



Sapindus Based Activated Carbon by Chemical Activation

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Abstract

Organic waste sapindus seeds hulls are activated chemically using concentrated sulphuric acid in the 1:1 weight ratio at the temperature of 160 °C for 24 h. Activated carbon (AC) is characterized for its various properties. A char yield of 60.8 % is obtained. Proximate analysis of AC shows an ash content of 5.08 % and volatile content of 71.8 %. Physical analysis of the AC highlights that the percentage of the carbon content existing in the AC is 53.7 %. Further, H/C ratio decreased from 0.15 of sapindus seed hulls to 0.069 for AC, indicating the richness of AC in terms of its carbon content. Surface morphology shows the generation of large number of pores on the surface of AC. IR spectrum reveals the presence of various functional groups on the surface of AC.

Keywords: Activated carbon, Sapindus seeds, Chemical activation.

Introduction

AC is a highly porous carbonaceous substance that contributes very high surface area up to 3000 m²/g of the adsorbent¹. The activation treatment results in the creation of pores and tuning of functional groups which facilitate adsorption of pollutants from their streams². Its common use as an adsorbent is because of fast adsorption rates, and ease of regeneration³.

AC is prepared by two methods. One method is physical activation and the other one is known as chemical activation. Physical activation is a two step process. Carbonization, in the absence of oxygen, is done in the first step whereas activation at higher temperature in the presence of an activating gas like carbon dioxide, etc is done in the second step. The tar formed during carbonization may block the pores resulting in low surface area. Chemical activation, on the other hand, is a single step process. Both carbonization and activation takes place in single step at lower temperature. Further, comparison among both the methods reveals that chemical activation results in lesser tar formation and results in the high yield since char burn-off is avoided⁴⁻⁵.

AC so far produced from conventional organic raw materials like coal, coconut shells is very expensive⁶. However, the persistent rise in the pollutants release in to the atmosphere has now demanded the low cost adsorbents. This demand can be met by utilizing locally available carbonaceous materials⁷. In this regard, the organic waste is the best choice for the synthesis of AC. So far, various researchers have worked out for the production of AC from various organic wastes that includes fruit stones like olive stones, cherry stones, plum stones, date pits, apricot stones and peach stones; fruit shells like walnut shells, palm fruit shells, hazelnut shells, almond shells; corn cobs;

coffee bean husks, rice husks, etc^{1,4,5,8-10}.

The literature survey reveals that the use of sapindus, also known as soap-nuts is limited to shampoo based industries¹¹⁻¹². The sapindus seeds hulls are not being used so far for the preparation of AC. The objective of this work is to fill this knowledge gap by preparing AC from sapindus seed hulls. AC is prepared by chemical activation method. Various properties of the AC are evaluated and compared with the data available in literature for organic waste based ACs.

Methodology

Materials: Raw material used in this work is sapindus (of Indian origin). It is purchased from the local market. Concentrated sulphuric acid (AR grade) procured from Fischer Scientific is used as an activating agent. Distilled water produced indigenously using Borosil double distillation unit is used for washing of the AC after the activation process.

Feed Preparation: The processing steps of preparation of feedstock (crushed hulls) from sapindus are shown in figure 1. Dried sapindus are manually broken in a traditional iron mortar-pestle and the seeds are extracted. The seeds are then broken; hulls (the stone type pericarp or hard shell of the seed) are separated from its internal soft part. The internal part is discarded as it is expected to have low adsorption capacity¹³. The seed hulls are washed with the distilled water and dried in an air oven (Universal make) at 100 °C for 3 hours. The dried seed hulls are crushed to smaller particles of size \approx 3-4 mm. Crushing is done in the roll crusher (Swastik make). Sapindus seed hulls are characterized for basic properties which are presented in table-1.

