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Comparative study of action of H_3PO_4 on different biomass samples

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ABSTRACT

This paper discusses the response of different lignocelluloses constituent to dehydrating agent H_3PO_4. Being weak acid the phosphoric acid only etches the surface of lignocelluloses. Further the comparison is presented with help of BET curve. It is found that lignin and cellulose content has impact on activation of carbon.

KEYWORDS: H_3PO_4,BET, coconut leaves, coconut shell, arecanut shell, SEM.

INTRODUCTION

Activated carbon is an extremely versatile material with high porosity and surface area. It has become one of the technically important materials for selective separations. The structure of activated carbon is mainly micro porous. Nevertheless, its application fields are restricted due to high cost.

The report presents the elemental analysis and BET results of the activated carbon prepared from areca nut shell, coconut shell and coconut leaves.

By BET (Brunauer, Emmett and Teller) the *specific surface area* of a sample is measured – including the pore size distribution. This information is used to predict the adsorption rate, as this rate is proportional to the specific surface area.

This difficulty has led to search for the use of cheap and efficient alternative materials such as rice husk [1], bamboo [2], sugarcane stalks [3], tamarind kernel powder [4], palm shell [5] babool wood [6], bagasse fly ash [7], ashoka leaf powder [8], coir pith [9] and banana pith [10] etc. Biomass wastes are considered to be a very important feedstock because they are renewable sources. Activate carbon such produced can be used as effective adsorbent because of high adsorptive capacity. However, continues production of activated carbon with reproducibility of characteristics is restricted by the seasonal availability of the starting materials.

This led us to use coconut shell, areca nut shell and coconut leaves, which are available throughout the year irrespective of season as starting materials for carbon preparation. Being in daily use in Indian continent as food ingredients and in some parts on auspicious occasions, the coconut shell is generated enormously. Areca nut is also chewed in Asian continent as mouth freshener and in India on auspicious occasions along with coconut.

For activation, the surface of carbon modifies to develop newer reactive cites. There are different agents used for activation of carbon. Each agent imparts different morphology to the resultant carbon. The ratio of lignin to cellulose and the nature of starting material play certain role in the attribution of activity to the resultant carbon. For the treatment with alkali, the surface modification is limited. The acid treatment enhances porosity, and in turn increases the yield of activated carbon. Ours is the activated carbon prepared by acid treatment to the agricultural waste lignocelluloses materials.

The aim of this paper is to report the production of activated carbon from lignocelluloses material from agricultural waste and to study the activation process using Phosphoric Acid [H_3PO_4] as dehydrating agent.

1. MATERIALS AND METHODS

1.1 Selection of materials: By finding out the acid soluble and alkali soluble content of the different agricultural waste, the coconut and the areca nut material were selected pertaining to the availability and the acid hydrolysable content.

Biomass waste such as coconut shell, areca nut shell and coconut leaves is used as the raw material for preparation of activated carbon. The biomass is first chopped into pieces of 2 cm wide and 5 cm long. Then washed with distilled water to remove dust particles, and then dried at 110^0c. Biomass waste was finally crushed and sieved to 180 mesh size.

METHODS -EXPERIMENTAL

1.2 Preparation of Activated Carbon: First preparation of activated carbon was done in three batch sizes of 50 gm, 100 gm, and 300 gm.

H_3PO_4 chemically pure quality [Merck and Co.] was used as activating agent. A known mass of activated agent was mixed with distilled water, and Biomass waste was impregnated in acidic solution. The mass ratio of activating agent to dried material was 1-3.

The impregnated sample was kept for 24hr. After 24hr the residual water was removed and kept in oven for 110^0C A Weighed amount of impregnated samples was kept in muffle furnace for 400^0C. The muffle furnace is purged with high purity nitrogen gas to avoid oxidation .Nitrogen flow was adjusted to 3^0C/min at 400^0C. The activated carbon was subsequently removed from furnace and cooled to room temperature.

After activation the samples, 3M hydrochloric acid used to remove the phosphoric acid compounds. The washed samples were dried at 110^0C for 6hr in oven and then ground to form a porous carbon powder.

