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Synthesis and characterization of chemically activated carbon derived from arecanut shell

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Abstract: Activated carbon (AC) was prepared from areca-nut shell (AS) by chemical activation using phosphoric acid (PA). Activated carbon was prepared in three batches using phosphoric acid of 50 gm, 100 gm, and 300 gm with varying impregnation ratios by weight of 1:1, 2:1 and 3:1, 4:1 each. Characterization of the prepared activated carbon was done by methylene blue number (MBN), iodine number (IN), acid adsorption test (AAT), and elemental composition. Activation was carried out at 400 ^{0}C. It was found that activated carbon derived from areca-nut shell shown improved results for methylene blue number (MBN), iodine number (IN), and acid adsorption test(AAT). Thermal analysis was carried out to know the weight loss and SEM was performed to know the morphology of AC.

Keywords: Areca-nut shell, activated carbon, phosphoric acid

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1. Introduction: Activated carbon is a generic term used for a family of highly porous carbonaceous materials. Activated carbons have enormous surface area which makes them effective adsorbent**.** The characteristics of activated carbon depend on chemical and physical properties and activation method. Agricultural waste is considered to be a very important feedstock for synthesis of activated carbon because of their renewable nature and lower cost. Several studies on the preparation of activated carbon from agricultural wastes such as fruit stones sugarcanes, almond shells, etc. have been reported **[1, 6]**. As the cost of activated carbon is high, there is continuing research for sorbent which are cost effective and can be produced locally from agro-waste materials **[7]**. In the present investigation, the arecanut shell is used for synthesis of activated carbon and used it as an adsorbent. Arecanut consists of a hard fibrous outer covering commonly called husk enclosing within it the endosperm which is edible nut.

High quality arecanut shells were obtained from Karnataka, India. Activated carbon can be made from a variety of agro-waste materials by various activation methods **[8]**. More recently, interest has been shown in the preparation of activated carbon using agricultural by-products as precursor material **[9-11]**. This will reduce the importation of activated carbon therefore increasing the economic base **[12]**. Several investigators have reported the composition, chemical characterisation, and functional properties of agricultural waste **[13 - 16]**.

The aim of the present investigation is production of activated carbon from arecanut shell and to study the activation process using phosphoric acid [H_3PO_4] as activating agent. The activated carbon is prepared with varying ratio of composition of phosphoric acid and agro-waste [viz. 1:1, 2:1, 3:1, 4:1].

Adsorption capacity was compared for varying batch size of 50 gm, 100 gm, and 300 gm with lead and copper.

2.0 Materials: Arecanut shell was used as the raw material for preparation of activated carbon. Arecanut shell was first washed with distilled water to remove dust particles and then dried at 110 ^{o}C. The arecanut shells are then chopped into pieces of ¼ size in wide and ½ long. IS-2230-1962 procedures were applied to know methylene blue number, iodine number, and acid adsorption. Arecanut was crushed and sieved to about 180 mesh.

3. Experimental

3.1 Preparation of activated carbon: Preparation of activated carbon was done in three batch sizes of 50 gm, 100 gm, and 300 gm. Phosphoric acid [H_3PO_4, Merck] was used as activating agent. A known mass of activating agent was mixed with distilled water; and arecanut shell was impregnated in acidic solution in the mass ratio of activating agent to dried material was 1 - 4.

The impregnated sample was kept for 24 hr. After 24 hr, the residual water was removed and kept in oven for 110 ^{o}C. A weighed amount of impregnated samples were kept in muffle furnace for 400 ^{o}C. The muffle furnace is purged with pure nitrogen gas to avoid oxidation. Nitrogen flow was adjusted. The activated carbon was subsequently removed from furnace and cooled to room temperature as shown in Figure (1).

After activation of the samples, 3 M hydrochloric acid (HCl) was used to wash the samples. The washed samples were dried at 110 ^{o}C for 6 hr in oven and then grounded to form carbon powder. The equipment was fabricated to hold the raw sample of 12 x 3.5 x 3.5 inch size as shown in Figure (1). Figure (2) shows the experimental set up for preparation of activated carbon from arecanut shell.