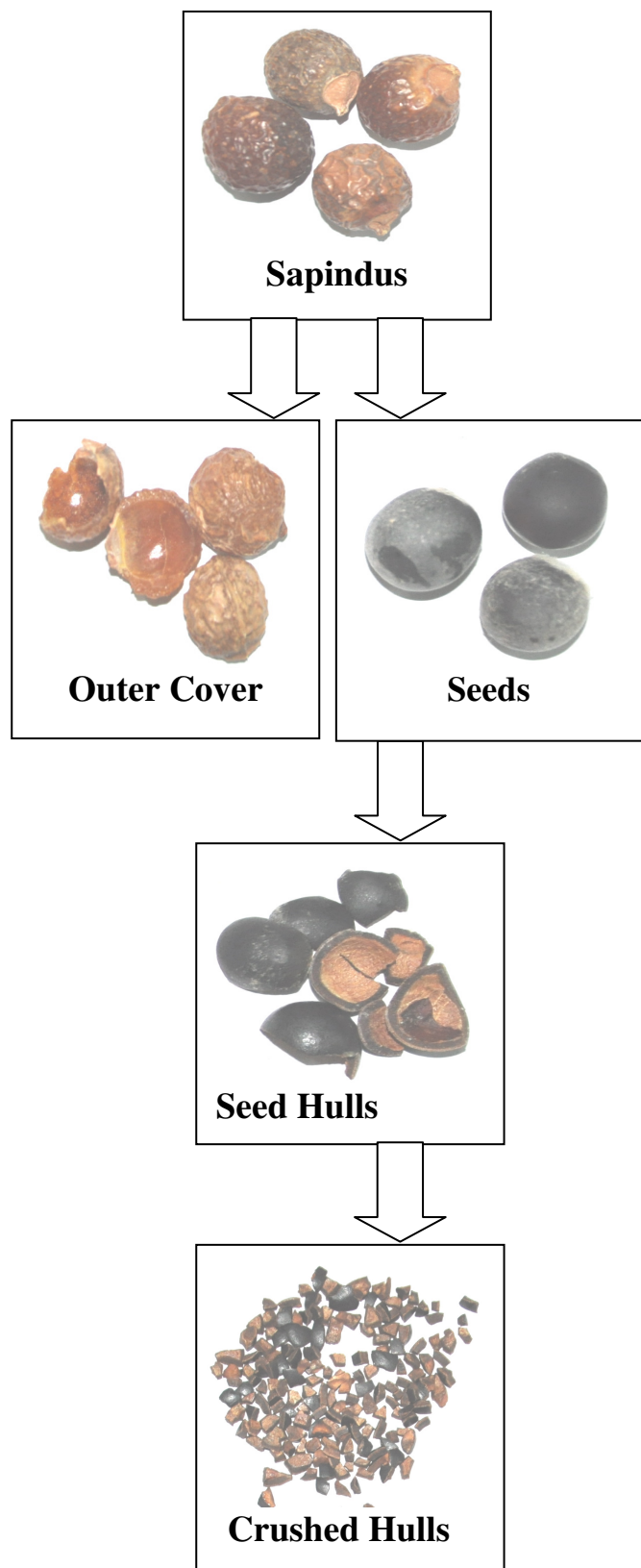


Figure-1

Process flow chart of feed preparation from Sapindus

Table-1
Sapindus seed hulls properties

Property	Value
Bulk density, g/cc	1.66
Ash content, %	4
Moisture content, %	7.1
Carbon, %	49.9
Hydrogen, %	7.5

AC Preparation: Granulated sapindus seed hulls (50 g) are mixed with the concentrated sulfuric acid in the 1:1 weight ratio. The mixture is heated to 160 ± 10 °C in an electric muffle furnace (Shivalik make) for 24 h. The whole operation is carried out in an air atmosphere. The processed material is then removed from the muffle furnace. It is placed in a desiccator (Tarsons make) and is allowed to cool to the room temperature. After cooling, the processed particles are washed several times with distilled water to eliminate traces of the free acid. The pH of the wash liquid is checked for alternate wash and continued till it attains the value of 6 as suggested by Ho and co-workers¹⁴. After removal of free acid, the AC is dried in the air oven at 105 °C for 5 h to remove wash water.