The equipment was fabricated to hold the raw sample of 12 * 3.5*3.5 inch size as shown in figure:-1. The Experimental set up of preparation of activated carbon from coconut shell, areca nut shell, and coconut leaves consists of muffle furnace associated with nitrogen gas cylinder is shown in figure no:2

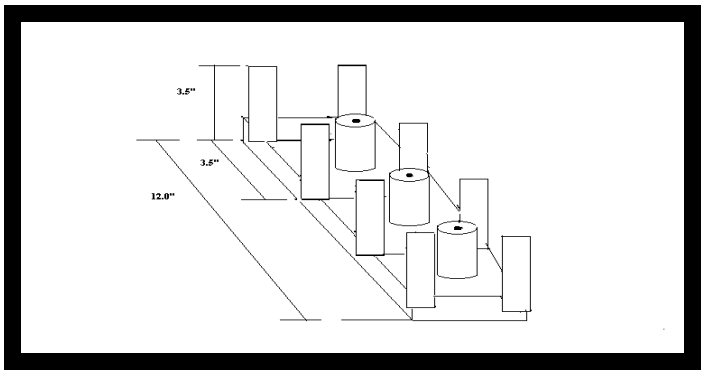

Figure no:-1 Fabricated Equipment to hold the sample

Figure no:-2 Experimental Set up

METHODS -ANALYSIS

1.3 Analysis of starting material: In order to find out the cellulose content as acid hydrolysable and lignin content as alkali soluble, 17% H_2SO_4 solution and 17% NaOH solutions were used. The pre-weighed sample was first digested in acid at room temperature for 4hrs with constant stirring. Oven dried to constant weight to know the weight difference. The weight difference corresponds to the cellulose and hemicelluloses content. The same sample was digested in NaOH solution at 80^0C for 2 hrs with constant stirring. The sample was oven dried till constant weight and weighed to find the lignin as alkali soluble content.

1.4 Analysis of activated carbon: The Ultimate Analysis of a sample determines the elemental composition of the sample. It is based on the principle of Dumas method which involves the complete and instantaneous oxidation of the sample by flash combustion. The results are in percentage composition of Carbon, Hydrogen, Nitrogen and Sulphur. From these results the oxygen composition is determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100.

The Ultimate Analysis was carried out in a CHNS Analyzer. The sample is fed into the analyzer along with excess supply of oxygen. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulphur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulphur dioxide respectively. The combustion products are separated by a chromatographic column and are detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample.

2.0 ACTIVATION OF CARBON:

The acid causes the wood to swell, opening the cellulose structure and stabilizes this structure, keeping it open. The acid is then washed out of the carbon.

2.1 LIGNOCELLULOSE CONTENT OF THE STARTING MATERIAL

Table –1 Lignin and cellulose content of the raw material

Sr. No.	Material	Cellulose % (as acid soluble)	Lignin % (as alkali soluble)	Weight of remainder
01	Coco nut shell	36%	16%	48%
02	Coco nut leaves	47%	40%	13%
03	Areca nut shell	58%	16%	26%

From the table no. – 1, it is observed that the acid hydrolysable is more in areca nut shell as compared to the other two materials. Three of the materials present three different classes of lignocellulosics. Coconut shell is the only woody material i.e. more complex and cross linked form of lignocelluloses. Areca nut shell is the material which has combination of fibrous and hard material. Whereas coconut leaves has on major watery content, comparatively simple form of polymer lignocelluloses.

The same trend is observed in ultimate analysis results. The coconut shell has got all the value, for ultimate analysis in moderate range as compare arecanut shell and coconut leaves exept the % fix carbon content. Which is the highest i.e. 81% followed by arecanut shell 75.9% and coconut leaves 75.3%.

