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The Effect of Activating Agents on the Activated Carbon Prepared from *Feronia limonia* (L.) Swingle (Wood Apple) Shell

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Abstract

Activated carbon samples are characterized by their high adsorption capacities. Although the highly active surface properties of the activated carbon are after attributed to the chemical functional groups, surface morphology plays a significant role in determining the surface availability. Micropores, mesopores and macropores distribution in activated carbon samples are closing related to their preparation methods. The objectives of this study were to evaluate the influence of activation methods on the characterization of activated carbon produced from *Feronia limonia* shell. The resulting samples were characterized by nitrogen adsorption measurements at 77 K to obtain surface area and pore size distributions. The morphology of the resulting sample was observed by scanning electron microscopy and the electronic structure was investigated by Fourier transformation infrared spectroscopy techniques. Results obtained indicate that the activated carbon prepared using *Feronia limonia (L.) Swingle (wood apple) shell* by $ZnCl_2$ carbonization process followed by activation at 800° C under a nitrogen atmosphere yielded activated carbon with the highest surface area and more developed micro, meso and macroporosity.

KEY WORDS: Feronia limonia shell; *Activated carbon; Carbonization processes*

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1. INTRODUCTION

Various dye/color removal methods like aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, diffusion, filtration, flotation, softening, hydrogen peroxide catalysis and reverse osmosis have been proposed from time to time. However, all these methods suffer from one or more limitations and none of them was successful in removing the color from wastewater completely.

For the past ten years, attention has been shifted towards adsorption technique, which emerged as one of the widely accepted methods for the removal contaminants from wastewater. Activated carbon adsorption has been cited by the US Environmental Protection Agency (USEPA) as one of the best available environmental pollution control technologies (Debyshire et al.2001).

One of the major challenges associated with adsorption using activated carbon is its cost-effectiveness. Researches in the recent past have mainly focused on the preparation of the activated from agricultural waste materials as an alternative for the commercial activated carbon. Peat mass (Chen et al. 2001), corncob (Bosinco et al.1996), coconut shell (Kirubakaran et al. 1991), pistachio shell (Abe et al. 1990), saw dust (Xiongzun et al. 1986), walnut shell Khan et al. 1985, tropical wood (Maniatis et al. 1992) and almond shell (Hayashi et al. 2000) are some of the agricultural waste materials, which have been fruitfully used for the preparation of activated carbon. The efforts do not go beyond some primary interpretations of the performance of the adsorbents in terms of their textural properties (porosity, surface area). More recently, some authors have started to interpret the surface chemistry of activated carbon with the adsorption performance (Manuel Fernando Peyeira et al. 2003).

Therefore, carbons with excellent surface properties and specific functionalities to be developed to create a high affinity for the adsorption of adsorbate in its solution. It will be beneficial to have an activated carbon with sufficient amount of super microporosity and mesoporosity for the enhanced solute adsorption.

In this study, activated carbons derived from *Feronia limonia* (L.) Swingle (wood apple) shell was analyzed with various techniques such as Scanning Electron Microscopy (SEM) and Fourier Transformation

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Infrared Spectroscopy (FT-IR) in order to understand the properties. The objective of this paper is to study the physico-chemical characteristics of activated carbon prepared from *Feronia limonia* (wood apple) shell by various physical and chemical activation process with a view to use them in the treatment of wastewater.

2. EXPERIMENTAL

2.1 Carbonization and activation

Feronia limonia (wood apple) shell as a precursor material collected from various parts of south India, cut into pieces of nearly 1 to 3 cm size and dried at 110° C for 3 hours in a hot air oven. In the $ZnCl_2$ impregnated process, the dried material was digested in a boiling solution of (10% w/v) anhydrous Zinc Chloride for 1 hour, then the remaining solution was drained off and oven dried at 110° C for 6 hours. This material was carbonized at 550° C for 1 hour and then activated in a tubular furnace under nitrogen atmosphere. The temperature was ramped from ambient temperature to 800° C at 10° C/min. for 2 hours. The sample was cooled in nitrogen atmosphere inside the furnace. After cooling, the sample was treated with 0.1M HCl solution maintained at 80° C for 24 hours and then washed with double distilled water and dried at 110° C for 6 hours. Activated carbon prepared from *Feronia limonia (wood apple) shell* by various processes shown in the table 1.