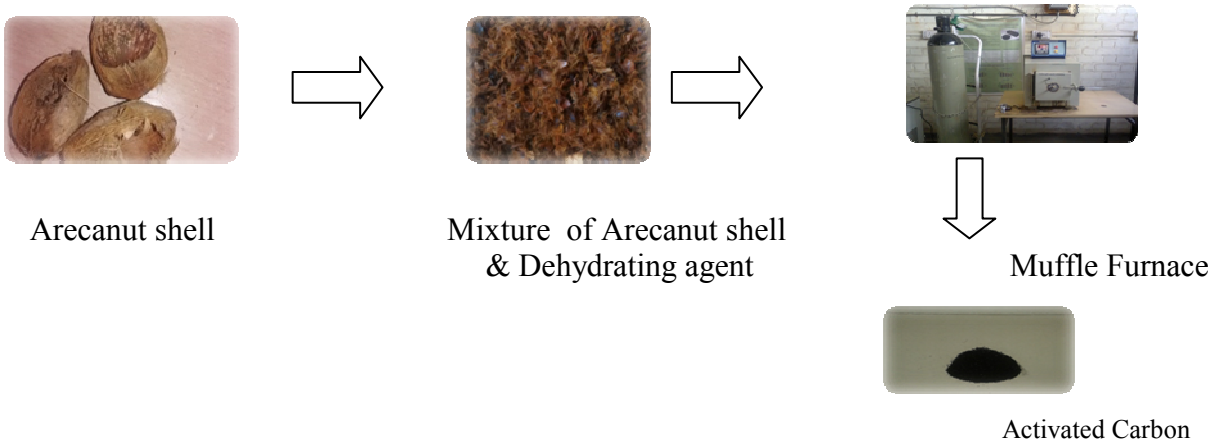


Figure (1): Preparation of activated carbon from arecanut shells.

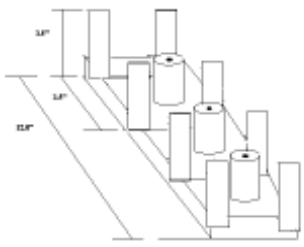


Figure (2): Fabricated Equipment to hold the sample

Figure (3): Experimental setup

Synthesized activated carbon was washed several times with distilled water until a pH range between 6 - 7 was obtained. The adsorbent is dried in an oven at 105 °C for a period of 24 hrs [2].

4. Characterisation of activated carbon produced derived arecanut shell: Characterisation was carried out to know decolorizing power, absorptive capacity, and acid adsorption. Elemental analysis was performed to know content of carbon, nitrogen and sulphur and other elements (if any). Thermal analysis was done by TG-DTA and surface morphology was studied by scanning electron microscopy (SEM).

4.1 Yield: The yield of activated carbon was calculated based on the following equation:

$$Yield = \frac{Weight\ of\ AC\ after\ Carbonization}{Weight\ of\ the\ raw\ material} * 100$$

The yield is defined as the ratio of final weight of the obtained product after washing and drying to the weight of dried precursor initially used.

4.2 Determination of decolorizing power of activated carbon:

Dissolve 0.15 g of methylene blue conforming to IS:2230-1962 in 100 ml of water.

Weigh accurately about 0.1 g of material with accuracy of 0.01 g and transfer to a 50 ml glass stoppered flask. Add 10 ml of methylene blue solution and shake for 5 minute. After the first 10 ml of MB solution gets decolorized, continue to add methylene blue solution (1 ml at a time) till the blue colour dose not disappear for 5 minutes. Decolourizing power of carbon is expressed in terms of milligrams of methylene blue adsorbed by 1 g of activated carbon. The methylene blue number (MBN) is a measure of mesoporosity (2 – 5 nm) present in AC.