Moisture Content: Moisture content of feed stock material and AC is measured by heating a known quantity (W_i) of sample in a preheated oven at 150 °C for 3 hour as per ASTM D2867-09. After heating, the sample is taken out from the oven and placed in a desiccator. It is allowed to cool to room temperature and weight (W_f) is measured. The loss in the weight of the sample is the moisture content and percentage moisture is calculated as follows:

$$\text{Moisture, \%} = (\text{weight loss} * 100) / W_i$$

Where, weight loss = ($W_i - W_f$), W_i = weight of the sample before heating, W_f = weight of the sample after removal from the oven

Volatile Content: Volatile content of AC is recorded after removal of moisture. The known quantity (w_1) of sample is heated to 900 ± 10 °C for 7 min in the electric muffle furnace. For this the test method described in the reference is adopted¹⁵. After heating, the sample is placed in the desiccator. It is then allowed to cool to room temperature. The final weight (w_2) of the sample is noted down. The difference in the weight of the sample is volatile content and percentage volatile is computed as follows:

$$\text{Volatile, \%} = (w_1 - w_2) * 100 / w_1$$

Where, w_1 = initial weight of the sample on dry basis, w_2 = final weight of the sample after heating followed by cooling to the room temperature

Ash Content: Ash content is recorded for both feed and AC. Ash content is determined as per procedure described by Aygun and co-workers¹⁶. Small amount (W_i) of the sample is placed in

the crucible and heated to 800 °C in the muffle furnace for 2 h. During this period, the carbon content will burn-off completely and the inorganic matter will be left behind. The burnt-off sample is then removed from the furnace and placed in the desiccator. It is allowed to cool to room temperature. The final weight (W_f) is measured. This inorganic matter is the ash. The percentage ash is calculated as follows:

$$\text{Ash, \%} = (W_f * 100) / W_i$$

Where, W_i = weight of the sample before heating, W_f = weight of the sample after burn off

Carbon Content: Carbon content of feedstock material and AC is evaluated by CHNS analyser (Perkin Elmer 2400 Series II). Small quantity (0.1 g) of the sample is burned with oxygen in the furnace at 1000 °C. The carbon, hydrogen, and nitrogen content get converted into carbon oxide, water, and nitrogen gas / nitrogen oxides respectively. The analysis of these combustion products is carried out by thermal conductivity detector.

Bulk Density: The bulk density of the feedstock material and AC is measured as per following relation:

Bulk density (ρ) = mass in gram / volume in cc including its pore volume

A single piece of the material is rubbed gently with the sand paper to make a uniform shape. For the determination of volume, the three dimensions of the piece are measured with the venire caliper. The volume is then calculated by multiplying all the three dimensions measured. The mass of the piece is measured using a digital weighing machine.

Char Yield, %: The char yield is the ratio of the weight of the AC produced divided by the weight of the feed, both on the dry basis. It is measured as per the procedure described by Diao and co-workers¹⁷.

$$\text{Char yield, \%} = (w_{ac} / w_f) * 100$$

Where, w_{ac} = weight of the AC on the dry basis after washing and drying, w_f = weight of the feed taken on dry basis

Attrition Percentage: Attrition percentage of AC is calculated as per the procedure described by Aygun and co-workers¹⁶. Small quantity (W_i) of the sample is mixed with 100 ml of 0.07 M sodium acetate – 0.03 M acetic acid buffer of pH 4.8. The mixture is stirred at 250 rpm. Stirring is done for 48 hours by the use of a magnetic stirrer (Tarsons make). After stirring for specified time, the mixture is filtered by 50 mesh sieve. The particles retained on the sieve are washed thoroughly with the distilled water and transferred on a pre-weighed glass watch and kept in the oven at 110 °C for 2 hours. Sample is then placed in the desiccator and allowed to cool to room temperature and the final weight (W_f) is taken. The percentage attrition is then computed as follows:

$$\text{Attrition, \%} = (\text{weight loss} * 100) / W_i$$

Where, weight loss = ($W_i - W_f$), W_i = initial weight of the sample, W_f = final weight of the sample after stirring

Morphology: Environment scanning electron microscope (Carl Zeiss SMT EVO 50) is used to get the images for feedstock material and AC. Images for SEM are taken using 80P air pressure. LaB6 filament is used while taking the images.