Another sample of carbon prepared by the same procedure stated above with activation at 800°C instead of nitrogen atmosphere and was designated as FAC2. In the dolomite ($CaCO_3$) process, the material was activated over the layer of powdered calcium carbonate in a closed graphite crucible at 550^0C for 30 min, followed by thermal activation at 750° C for 30 min. After the activation the material was repeatedly washed with plenty of distilled water and dried at 110° C for 6 hours

In acid process, activated carbon was prepared by treating the cleaned raw material with 1:1.8 parts of concentrated sulphuric acid and kept in a hot air oven at 80° C for 12 hours. The carbonized material was washed with plenty of water and finally with distilled water to remove free acid. Then it was soaked in 1% (w/v) sodium bicarbonate solution for 12 hrs to remove any residual acid and the material subjected to thermal activation at 750° C for 30 min. After activation the carbon was washed with double distilled water and dried at 110° C for 6 hours.

Activated carbon also prepared using the activating agents like hydrogen peroxide and Ammonium persulphate. In addition to 1.8 parts sulphuric acid, 0.4 parts of H_2O_2 in the case of FAC6 and 0.1 parts of ammonium persulphate added for the preparation of FAC4.

Table 1. Activated carbons prepared from *Feronia limonia* shell by different activation Processes

Sample	Treatment process
FAC1	$ZnCl_2$ impregnation process + Thermal Activation under N_2 flow
FAC2	$ZnCl_2$ impregnation process + Thermal Activation without N_2 flow
FAC3	$CaCO_3$ Process + Thermal Activation
FAC4	H_2SO_4 Process with $NH_4S_2O_8$ + Thermal Activation
FAC5	H_2SO_4 Process + Thermal Activation
FAC6	H_2SO_4 Process with H_2O_2 + Thermal Activation

2.2 Characterization of the activated carbon

pH and conductivity were analyzed using Elico make pH meter (model L1-120) and conductivity meter (model M-180), respectively. Moisture content (%) by mass, Ash (on dry basis) % by mass, Volatile matter, Bulk density, Specific Gravity, Porosity, Meter soluble in water, Matter soluble in Acid, pH_{zpc}, Iodine Number were analyzed as per standard procedures.

2.3 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, Quanto Chrome Corporation) in order to determine the surface area and total 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 estimated using liquid volume of adsorbate (N_2) at a relative pressure of 0.99. All the surface area calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule was 0.162 nm^2.

2.4 FT-IR spectra and SEM

The electronic structure of carbon samples were examined suing FT-IR 1725 x (perkin-Elmer) spectrometer. The measurements were carried out over were stirred with dry KBr (Merk, spectroscopy grade) and then pressed to form appropriate tablets. The surface morphology of carbon samples observed with SEM (HITACHI S3000N).

3. RESULTS AND DISCUSSION

The characteristics of activated carbon prepared from *Feronia limonia* (wood apple) shell in different activation methods were given in the Tables 2 and 3. The evolution of characteristics of carbon (Table 2) indicated that the density of carbon prepared from different processes were close to each other. No major deviations noticed in bulk density values. The uniform bulk densities of the activated carbon imply that *Feronia limonia* (wood apple) shell has moderate resistance towards chemicals.

From Table 2 the moisture content found to be high in FAC1 & FAC2. The result implies that extensive porosity introduced by chloride process in the carbon structure. Even though moisture content of the carbon has no effect on its adsorptive power, moisture necessitates the use of additional weight of carbon during treatment process. Among the carbons prepared by various methods, the carbon obtained by dolomite process contains less moisture. Ash content generally the range 4000 – 400cm^{-1}. Carbon samples (0.33 wt%) gives an idea about inorganic constituents associated with carbon obtained by different carbonization methods. The ash content values from Table 2 indicate that the overall ash content for all the varieties of carbon were comparatively lesser values. This may be attributed to lower inorganic content and higher fixed carbon, which is inherent to the organic nature of the material.

Solubility studies of carbon in acid and water were performed to evaluate the amount of impurities present in the carbon prepared by different carbonization processes. The high value of water soluble matter in the carbon prepared by dolomite process indicates that a large amount of carbonate salts would have been incorporated into the carbon structure the same trend noticed for matter soluble in acid also.

The matter soluble in water and matter soluble in acid in the carbon prepared from acid processes were very low. Due to high charring and high solubility of acid, low impurities are there for water and dil. HCl to dissolve from the carbon.

The carbon derived in acid process is acidic in nature with moderate conductivity compared with the carbon prepared by other carbonization processes.