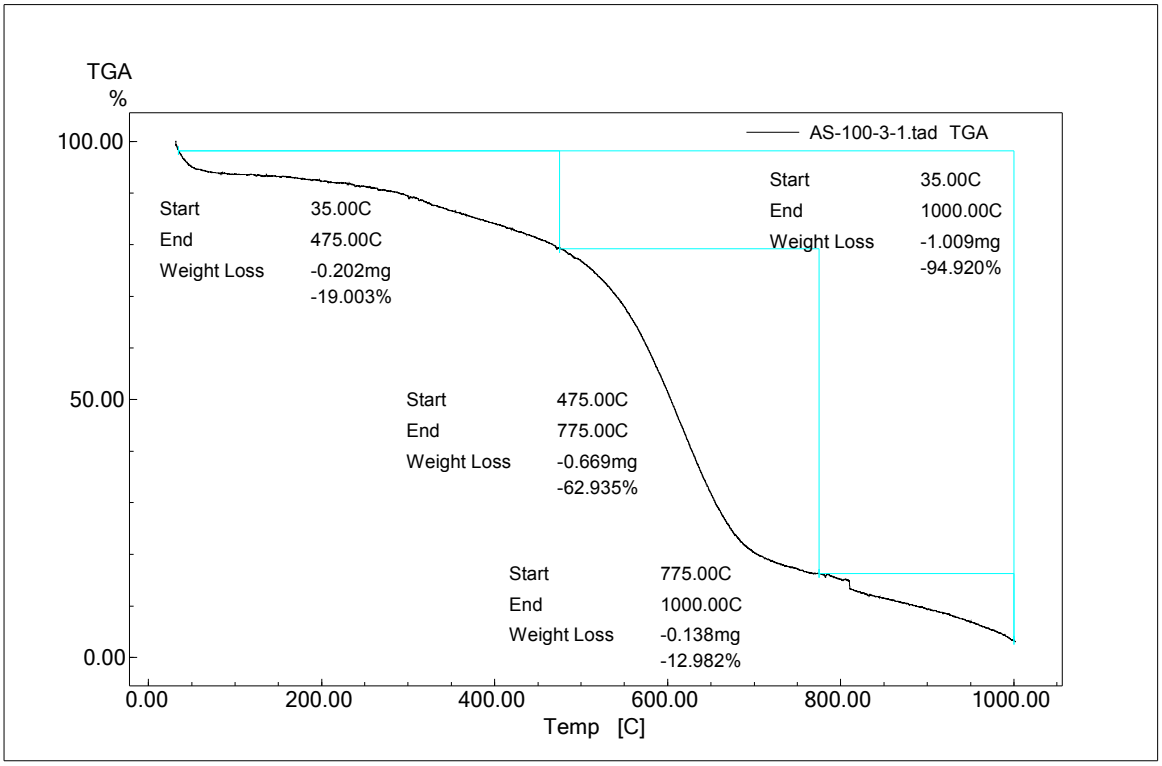
Decolourizing power = 15×V/ (10 × M)

where, V= Volume in ml of methylene blue solution consumed and M = Mass in gm of material taken for the test .

4.3 Deteremination of iodine number of activated carbon: The iodine number is defined as the *mg* of iodine adsorbed by 1 g of activated carbon when the iodine concentration of the residual filtrate is 0.02 N from 100 ml of 0.1 N iodine solution. The iodine number (IN) is a relative indicator of porosity in an activated carbon. It is a measure of micropore content of the AC (up to 2 nm). The iodine number is determined according to the ASTM D4607-94 method.

