activated carbons obtained by different impregnation process. The peaks observed in XRD patterns 2ɵ=25, 45, and 48 for all the carbon samples are due to the presence of graphitic crystallites of carbon which correspond to the (002), (100) and (101) planes of the graphitic structures.

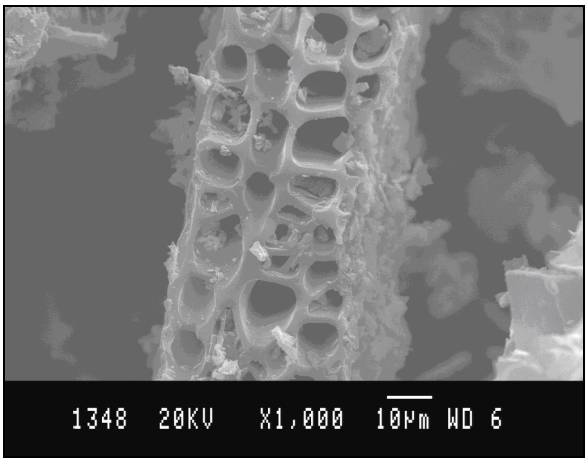
FTIR

The presence of different functional groups in the activated carbon prepared from *Leucaena leucocephala* seed shell waste was determined by IR measurements and the results were shown in the Fig-3 (a to e). Most of the carbons exhibit similar IR spectroscopic features. Those are very intense/sharp –OH stretching absorption. The broad band observed in the region of 1000 to 1250 cm^{-1} was assigned due to a characteristic absorption of –OH group. These results are in good agreement with the findings of many investigators[26]. An absorption peaks appearing at 2850 to 2920 cm^{-1} for LSAC1 suggests the presence of CH stretching vibration and CH_2 asymmetrical vibrations. 1500 cm^{-1} showed the presence of

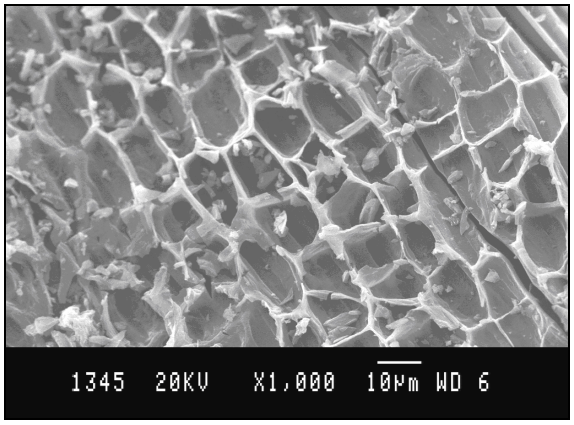
(C=C) bond in alkenes. Similarly the peaks at 1552 cm^{-1} and 1571 cm^{-1} are assigned to C=O stretching band in LSAC2, LSAC3, LSAC4 and LSAC5.