The % yield of carbonisation process also follows the same trend as shown in above analysis

2.2 ELEMENTAL ANALYSIS

Table no: 2 Ultimate Analysis

Parameters	Lignocellulosic wastes (wt%) dry basis		
	Arecanut Shell	**Coconut leaves**	**Coconut Shell**
Proximate Analysis			
Moisture	15.46	8.167	11.93
Ash	6.473	2.39	4.90
Fixed Carbon	75.9	75.38	81.44
Volatile Matter	6.47	14.06	4.985
Ultimate Analysis			
Carbon	54.86	23.56	57.62
Hydrogen	4.486	0.916	3.432
Nitr ogen	0.475	0.889	0.191
Sulphur	0.251	0.115	0.119

3.0 SCANNING ELECTRON MICROSCOPE (SEM) ANAYSIS

The prepared activated carbons were examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM micrographs of the chemically activated carbons by H3PO4 are presented in Figure 3. In all three cases, well-developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer (μm) range. These pores are considered as channels to the microporous network. From the figures below, it can be observed that all the adsorbents have rough texture with heterogeneous surface and a variety of randomly distributed pore size.

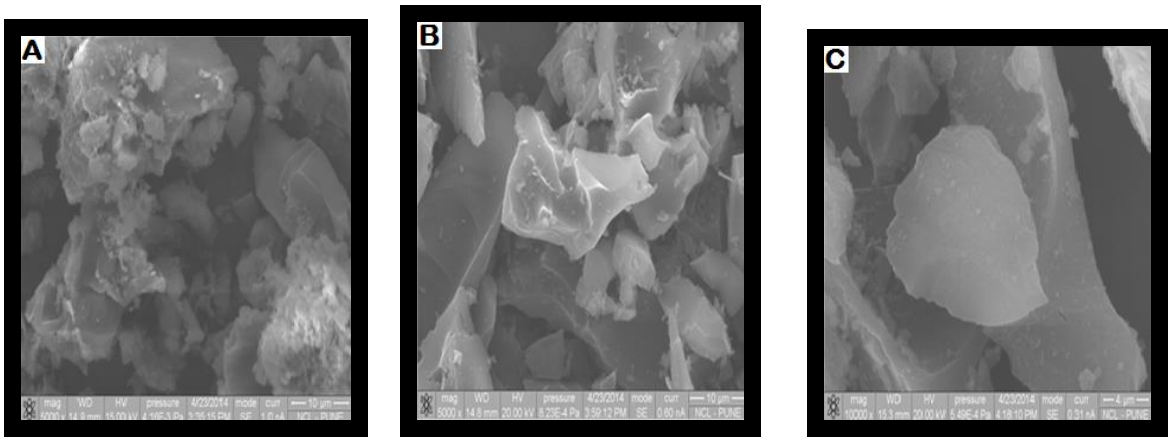

Fig 3: SEM images of chemically activated adsorbent, for 1:1 Acid: Adsorbent ratio.

Coconut Leaves (B) Coconut shell (C) Areca nut Shell

3.1 SURFACE MORPHOLOGY

The total surface area of adsorbent is commonly measured by Brunauer-Emmet-Teller (BET) method. Determination of surface area of adsorbent is accomplished by using N_2 adsorption liquid N_2 temperature in which adsorbed N_2 molecules adhere on surface site as monolayer. The surface area of adsorbents with its modified forms are tabulated in Table 3. The Table reveals that CLC has the highest surface area. The presence of micro pores may be contributing to the high surface area of CL, presented in Table

Table 3 Result of petrol swelling test hardness, tensile test for NBR, Arecanut Shell. Coconut Shell

Sr. No	Sample	% deviation in density	% deviation in hardness	Remark
01	NBR	87.18	54.16	This is matrix material
02	AS	11	82	This can be used for fuel tube application
03	CS	28.3	54	This can be used for hose pipe application
04	CL	61.9	68	Needs to be studied further

4.0 ADSORPTION ANALYSIS

The surface area of different carbons follows the order: CL > CS > AS. N_2 adsorption-desorption isotherms on CL, CS and AS are presented in Fig.5. The figure shows that Coconut leaf has the highest N_2 adsorption characteristics among the three adsorbents and higher surface area. CL and CS exhibit similar nitrogen adsorption capacity in relative pressure up to 0.9. Beyond this, the adsorption capacity of CL increases as it is Type IV isotherm pattern.