Adsorption of iodine from an aqueous solution has been used to indicate absorptive capacity.
Iodine Number (Dry Basis) = F(mg of I_2 at Outset-mg of I_2 at end of test)
where F = Filterate Normality= VN /50
V=Volume Of Sodium Thiosufate Solution (ml) and
N= Normality of sodium thiosulphate solution

4.4 Thermal (TGA-DTA) Analysis: The carbonization behaviour was measured by using thermobalance (DTG-60, Shimadzu Corporation) on the aspect of the weight loss behaviour. Temperature range is from ambient to 1373 ^{0}K. Heating rate was from 0.01^0 to 60 ^{0}C /min. TGA study was performed on the activation of activated carbon impregnated with the activating agents H_3PO_4. For each experimental run, a known weight of 6±0.5 mg was placed on a platinum sample pan. The samples were heated from 35 ^{o}C to 1000 ^{o}C at a rate of 10 ^{o}C/min in a nitrogen atmosphere.



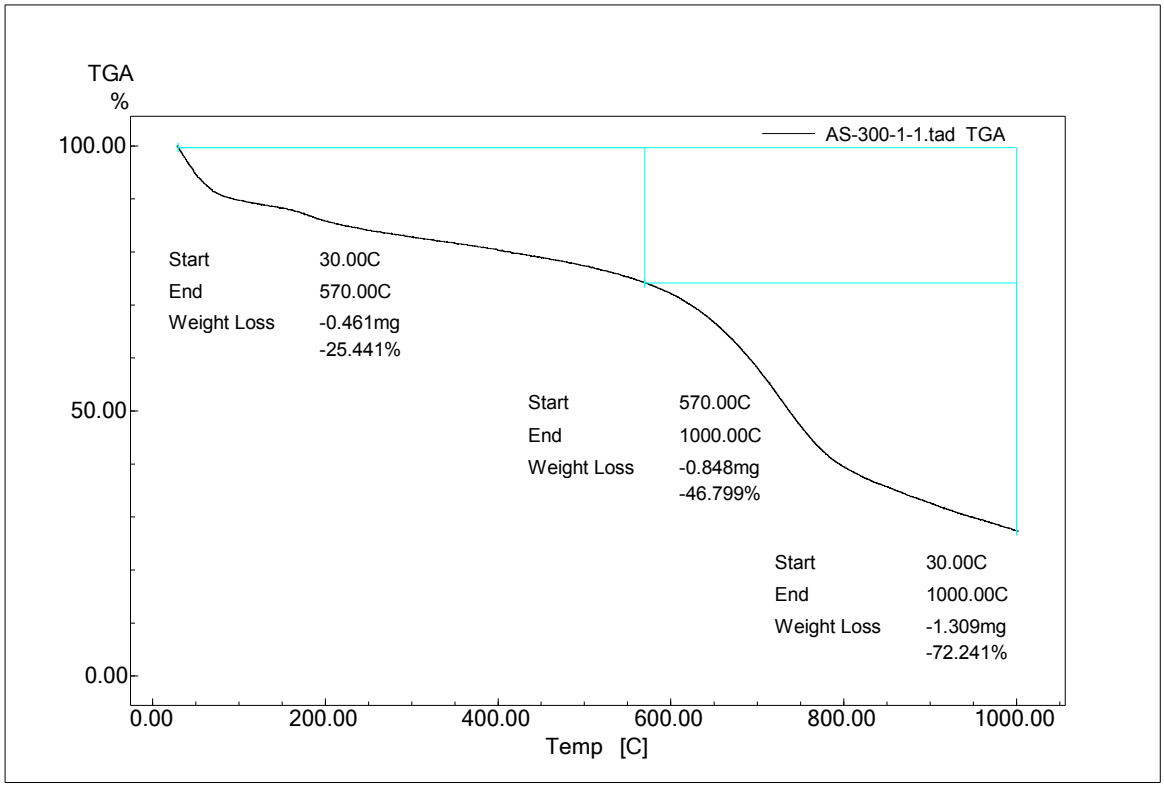


Figure (4): TGA Analysis of arecanut shell (100 gm - 3:1) and (300 gm-1:1) (400^0C).