FT-IR: The FT-IR spectrum of AC is taken. It is generated using Perkin Elmer Frontier in the range of 400-4000 cm^{-1} at room temperature. FTIR spectrum is taken at room temperature. The powdered sample of AC is mixed with 0.3 g of KBr in 2:100 ratio and pellets are formed by compacting the mixture in a dye. For compaction of mixture a pressure of 7-8 ton is applied through hydraulic press. The pellets obtained are approximately 1 mm thick. The spectrum of the pellets is recorded with resolution of 4 cm^{-1} and 16 scans per sample. Baseline correction is done with Spectrum 10 software.

Results and Discussion

Result of moisture content of AC is shown in Table-2. Moisture content of AC is reduced compared to feed material. It reaches the lower value than that reported (5.21 %) for banana empty fruit bunch (BEFB) based AC produced by chemical activation¹⁸. The moisture content of AC is reduced compared to feed.

Table-2
Properties of AC

Properties	Value
Moisture content, %	3.5
Volatile content, %	71.5
Ash content, %	5.08
Carbon content, %	53.7
Hydrogen, %	3.7
Bulk density, g/cc	1.06
Yield, %	60.8
Attrition, %	12

Volatile content of AC prepared from sapindus seed hulls is shown in Table-2. It is found to be lower than that reported for delonix regia fruit pod (DRFP) based AC (92.03 %) and BEFB based AC (78.83 %) by Sugumaran and co-workers¹⁸.

Volatile content in AC is mainly due to the presence of non-carbonaceous matters. The elimination of non-carbonaceous matters is controlled by activating agent and temperature. The acid attacks non-carbonaceous matters present in the feed and detaches them from their native sites. The deep penetration of acid detaches more non-carbonaceous matters. The application of temperature aids in moving these matters from the surface during activation.

Micrographs of AC synthesized from sapindus seed hulls show

lack of deep penetration of acid into the sapindus seed hulls. The activation temperature is also same as that used by Sugumaran and co-workers¹⁸. Even then the volatile content of sapindus seed hulls based AC is lower. It shows that the content of non-carbonaceous matters present in sapindus seed hulls is low.

Volatile content can be further reduced by using lower feed size as more surfaces will be exposed for acid attack. It is also expected that increase in activation temperature may aid in the elimination of more non-carbonaceous matters resulting further reduction in volatile content.

Table-1 shows 4 % of ash content for sapindus feed. Ash represents in-organic matters. Generally, ash content lies in the range of 1-20% and its value in AC produced depends upon the origin^{7, 19}. Lower ash content organic feed is good for AC synthesis as it does not aid much in the adsorption capacity. It means sapindus seed hulls are good feed for the synthesis of AC. The percentage ash content of AC is shown in Table-2. The total weight of ash present in the feed is expected to remain as such in AC at low temperature. But a little drop in the total weight of ash has been observed that indicates the probable volatilization of some in-organic matter from the surface owing to acid attack.

The removal of non-carbonaceous matters from the precursor during the activation process results in the enhancement of the carbon percentage from 49.9 % of the precursor to 53.7 % in AC. Sugumaran and co-workers have reported 41.75 % carbon content for BEFB based AC and 34.22 % carbon content for DRFP based AC¹⁸. Therefore, the high value of carbon content in the AC produced from sapindus seeds hulls indicates its feasible use as an adsorbent. The H/C ratio has shown reduction from 0.15 for feedstock to 0.069 of AC which is again lower than that of the above stated reference. The reduction in this ratio shows the enrichment of the material with respect to carbon.

Bulk density of AC is shown in Table-2. Density of AC as expected is reduced compared to feed due to the elimination of non-carbonaceous matters which left behind porosity. In general, chemical activation results in high bulk density of AC and same is observed here. However, it is in accordance with the bulk density of 1.05 g/cc which is reported for sludge based AC prepared through chemical activation process². It may be reduced by the application of high temperature during activation. Lower particle size of feed may also affect the density as it will permit acid to attack large surface area of precursor to detach more non-carbonaceous matters which will lead to more porosity.