Table 2. *Feroina limonia* Shell Activated Carbon Properties

Properties	Activated Carbon					
	FAC1	FAC2	FAC3	FAC4	FAC5	FAC6
pH	6.0	6.2	8.3	6.8	5.7	7.1
Moisture content, %	17.20	17.80	6.80	11.80	11.20	13.80
Ash Content, %	10.16	14.20	13.89	8.86	14.46	8.36
Conductivity, mS / cm	0.51	0.34	0.13	0.42	0.40	0.39
Specific Gravity	1.49	1.32	0.89	1.37	1.33	1.88
Bulk Density, g / ml	0.757	0.744	0.657	0.759	0.750	0.699
Porosity, %	49.19	43.64	26.18	44.60	43.61	62.82
Matter Soluble in water, %	1.12	1.43	1.50	0.44	0.23	0.81
Matter Soluble in 0.25M HCl, %	1.78	2.06	2.03	1.84	1.48	1.81
Surface Area, m^2/g	925.00	844.66	223.77	309.61	229.67	539.70
Iodine Number, mg/g	826	814	182	276	201	509
pH$_{ZPC}$	3.9	4.2	6.9	3.6	5.2	3.3
Yield, %	42	37	49	51	55	52

As reported, this may be due to the incorporation of acid in the carbon structure (Sivakumar, 2002). Chloride impregnated carbon is also found to exhibit moderate conductivity. This may be due to the development of exchangeable sites on the surface of the activated carbon.

The surface area of carbon prepared by various processes found in the following order.

FAC1 > FAC2 > FAC6 > FAC4 > FAC5 > FAC3

The higher surface area of carbon FAC1 & FAC2 prepared by zinc chloride processes ($ZnCl_2$ + N_2 & $ZnCl_2$) may due to the restricted pore shrinkage during activation. The iodine numbers of all the carbon were found in the same order as that of surface area. This indicates that the carbon FAC1 & FAC2 have the maximum adsorption capacity. Carbons with high surface area considered the most superior for adsorption of organic substances (Hu & Srinivasan 1997). The nitrogen adsorption-isotherm data at liquid nitrogen temperature (77 K) on the carbon samples activated by different processes shown in Table 3 and the corresponding isotherms are shown in figures 1a and 1b.

The isotherm of the activated carbons FAC3, FAC4 and FAC5 are typical type II isotherms, indicating that the carbon is almost non porous. Moreover, visible hysteresis loops for carbons FAC1, FAC2 and FAC6 means that they contain some mesopores.

Another important feature of the isotherms of the carbon samples FAC4 and FAC5 are the hysteresis extending to low relative pressure; such hysteresis is associated with very narrow micropores (Gregg & Sing 1982).

All carbon samples show significant nitrogen uptake at low relative pressure. That can be described to the strong interaction between nitrogen molecules and the wall with closely spaced pores. Nitrogen adsorption for the FAC3, FAC4 and FAC5 samples were low since the samples have such a low degree of activation and a low pore volume.

The highest surface area obtained for activated carbon prepared using *Feronia limonia (L.)* Swingle (wood apple) shell by $ZnCl_2$ process followed by activation at 800^0C under a nitrogen atmosphere (925.00 m^2/g).