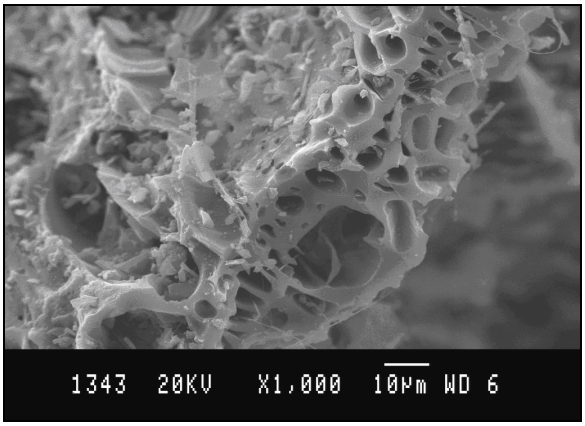
(a.) SEM image of LSAC1



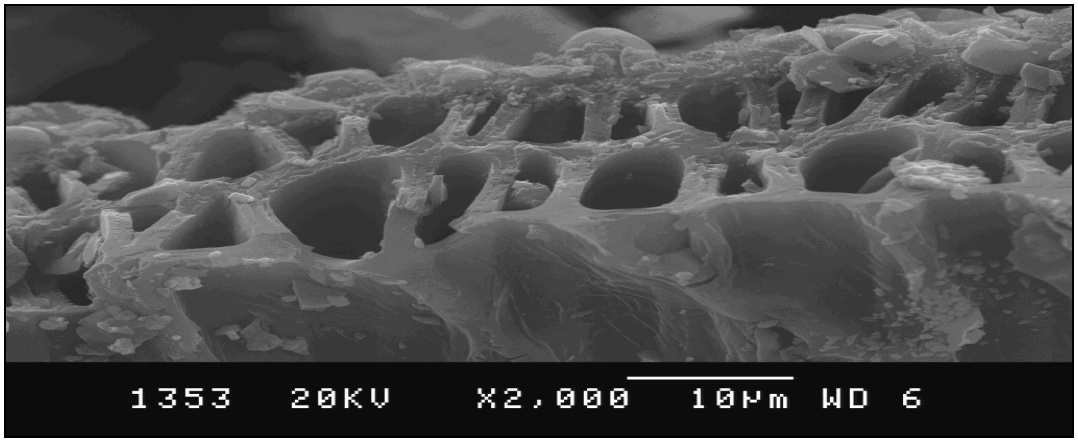
(b.) SEM image of LSAC2



(c.) SEM image of LSAC3

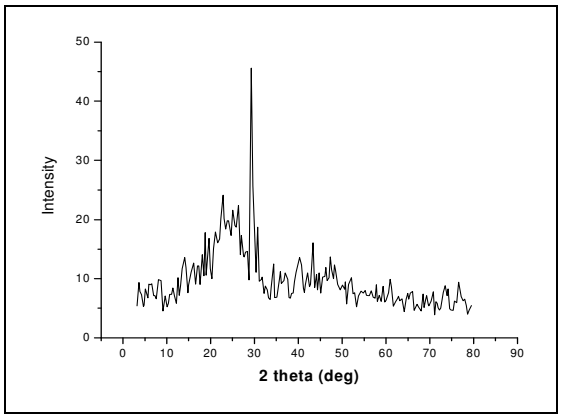


(d.) SEM image of LSAC4

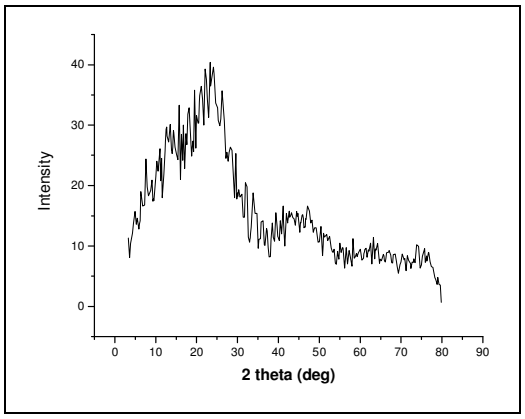


(e.) SEM image of LSAC5

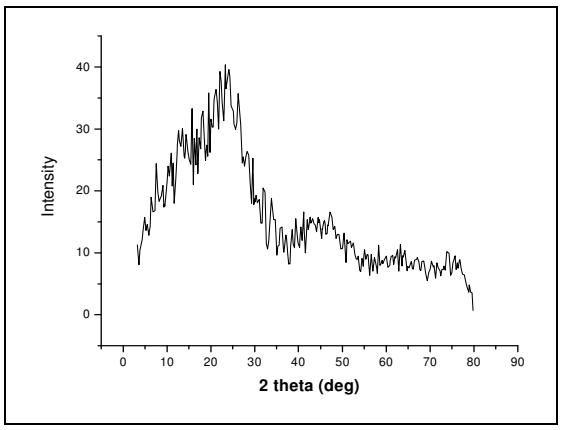
Fig.-1: SEM Photograph of (a) LSAC1, (b) LSAC2, (c) LSAC3, (d) LSAC4 and (e) LSAC5.