The char yield is evaluated to be 60.8 % in this work. Higher value of char yield implies either less elimination of the non-carbonaceous content from the precursor or better productivity of the feed w.r.t AC. But here it is found due to less elimination

of non-carbonaceous content from the precursor. The exclusion of non-carbonaceous content is aided by the acid which results in an early cleavage of the bonds²⁰. For better release of non-carbonaceous contents, the molecules of the acid have to pierce through the surface in to the feed particle. Hence, particle size as well as surface rigidity plays an important role in the elimination of these matters. Since the particles size of sapindus feedstock used in this work is large hence it might have resulted in higher char yield. Apart from it, char yield is also affected by the activation temperature and decreases at higher temperatures⁴. The fall in yield at higher temperature too examine by Evans and co-workers²¹. Thus, the temperature employed during activation has an undeviating influence on the yield likewise on the bulk density and volatile content. In this study, low temperature is employed that might have resulted in high char yield. However, Teng and co-workers have reported higher char yield for the ACs processed even at higher temperature²⁰. They got up to 71 % for physical activation of few samples of bituminous coal and 78 % for physical activation of bituminous coal after chemical treatment with phosphoric acid. Similarly, Mdoe and co-workers reported very high char yield of 79 % for AC synthesized at 200 °C from rice husks using sodium chloride as an activating agent⁴. Abdullah and co-workers have reported the char yield reaching to 65 % when concentration of activating agent is increased to 10 % for gelam wood bark based AC¹⁹.

Granular AC may face challenges of intra-particle abrasion in some applications, so attrition value plays an important role in deciding the commercial usability of AC. The AC produced by chemical activation in this work gives attrition value of 12 % when the stirring is done at 250 rpm for 24 hours. However, as the time of stirring increased up to 48 hours, the attrition percentage reaches to 31 %. The increment in the value of attrition with increase in stirring time is due to the extra crushing done by the rotating magnet that weighs 10.2 g. Over grinding of the AC particles turned up in excess loss of sample weight during sieving and resulted in the high attrition value. Also, the activation method has control over the quality of the AC as clear from the attrition percent 41 % of AC prepared by continuous method²². Lower value of attrition makes sapindus based AC more competent for industrial applications than ACs produced from various other organic wastes.

The microstructure of the sapindus seed hulls before and after chemical treatment is taken. The images are presented in figure 2-5. The SEM images for feed which is sapindus seed hulls depicts that the surface does not contain any pores; however, cracks do exist as clearly seen in figure 2-3. The width of these cracks varies from 3.6 to 8.02 μm . Some cracks of further lower dimensions also do exist. When it is compared with the SEM images of AC presented in figure 4-5, it is examined that tremendous pores are created on the surface after chemical treatment with H_2SO_4 .