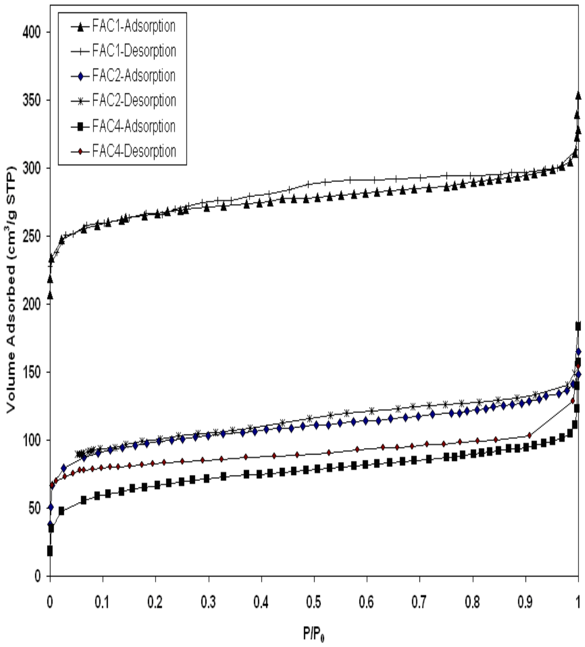

Fig. 1a : Adsorption and Desorption Isotherms of Carbon Samples

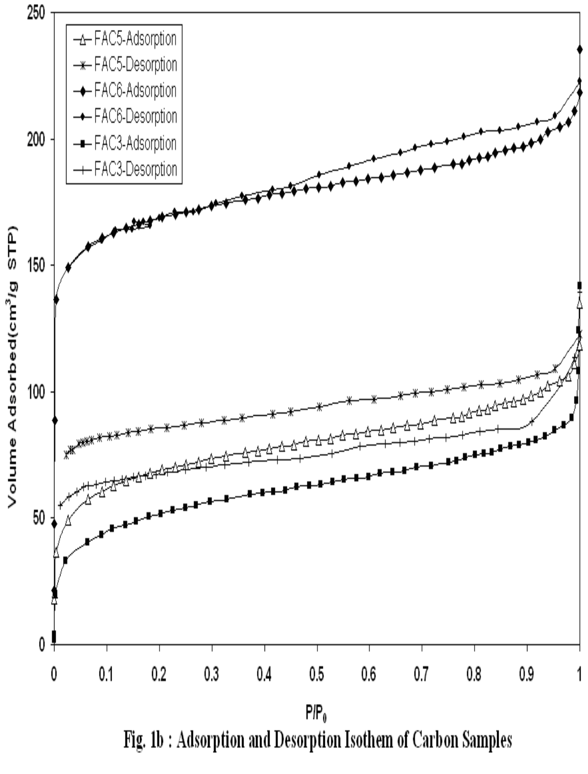

Fig. 1b : Adsorption and Desorption Isothem of Carbon Samples

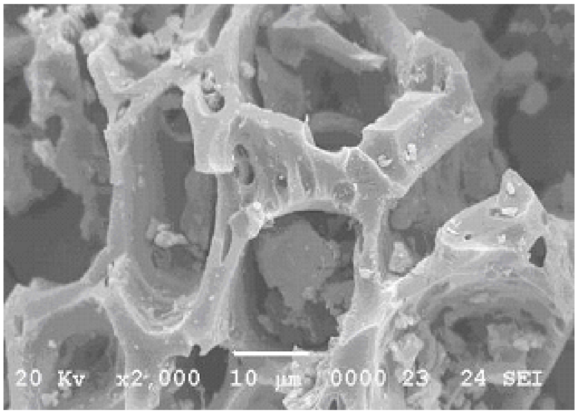

Fig. 2a SEM photograph of FAC1

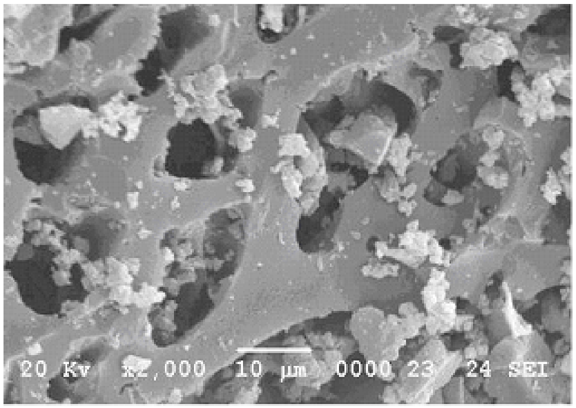

Fig. 2b SEM photograph of FAC2

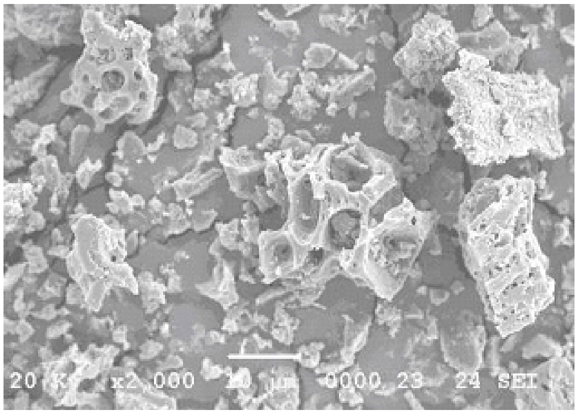

Fig. 2c SEM photograph of FAC3

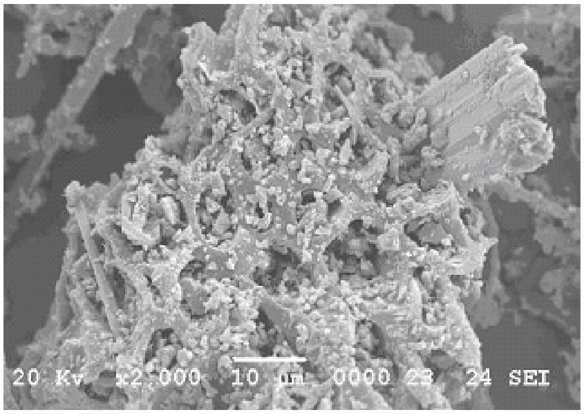

Fig. 2d SEM photograph of FAC4

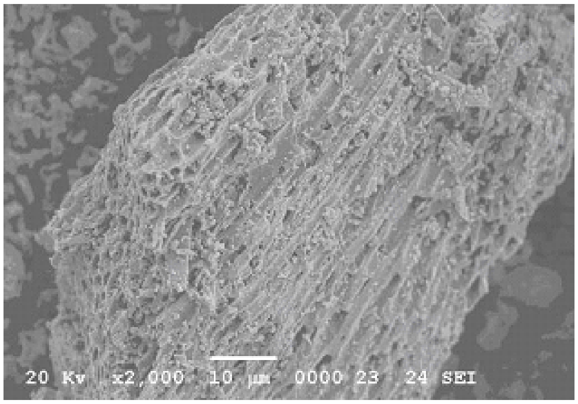

Fig. 2e SEM photograph of FAC5

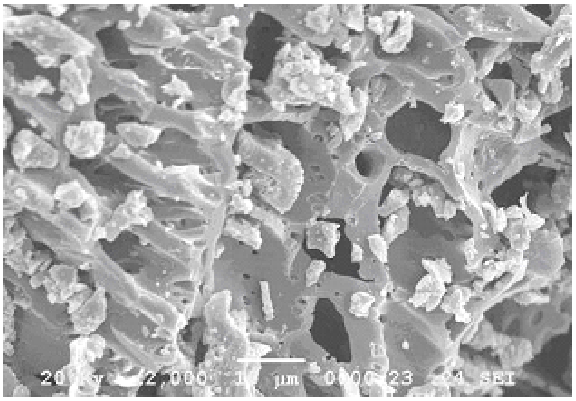

Fig. 2f SEM photograph of FAC6

Table 3. Porosity Characteristics of *Feroina limonia* Shell Activated Carbon

Properties	Activated Carbon					
	FAC1	FAC2	FAC3	FAC4	FAC5	FAC6
$S_{BET,}$ m^2/g	925.00	844.66	223.77	309.61	229.67	539.70
S_{Ext}, m^2/g	143.33	142.46	1.92	113.67	142.46	142.46
V_{micro}, cm^3/g	0.349	0.35	0.15	0.0926	0.043	0.197
S_{micro}, m^2/g	702.97	702.19	221.85	195.94	87.21	397.24
S_{IP}	188.00	191.13	47.12	64.53	49.03	120.08
$V_{Total,}$ cm^3 / g	0.59	0.492	0.216	0.206	0.183	0.337
Average pore diameter, °A	28.041	23.316	38.567	25.913	31.872	25.027

Hu and Vansant 1995 reported that $ZnCl_2$ activation process at 600-950° C converted coal waste to an efficient adsorbent. It was found that the surface area decreased with increasing activation temperature from 600-700° C, it increased from 750-950 °C. Although the details of activation are not clear, the surface area with activation temperature could be related to the boiling point of $ZnCl_2$ (732° C). The $ZnCl_2$-chemical activation at high temperature of 800 °C could produce high surface area carbons from coconut shells (Hu & Srinivasan 1997).

Pyrolysis of $ZnCl_2$ impregnated coconut shell under N_2 and CO_2 flow carried out to study the influence of gas phase on the porosity development of activated carbon and suggested that the formation of mesopores was the result of widening micropores by N_2 gas activation (Hu et al. 2001). These authors also suggested that $ZnCl_2$ acts as dehydrating agent, which may alter the pyrolysis behavior of carbonaceous materials and alters the course of reactions in the pyrolysis. $ZnCl_2$ causes hydrogen and oxygen atoms in the source materials to be stripped away as water rather than as hydrocarbons or as oxygenated organic compounds. As a result, the carbon yield is much high than that from physical activation (Hassler 1974).

The morphological study by SEM of the above adsorbents shown in the figure 2a to 2f revealed that, it is highly porous in nature. From the SEM results, it was found that there are holes and cave type openings on the surface of the specimen that would definitely have increased the surface that are available for the adsorption (Khattri & Singh 1999). The FT-IR spectrum of the *Feronia limonia* shell activated carbon prepared by various treatment processes shown in the figures 3a and 3b revealed that, but not all, of the carbons evaluated contain four classes of surface oxides: carboxyls, lactones, phenols and carbonyls.