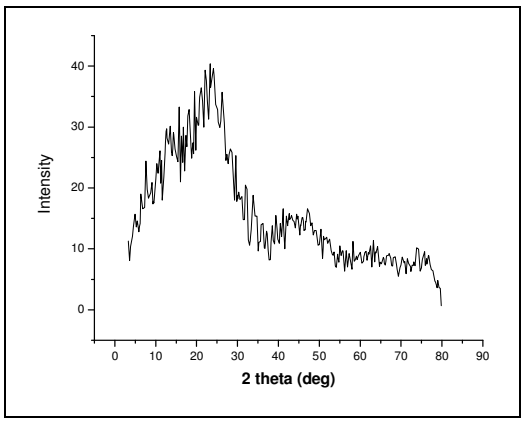
(a.) XRD image of LSAC1



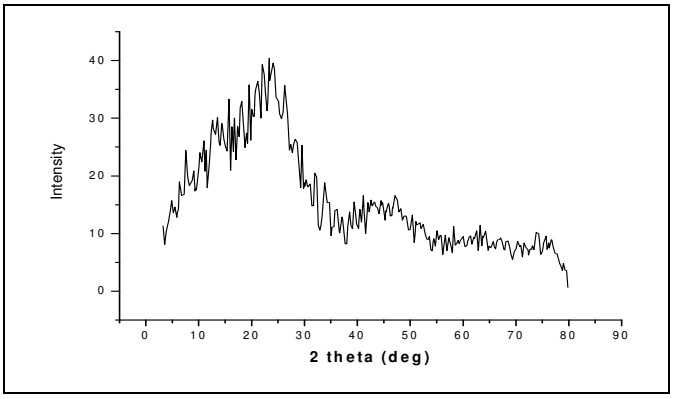
(b.) XRD image of LSAC2



(c.) XRD image of LSAC3

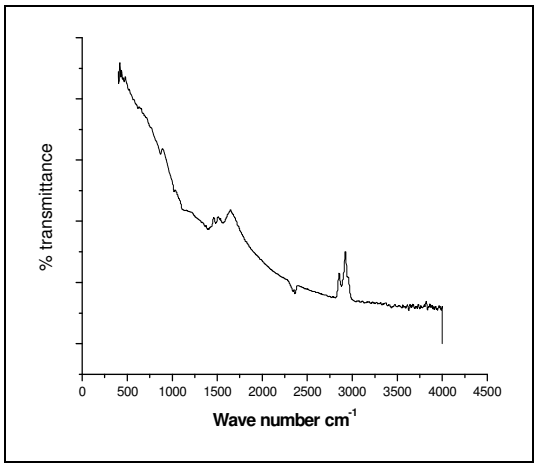


(d.) XRD image of LSAC4

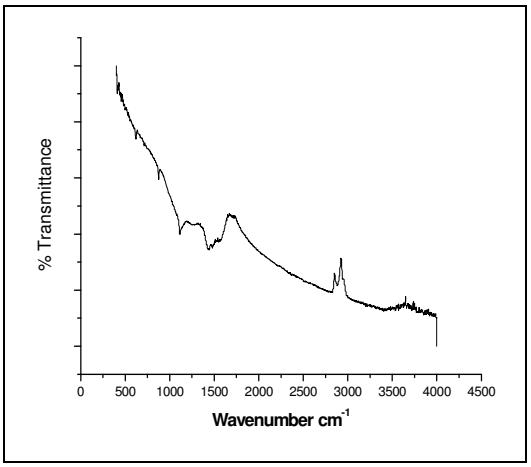


(e.) XRD image of LSAC5

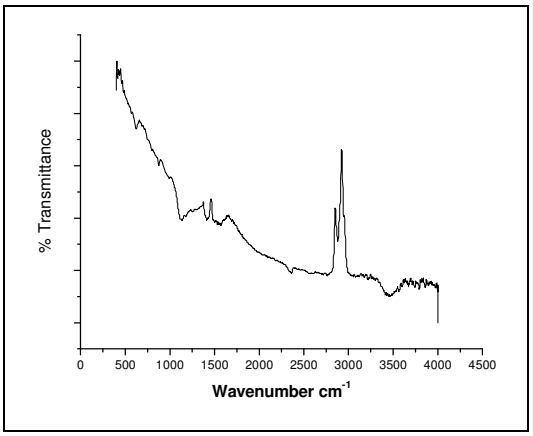
Fig.-2: XRD pattern of (a) LSAC1, (b) LSAC2, (c) LSAC3, (d) LSAC4 and (e) LSAC5



