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Ferets diameter estimation of activated carbon for effluent treatment application

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In this paper, activated carbon was produced of by chemical activation with phosphoric acid of agricultural wastes such as *Arecanut shell* of 25 micronmeter at 400°C by slow pyrolysis. The BET surface area and iodine number surface area is calculated and compared. The FTIR spectra show the presence of activated carbon. The TGA revealed, activated carbon is thermally stable at 480°C. The SEM shows the incorporation of activated carbon particles leads to the systematic change in morphology of activated carbon. Surface area plot shows the details of morphological change caused by iodine number surface area. Ferets diameter is estimated to know circularity of the particle. Methylene blue number, acid adsorption value is calculated to know adsorption capacity of the carbon. Thus results proves selection of ferets diameter, activation temperature, and impregnation ratio is important in determining the quality of activated carbon obtained and its use in industrial waste water treatment.

Keywords: *Arecanut shell*, activated carbon, phosphoric acid, feret diameter.

Introduction

Arecanut shell is not a consumable part and is usually discarded as waste. *Arecanut shell* has become important species since its demand for export has increased tremendously. To make better use of cheap and abundant agricultural waste, it is proposed to convert *Arecanut shell* waste into activated carbon. This conversion will address problems of unwanted agricultural wastes been converted into useful, value-added adsorbent and also the use of agriculture by-products to represent potential source of filler which will largely address problems of waste management. However, not many studies have been reported on converting *Arecanut shell* into activated carbon. In the present study, the optimal experimental conditions required to obtain adequate activated carbon with desirable properties in terms of carbon yield, BET surface area, iodine number surface area and ash content, methylene blue number, iodine number, ferets diameter which is critical in determining a good quality activated carbon is studied. A good quality activated carbon should have low ash content as possible[1], suggests that typical values of ash content should be in the range of 5–7% and about 85–90% for carbon content. As the carbon content of the activated carbon increase, the surface area also increases. High carbon content value is desired to achieve high surface area. Activated charcoal produced from residues would reduce the pressure on forests since wood is also commonly used for this purpose[2]. Many agricultural by-products such as coconut shell[3,4], grain sorghum[5], coffee bean husks[6], rubber wood sawdust[7], chestnut wood[8], have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents. Agricultural wastes are considered to be a very important feedstock because of especially two facts: they are renewable sources and low cost materials. A considerable amount of such materials as waste by products are being generated through agricultural practices mainly from various agro based industries. Sadly, much of the agro waste

is often disposed of by burning, which is not restricted to developing countries alone. Recently agro waste have gained increasing research interests and special importance because of their renewable nature. Therefore, the huge amounts of agro waste can potentially be converted into different high value products.

Materials and methods:

Preparation of activated carbon:

First preparation of activated carbon was done in three batch sizes of 50 g, 100 g, and 300 g. 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 amount of phosphoric acid solution used was adjusted to give a certain impregnation ratio (weight of activating agent/ weight of raw material) of 1:1, 2:1, 3:1, and 4:1. The impregnated sample was kept for 24 h. After 24 h the residual water was removed and kept in oven for 110°C. A weighed amount of impregnated samples was kept in muffle furnace for 400°C. The muffle furnace is purged with high purity nitrogen gas to avoid oxidation. Nitrogen flow was adjusted to 3 ml/°C at 400°C. The activated carbon was subsequently removed from furnace and cooled to room temperature. After activation the samples, 3 *M* hydrochloric acid used to remove the phosphoric acid compounds. The washed samples were dried at 110°C for 6 h in oven and then ground to form a porous carbon powder.

Results and discussion

Proximate analysis:

Proximate analysis of *Arecanut shell* is given in Table 1. This table reveals that the precursor used in this study has high carbon content approximately 75% and low ash content about 6.4% indicate that *Arecanut shell* is suitable to be used as activated carbon precursor.

Effect of impregnation ratio on Methylene blue number:

Increase in methylene blue concentration showed no significant changes. This is due to the fact that with increased MB concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface. Above optimal methylene blue concentration, the active sites required for the adsorption of will lack. This retard the overall MB adsorption by activated carbon. Methylene blue number is an indication of ability of a carbon to adsorb high molecular weight substances like dye molecule. Methylene blue number of greater than 400, indicates that the carbon is good for dye adsorption.