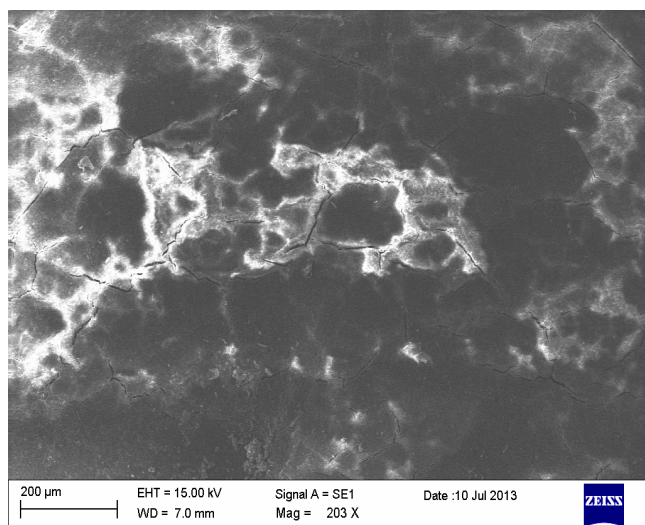


Figure-2
203 X SEM micrograph of Sapindus feed

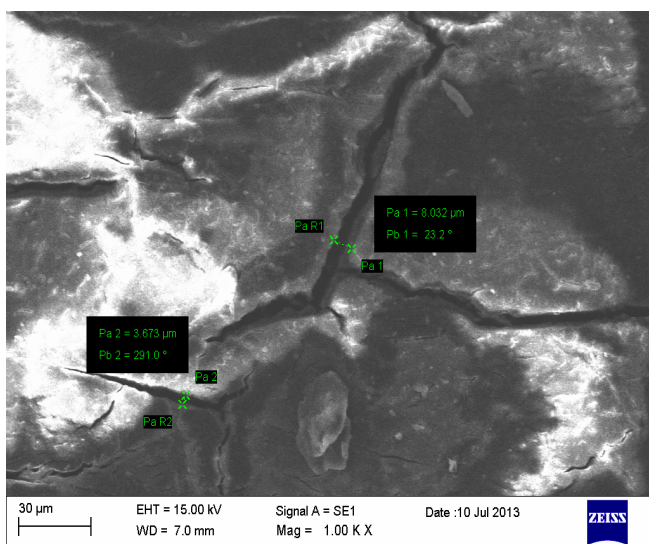


Figure-3
1000 X SEM micrograph of Sapindus feed

The maturity of the pores results in the augmentation of the adsorption capacity. It is, further, observed from figure 4-5 that the pores developed are highly non-uniform. Most of the pores are of circular size. But some pores of irregular size also do exist. The circular pores are of two dimensions viz smaller and bigger diameter. The size of bigger diameter pores varies from 42.46 to 48.93 μm . It is also being observed that the pores are developed on the surface and do not extend up to the center of the particle. This is evident from the figure 4 that shows widening of the pore at mouth is more than the tail of the pore. It can be explained by the fact that the rigid surface of the feed may have hindered the acid molecules to pierce deep through the precursor. To easily penetrate into the hard structure of the bigger feed particles, molecules of the activating agent require high state of energy level that can be achieved at high

temperature of activation. Also, at high temperature, it is expected that the feed elements bonds get weakens and sulphuric acid can then easily break the bonds. But the low temperature application could not take the advantage of deep penetration of the acid molecules in to the feed material.

The FT-IR spectrum of AC produced is shown in Fig 6. The AC spectrum shows three main absorption bands for 3300-3500 cm^{-1} , 2800-3000 cm^{-1} and 1600-1000 cm^{-1} . The peak in the first band i.e. 3402 cm^{-1} is attributed to the O-H stretching of the hydroxyl group. The presence of this group may be due to the water molecules absorption. The regions of the band 2800-3000 cm^{-1} at 2918 cm^{-1} and 2848 cm^{-1} represent C-H interaction of alkyl groups and $-\text{O}-\text{CH}_3$ respectively.