This study defines the remaining amount of sample decomposed in nitrogen as W/Wo, where Wo and W represent the initial and instantaneous mass of the sample, respectively. The TGA and DTA curves were

recorded simultaneously as the temperature increases. Starting temperature was 35 ^{o}C and the end temperature was 1000 ^{o}C. The total weight loss occurred was 94.920 % for ASAC sample 100 (3:1) and for 300 (1:1) is 72.241 %. Samples were selected randomly according to observations made from methylene blue test and iodine number value. TGA-DTA characterization was done to know the thermobalance of the samples prepared. TGA study indicates that carbon derived from arecanut shell can with stand upto 475 ^{o}C.

4.5 SEM analysis and elemental composition: Scanning electron microscope (SEM) - Joel, Japan, JSM 6390LV was used for SEM observations. The surface morphology of the activated carbon samples were studied by scanning electron microscopy. Elemental composition was studied by M/s Elementar Germany:Vario EL III, Combustion temperature was used from 950 ^{o}C – 1200 ^{o}C. Carrier gas used was helium.

5. Result and Discussion

5.1 Effect of Yield: Activated carbon is prepared from areca-nut shell in varying batch sizes of 50 gm, 100 gm, 300 gm. From Table (1, 2 and 3), it is observable that as batch size of areca nut prepared activated carbon increases with phosphoric acid; amount of carbon obtained increases. Following observation table of arecanut shell derived activated carbon states that after increasing the batch size from 50 gm, 100 gm, and 300 gm with variation in phosphoric acid concentration, activated carbon yield increases. But decreases as impregnation ratio is increased to 4:1.

Table (1): Yield of Areca nut shell derived activated carbon.

Sample	Yield% (50gm)	Yield% (100gm)	Yield% (300gm)
AS-PA-01(1:1)	60.6	65.3	50.3
AS-PA-02(2:1)	77.2	77	73.33
AS-PA-03(3:1)	84	88	83.33
AS-PA-04(4:1)	70	80	75.23

5.2 Effect of methylene blue number (Decolorizing power):

Table (2): Methylene blue number of areca-nut shell derived activated carbon.

Sample	**MBN (50gm)**	**MBN (100gm)**	**MBN (300gm)**
AS-PA-01(1;1)	190	200	330
AS-PA- 02(2:1)	200	300	345
AS-PA- 03(3:1)	330	375	255
AS-PA- 04(4:1)	275	290	225

From Table (2), decolorizing power is calculated for varying batch sizes of 50 gm, 100 gm and 300 gm with respect to varying phosphoric acid to activated carbon ratio by weight basis. Decolorizing power increases with increase in ratio of phosphoric acid to activated carbon (ASAC). Decolorizing power is calculated by methylene blue test. Figure (5) shows increment of methylene blue value for various samples. Activated carbon prepared from 300 gm shows improved result. Methylene blue number is an indication of ability of a carbon to adsorb high molecular weight substances. ASAC showing methylene blue number smaller than 400, indicates that the carbon will not be able to adsorb dye molecules.

Optimization weight 300 gm is considered, because the decolorizing power decreases from impregnation ratio 3:1 to 4:1. Hence to validate the adsorption capacity; iodine number is calculated.

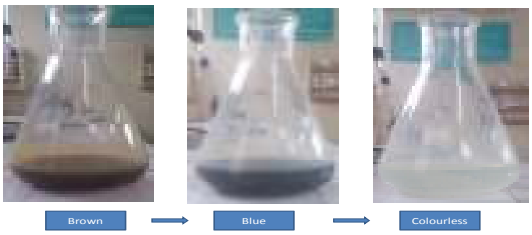


Figure (5): Decolorization of activated carbon using methylene blue test.

5.3 Effect of iodine number: It become necessary to know adsorptive capacity of AC. Adsorption of iodine from an aqueous solution has been used to indicate absorptive capacity. It is observable from Table (2) that iodine number increases for varying batch sizes from 50 gm, 100 gm and 300 gm with different varying ratio of phosphorous acid to activated carbon. Iodine number increase from 857 to 976.6 predicts the increase in porosity of activated carbon. Similar behaviour was observed with 100 gm and 300 gm samples. Iodine number is measure of activity level (higher number indicates higher degree of activation). Higher iodine number indicates better quality of the activated carbon. Iodine number is often reported in mg/g (typical range 500 – 1200 mg/g). Adsorption capacity of our AC was found to be good.