Table 1. Proximate analysis of *Arecanut shell*

Material	Weight (%)
Ash	6.4
Moisture	11.46
Volatile matter	6.24
Fixed carbon	75.9
Total	100

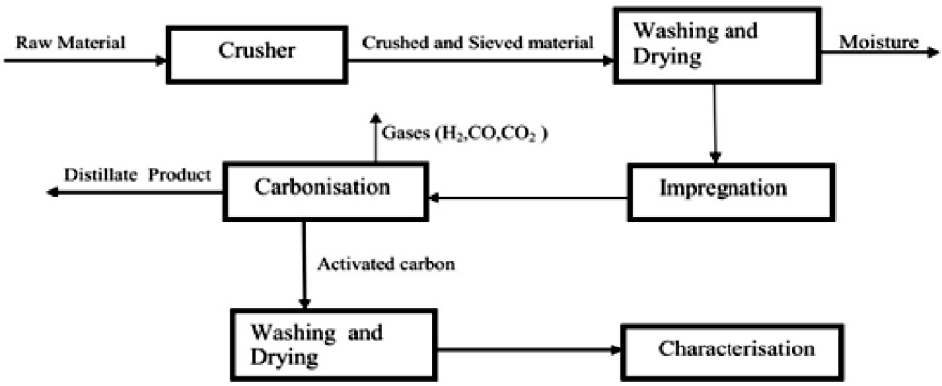


Fig. 1. Schematic diagram for preparation of activated carbon from *Arecanut shell*.

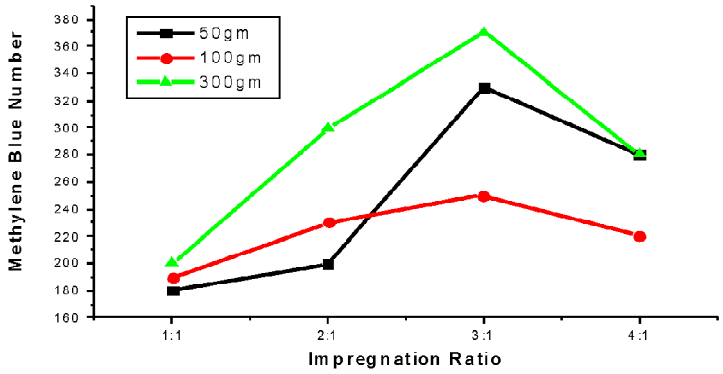


Fig. 2. Effect of impregnation ratio on methylene blue number activated carbon.

From above figure methylene blue number increases uptill 3:1 ratio and decreases thereafter to 4:1. Hence suitability for dye adsorption made us to calculate the effect of impregnation ratio on iodine number which discussed further.

Effect of impregnation ratio on iodine number:

Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. From the result of methylene blue value , it become necessary to know adsorptive capacity. Adsorption of iodine from an aqueous solution has been used to indicate absorptive capacity, iodine number increases for varying batch sizes from 50 g,100 g and 300 g with different varying ratio of phosphorous acid (1:1–4:1) to activated carbon. As iodine number increases there is increase in porosity of activated carbon, it is a measure of activity level. From Fig. 3 is seen that iodine number decreases from ratio 3:1–4:1 for all batches, indicates that degree of activation decreases i.e. activity level decreases.

Effect of acid adsorption:

Water soluble matter and acid soluble matter give the information about the amount of impurities present in carbon which affect the quality of water. But in our analysis, the data show that all the carbons contain very low amount of impurities. Here as impregnation ratio increases from 1:1–4:1, water soluble content increases uptill impregnation ratio of 3:1 and decreases from 3:1–4:1, for all batches from 50 g. 100 g and 300 g. It is observed that 300 g contains very less amount of impurities present as compared to the 50 g and 100 g.

TGA study:

The thermo gravimetric analysis of samples graph is pre-

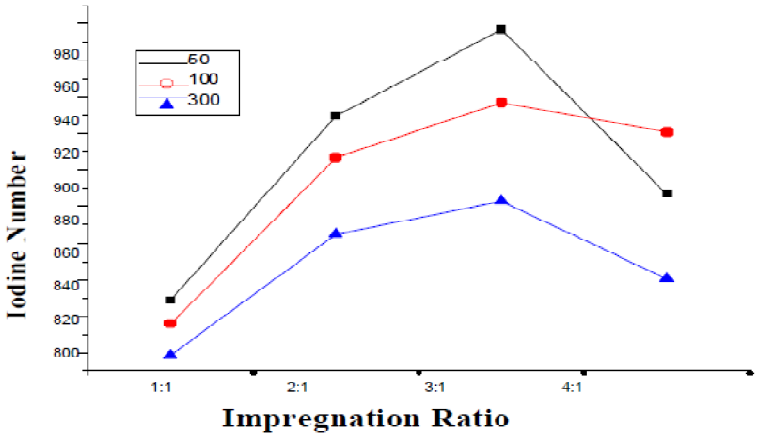


Fig. 3. Effect of impregnation ratio on iodine number.