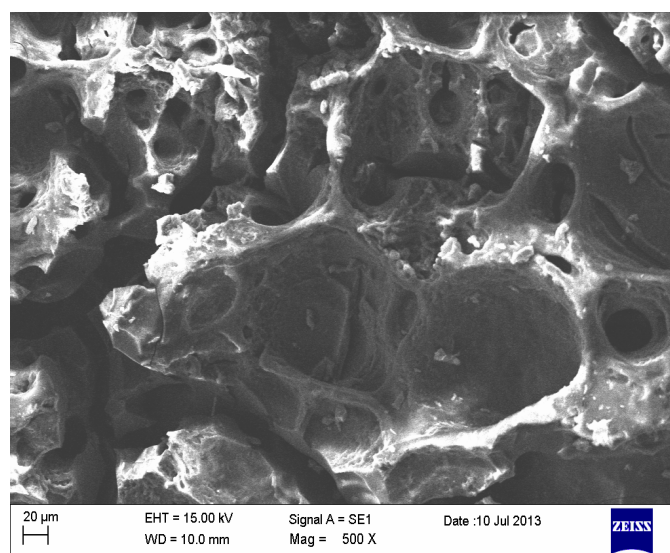


Figure-4
500 X SEM micrograph of Sapindus based AC

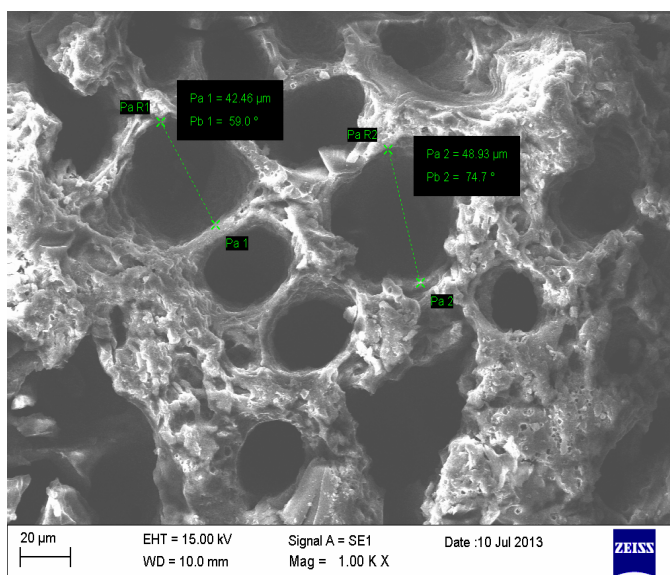


Figure-5
1000 X SEM micrograph of Sapindus based AC

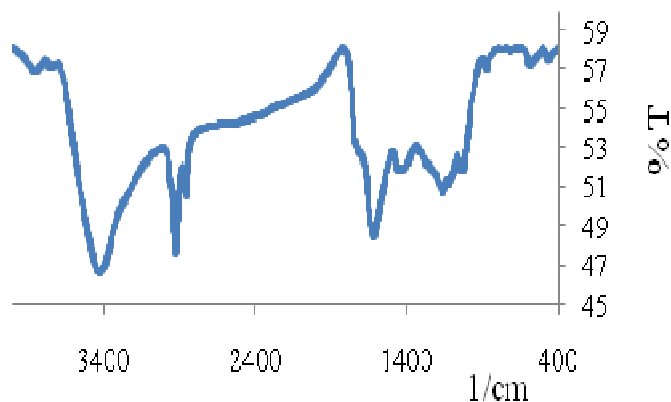


Figure-6
FTIR spectrum of AC

Another wider band from 1000-1600 cm^{-1} contains several peaks. The peak at 1595 cm^{-1} is expected either due to amide group (N-H) or carbonyl group. The peak at 1419 cm^{-1} may be due to O-H from either hydroxyl or carboxylic group. The 1137 cm^{-1} peak is resulted by the presence of C-O function of alcohols and 1012 cm^{-1} peak can be the result of amine C-N group, alkyl halide C-F or C-O of alcohol group^{2,23}. The presence of these functional groups will bend the pH nature of the AC. The sharp peaks for hydroxyl and carbonyl groups will form the ground of its basic character. The unsaturated bonds or electron donating features of these functional groups will result in the inclination of AC towards the acceptance of positive ions from the aqueous solutions²³.

Conclusion

This work intends to introduce an organic waste i.e. sapindus seeds hulls based AC. This material is first time tried for such type of work and never been used so far. Excellent set of properties of AC as presented in this paper have proved potential of sapindus feedstock material for converting it into AC through chemical activation.

Char yield of 60.8 % after activation is obtained and carbon content of 53.7 % is observed. The H/C ratio lowers to 0.069 % from initial value of 0.15 % in the precursor. Low activation temperature and large particle size chosen, results in the retention of large volatile content 71.5 % in the AC. Molecules of the activating agent could effectively pierce in the vicinity of the surface rather than deep in to the precursor. It could release sufficient amount of the non-carbonaceous matter. The attrition value 12 % depicts its mechanical strength but crushing of the particles with revolving magnet caused the percentage to increase further up to 31 % when stirring time is continued for 48 hours. Surface morphology could explain the development of the

non-uniform pores on the hard surface of non-porous precursor. The IR spectrum shows the presence of various functional groups which state the nature of the surface of the pores within the AC. The inclination of spectrum towards the hydroxyl and carbonyl functional groups makes its tendency to attract protons or positive ions.

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