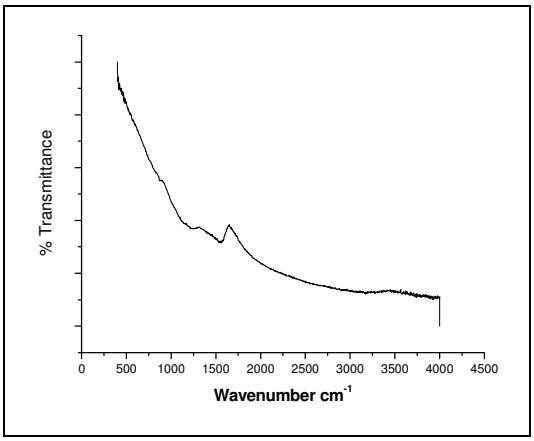
(a.) FTIR image of LSAC1



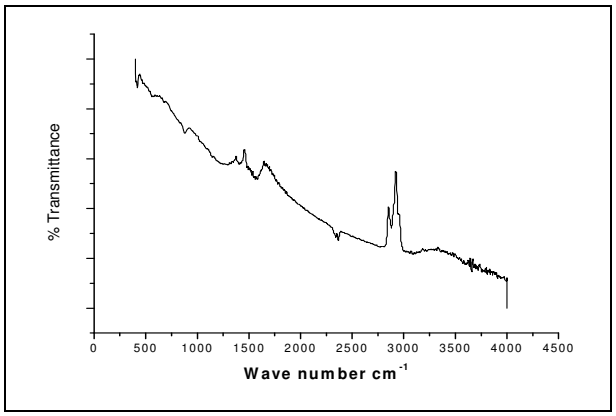
(b.) FTIR image of LSAC2



(c.) FTIR image of LSAC3



(d.) FTIR image of LSAC4



(e.) FTIR image of LSAC5

Fig.-3: FT-IR spectra of (a) LSAC1,(b) LSAC2, (c) LSAC3,(d) LSAC4 and (e) LSAC5.

Evaluation of Activated carbon samples for the removal of dyes

The acid, reactive and direct dyes have anionic character and basic dyes are cationic nature. Fig-4 shows the percentage of anionic and cationic dye removal for five different activated carbons prepared from *Leucaena leucocephala* seed shell waste. A safe connection between surface area and surface groups of the specially made activated carbon and percentage of dye removal through adsorption can be observed. Five types of activated carbons prepared from *Leucaena leucocephala* seed shell waste a similar behavior was observed for anionic dyes (i.e. acid, reactive and direct dyes) following an increase in the adsorption capacity with increase in the surface area. Different performances are obtained for the material tested, varying from 88.2% to 96.1% (for sample LSAC1) of anionic dye removal for the *Leucaena leucocephala* seed shell waste activated carbon. Sample LSAC1 is the most efficient adsorbent for the adsorption of all anionic dyes. LSAC1 has higher surface area and adsorps larger amount of anionic dyes than LSAC4.

CONCLUSION

From the present investigation, Activated carbons prepared from *Leucaena leucocephala* seed shell waste showed considerable surface area obtained. The difference in textural characteristic gave an account to the activation processes. The highest surface area obtained for activated carbon prepared using *Leucaena leucocephala* seed shell waste by H_3PO_4 process followed by activation at 800 ^oC under a nitrogen atmosphere (505 m^2g^{-1}). The concentration of the surface groups varied depending on the various types of activation conditions. Among the five carbons investigated LSAC1 showed the highest concentration of surface groups. Carbon prepared from above process and materials can be economic and conveniently used for both organic and inorganic effluent removal. On the basis of surface area, the following activated carbons/processes are compared with commercially available activated carbons such as LSAC1, LSAC2, LSAC3, LSAC4 and LSAC5. These carbons can be used for the removal of textile effluent because of the capability of adsorbing organics from the solution. The adsorption of various dyes with LSAC1 is more effective adsorbent than the other processes.

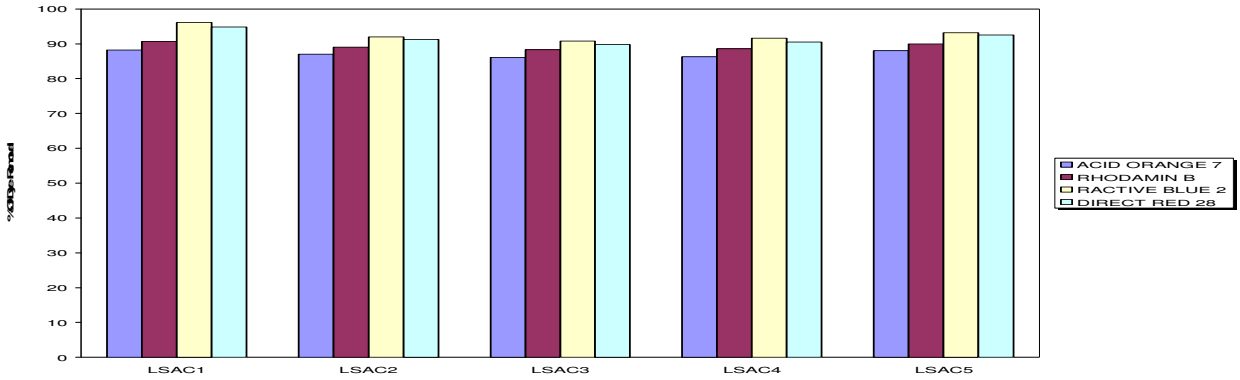


Fig.-4: Percentage of dye removal by *Leucaena leucocephala* seed shell waste Activated Carbons.

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