Table (3): Effect of iodine number on activated carbon yield.

Sample	Iodine Number (50 gm)	Iodine Number (100 gm)	Iodine Number (300 gm)
AS-PA-01(1;1)	857	829.63	742.06
AS-PA- 02(2:1)	906.67	937.93	786
AS-PA- 03(3:1)	937.93	976.6	976.6
AS-PA-04(4:1)	800.10	900	880

5.4 Effect of acid adsorption value: Acid adsorption test was carried out on activated carbon prepared for batch size of 50 gm, 100 gm and 300 gm. Acid adsorption increases as ratio of phosphoric acid (H_3PO_4) to activated carbon increases; thus indicating increase in porosity of the sample. From Table (4), result of acid adsorbed found linear for 300 gm sample of AC. Thus this test concludes ASAC prepared from 300 gm is having enhanced porosity and adsorption capacity.

Table (4): Effect of acid adsorption value on activated carbon yield.

Sample	Acid Adsorbed by ASAC (50 gm)	Acid Adsorbed by ASAC (100 gm)	Acid Adsorbed by ASAC (300 gm)
AS-PA-01(1:1)	4.4	6.34	5.30
AS-PA-02(2:1)	6.9	7.34	5.38
AS-PA-03(3:1)	7.3	8.31	6.2
AS-PA-04(4:1)	6.9	8.00	5.00

5.4 Elemental composition of AC: Carbon content of the activated carbon was higher for 1:1 ratio and 3:1 ratio of H_3PO_4-Areca nut produced activated carbon than that of the activated carbon for 2:1 H_3PO_4-Areca nut produced activated carbon. It is observed that carbon content is higher and increases with

increase in C/N ratio. For ASAC 100 gm (1:1) C/N ratio observed to 86.28, carbon content obtained is 61.52 %. For ASAC 100 gm (2:1) sample, C/N ratio observed to 115.5, carbon content obtained 54.86 %. For ASAC 100 gm (3:1) sample C/N ratio was observed to 140.9, carbon content obtained is 63.18 %. It is clear that carbon content value increases as C/N ratio increases for H_3PO_4 -areca nut shell activated carbon along with hydrogen.

Table (5): Elemental analysis of areca nut shell (100 gm).

H_3PO_4/Biomass Ratio	C	H	N	S
AS-PA-01(1:1)	61.52	3.734	0.734	0.144
AS-PA-02(2:1)	54.86	4.48	0.475	0.251
AS-PA-03(3:1)	63.18	3.368	0.448	0.11
AS-PA-04(4:1)	58.2	2.58	0.235	0.05

5.5 SEM analysis: Figure (6) shows scanning electron micrographs of the porous activated carbon. As magnification range is increased from 200x to 10000x. SEM micrographs of activated carbon particles showed cavities, pores and rough surfaces. Granular pores and cavities will increase the surface area of the adsorbent. SEM photograph shows that the surface is pitted and fragmented due to the carbonization with H_3PO_4 acid and activation process. The surface area is enhanced by the presence of more porosity, which can hold more solute from solution during adsorption.