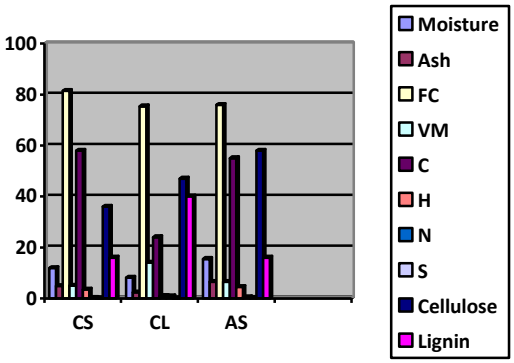

Fig. 4 Comparison on different parameters of biomass samples

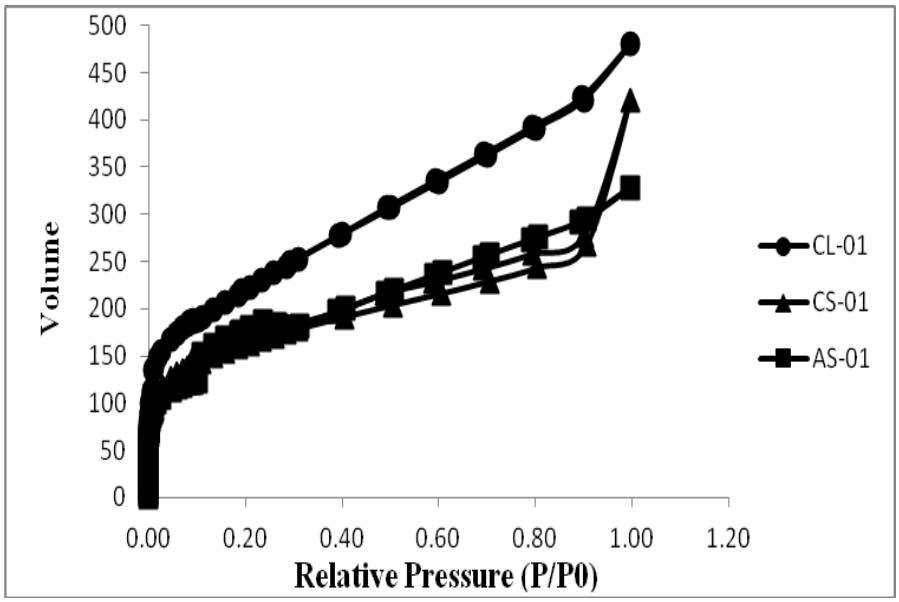

Fig. 5 Graph of Total analysis (BET) of samples like Coconut Leaves, Coconut Shell, Areca nut Shell.