The concentration of the surface groups varied, depending on the various types of activation conditions. Among the six carbons investigated, activated carbon prepared by $ZnCl_2$ process followed by N_2 gas activation method showed the highest concentration of surface groups. The assignment of the specific wave number to a given functional group was not possible because the adsorption bands of various functional groups overlap and shift depending on their molecular structure and environment.

Shifts in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, steric effect and degree of conjugation. For instance, within its given range, the position of C=O stretching band (common to carbonyls, carboxylic acids and lactones) is determined by many factors, such as:

1. The physical state
2. Electronic and mass effects of neighboring substituents
3. Conjugation
4. Hydrogen bonding and
5. Ring strain (Kendall 1996).

The FT-IR absorption bands of oxygen groups on the surface of activated carbon prepared using *Feronia* *limonia (L.)* Swingle (wood apple) shell by various processes were likely to be affected by some or all of the factors listed above.

Most of the carbons exhibit similar IR spectroscopic features; those are very intense/sharp H-bonded –OH stretching of carboxyl, phenol and alcohol vibration from 3600–3000 cm^{-1} and aliphatic C-H stretching absorption from 2750 to 3000 cm^{-1}.

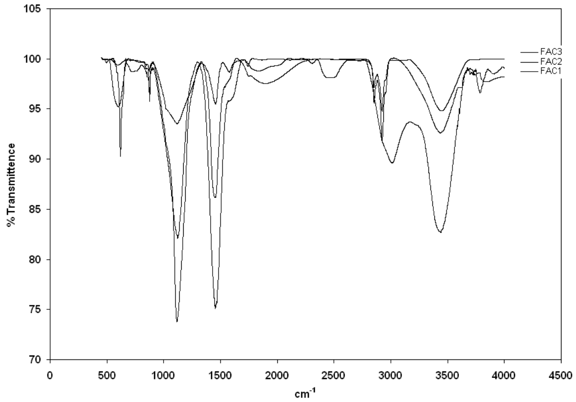

Fig. 3a : FT-IR Spectra for *Feronia limonia* shell waste activated carbon

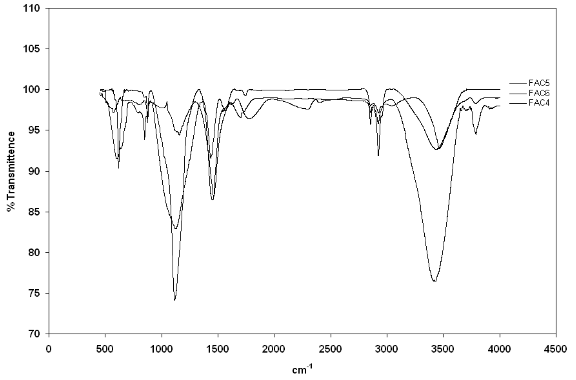

Fig. 3b : FT-IR Spectra for *Feronia limonia* shell waste activated carbon

Saturated aliphatic ethers show a strong band in the region 1070 to 1150 cm^{-1} for asymmetric C-O-C stretching. Esters, aldehydes, ketones, lactones, quinonoid carbonyl groups, chromene structure etc., shows a broad band in the region 1650 to 1900 cm^{-1} due to C=O stretching. The group of bands appeared in the region 1420 to 1460 cm^{-1} corresponding to -C-H def is characteristic of alkyl group provided, it is not under the some electrical influence. The broad band observed in spectrum of -OH derivatives between 1000 to 1250 cm^{-1} was assigned due to a characteristic absorption of -C-OH group. These results are in good agreement with the findings of many investigators (Zawadski 1981).

4. CONCLUSION

Activated carbons with moderate surface area obtained from *Feronia limonia* shell. The difference in textural characteristics related to the activation processes. The highest surface area obtained for activated carbon prepared using *Feronia limonia (L.)* Swingle (wood apple) shell by $ZnCl_2$ process followed by activation at 800 °C under a nitrogen atmosphere (925 m^2/g). The concentration of the surface groups varied, depending on the various types of activation conditions. Among the nine carbons investigated, activated carbon prepared by $ZnCl_2$ process followed by N_2 gas activation method showed the highest concentration of surface groups. Carbon prepared from above process and materials conveniently used for both organic and inorganic effluent removal.

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