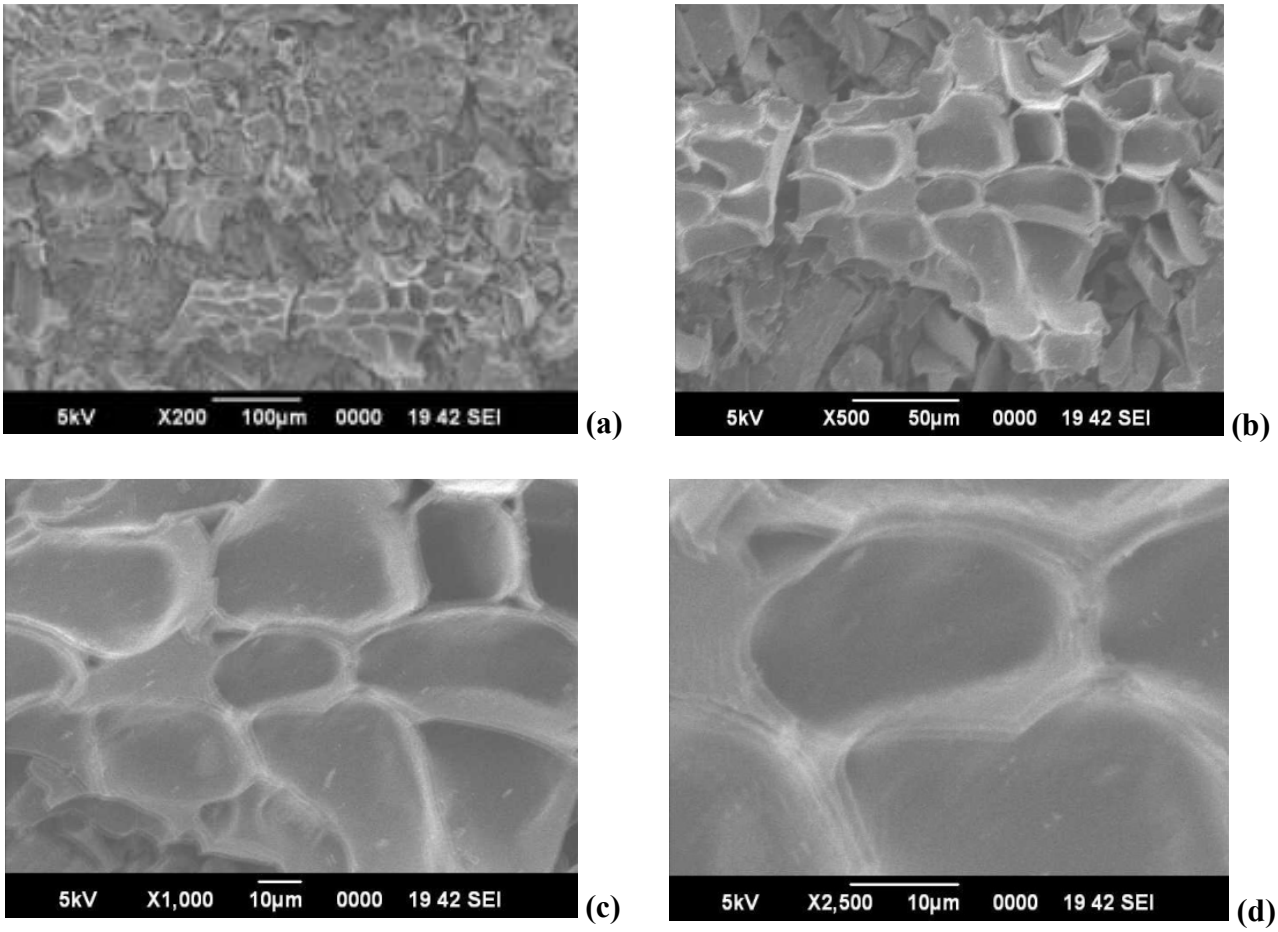


Figure (6): SEM photographs of AC synthesized.

6. Conclusion: Activated carbon was successfully prepared from arecanut shell by chemical activation method using phosphoric acid. Methylene blue adsorption test, iodine number, and acid adsorption value – all are observed to increase with increase in phosphoric acid (H_3PO_4) to biomass ratio. Iodine number value is above 700 which suggest good porosity which can satisfy commercial useablity criteria. All test carried for AC signifies that there is increase in the pore volume and porosity. Activated carbon prepared from arecanut shell is observed to be an effective dye adsorbent. Optimum impregnation ratio was observed to be 3:1.

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