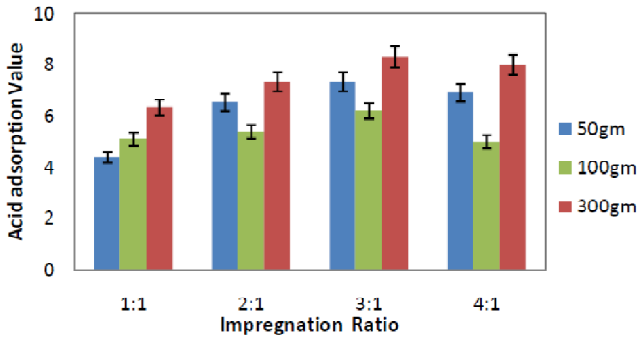


Fig. 4. Effect of impregnation ratio on acid adsorption.

thermally stable upto 150°C no appreciable weight loss. However they show weight loss of 10% in the first step, followed by weight loss of 11% in second step (150–500°C) and major weight loss of 50 to 55% form char residues 0–55% in the steep third step ascribed to the thermal decomposition of polymeric backbone and carbonisation of the fragments as well as AC particles.

Effect of impregnation ratio on BET surface area:

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 coconut leaves has the highest surface area. The surface area of different carbons follows the order: 50 g > 100 g > 300 g with

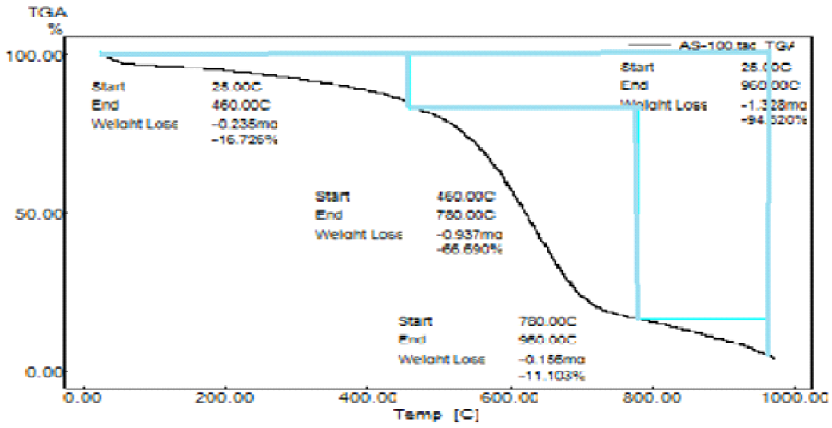


Fig. 5. TGA curve of *Arecanut shell* activated carbon.

sented in Fig. 5. Samples were analysed by taking weight of sample: 0.01 g, temperature range: 30–900°C and rate of heating: 10°C/min. 12% weight loss have been observed for *Arecanut shell* activated carbon weight loss of sample during analysis was 14%. It is seen that activated carbon are

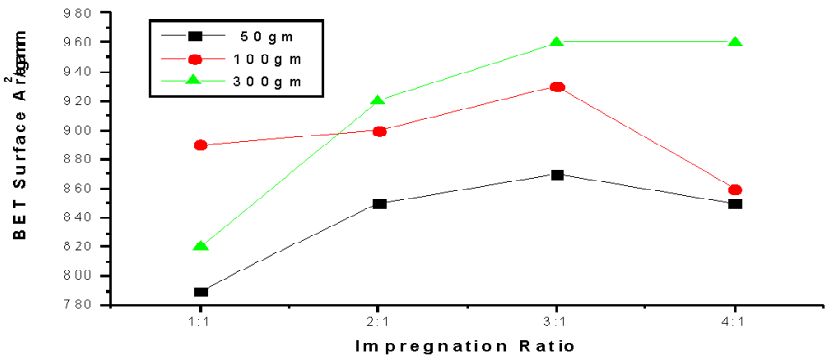


Fig. 6. Effect of impregnation ratio on BET surface area.

increase in impregnation ratio. N_2 adsorption-desorption isotherms on *Arecanut shell*, presented in Fig. 10. The figure shows that *Arecanut shell* has the highest N_2 adsorption characteristics, while surface area increases from 1:1–3:1, and decreases from 3:1–4:1 for ratio 1:1 of 50 g surface area shows little variation, other than 100 g and 300 g batch size. The BET does not predict surface areas of microporous carbon. Thus it became necessary to calculate the surface area using iodine number. 300 g sample shows steady deviation.