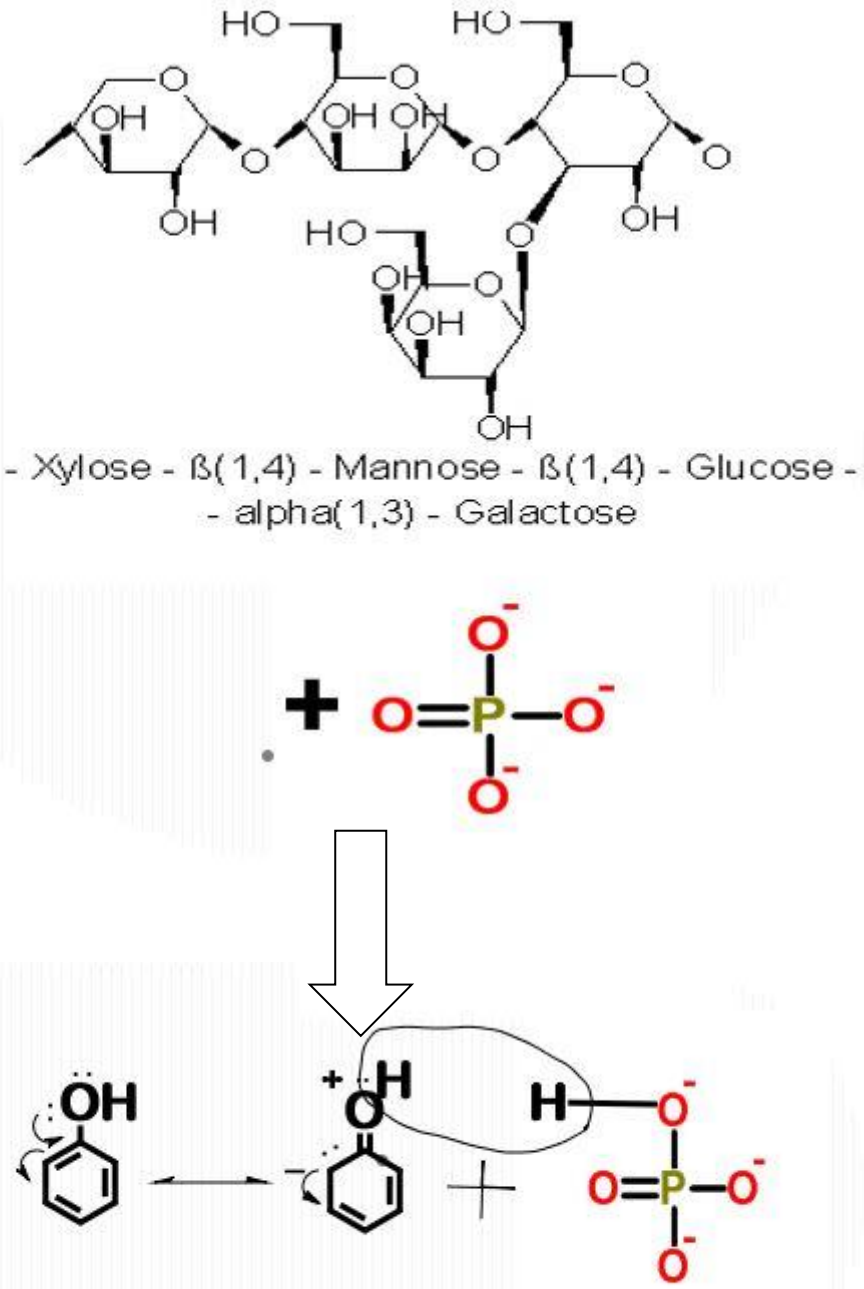

Fig. 6. Proposed Reaction Mechanism

Discussion:

1) In Arecanut shell, Coconut leaves, Coconut shell has a carbon composite 55.86%, 23.56%, 75.62% respectively. While cellulose content is 58%, 47%, 36% and lignin content is 16%, 40%, 16% respectively.

2) Etching to the surface of samples with reference to water content changes. As volatile content in Arecanut shell, Coconut leaves, Coconut shell is 6.47%, 14.06%, 4.98%. Water content is 15.46%, 8.16%, 11.93% respectively [14].

3) In case of reaction with ether and ester from our biomass samples we are treating it with weak acid that is H_3PO_4, the resonating structures of the NBR rubber is reacted at the OH bond as shown in the Fig no.6. And it forms chain structure with H_3PO_4 which is a divalent in nature and the proposed reaction mechanism is shown in the figure no 6. It goes in line with our earlier experimental work presented [15].

4.0 CONCLUSION: From the earlier studies and the results so far, we can conclude:

- Lignocellulose agricultural waste can be a starting material for the preparation of activated carbon.
- Elemental analysis and the BET study have shown surface modification carbon.
- Maximum volatile matter is present in coconut leaves which leads to surface etching and hence maximum surface area we are getting in the case of coconut leaves.
- The maximum carbon percent is present in case of the coconut shell, so to prepare a better activated carbon coconut shell is preferred.
- Further the results of this study showed that coconut shell, coconut leaves and areca nut shell can be successfully converted into activated carbon by using H_3PO_4 as dehydrating agent. The activated carbon has developed ether, ester and carbonyl groups over the surface for H_3PO_4 treatment.
- Proximate analysis and ultimate analysis may be the guideline to obtain carbon after activation of lignocellulose
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