Effect of impregnation ratio iodine number surface area:

Determination of the iodine adsorption number comprises the measurement of iodine amount in the adsorption layer of an activated carbon sample (in mg iodine/g adsorbent). Iodine number surface area is calculated to characterize the quality of activated carbon. Table 2 depicts that iodine number surface area of the *Arecanut shell*, iodine number surface area increases initially for batch size of $S_{IN(50\,g)}$, $S_{IN(100\,g)}$ and $S_{IN(300\,g)}$ and for varying impregnation ratio from 1:1–3:1 and decreases from 3:1–4:1. This happens due to the

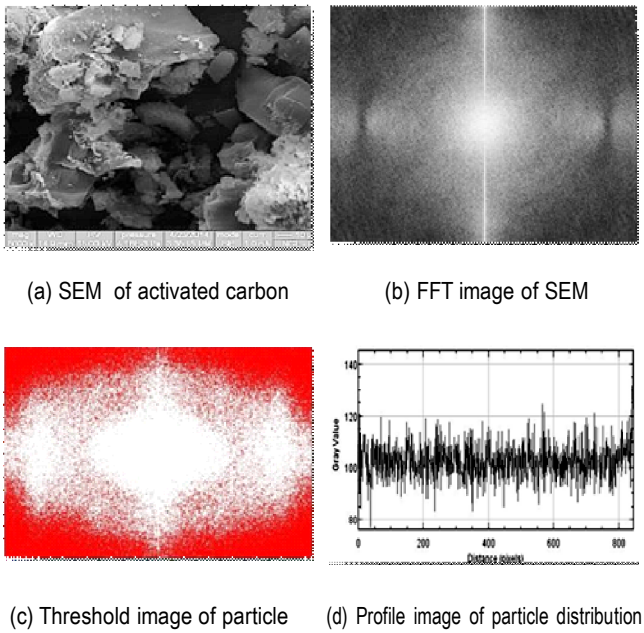
Table 2. Iodine number surface area of 50 g, 100 g, 300 g activated carbon derived from *Arecanut shell*

Sample	S_{IN} (50 g)	S_{IN} (100 g)	S_{IN} (300 g)
AS-PA-01 (1:1)	496.06	653.45	639.56
AS-PA-02 (2:1)	556.57	738.71	667.88
AS-PA-03 (3:1)	647.85	769.46	713.56
AS-PA-04 (4:1)	630.15	708.84	693.08

change of the bulk concentration results in the changes in the composition of the interfacial layers, which induces mutual displacements of the solution components from the adsorbed layer (Jankowska *et al.*, 1991). During excess adsorption from the solution there are no unoccupied sites on the surface, which implies that the same iodine amount occupies the same surface in the different carbon samples.

Comparison of the external surfaces of resulting carbon using SEM:

Scanning electron micrographs of the surface morphology of several samples of the activated carbons are given in Fig. 7. This figure shows the differences of the external surfaces of the activated carbons prepared. From this figure, it is obvious that the activated carbons produced at 400°C has cavities on their external surface. It can be predicted that the cavities on the surfaces of carbons resulted from the evaporation of the activating agent in this case is phosphoric acid during carbonization, leaving the space previously occupied by the activating agent. Similarly fast Fourier transform gives details of particle distribution of *Arecanut shell* particles.



(a) SEM of activated carbon (b) FFT image of SEM

(c) Threshold image of particle (d) Profile image of particle distribution

Fig. 7. SEM, FFT, threshold and profile plot of *Arecanut shell* particle.

Fourier transform infra red spectra:

FTIR spectra of *Arecanut shell* activated carbons with various impregnation ratios at each activation temperature are illustrated in Fig. 8. All of spectra show broad absorption band around 2999–2400 cm^{-1}. A peak around 1500 cm^{-1} shows the presence of stretching vibration of CO in ketones, aldehyde, lactone, and carboxyl.

The presence of broadband around 2999–2400 cm^{-1} and peak around 1510 cm^{-1} indicates the presence of carboxylic acid[16,17]. A relative low intensity peak at wavenumber around 3100 cm^{-1} of the broadband around 2999–2400 cm^{-1} may also represent OH stretching vibration in phenol. Very weak peak around 2900 cm^{-1} is CH stretching vibration in methyl group[17]. A strong band at 1590 cm^{-1} can be ascribed to C-C aromatic ring stretching vibration enhanced by polar func-

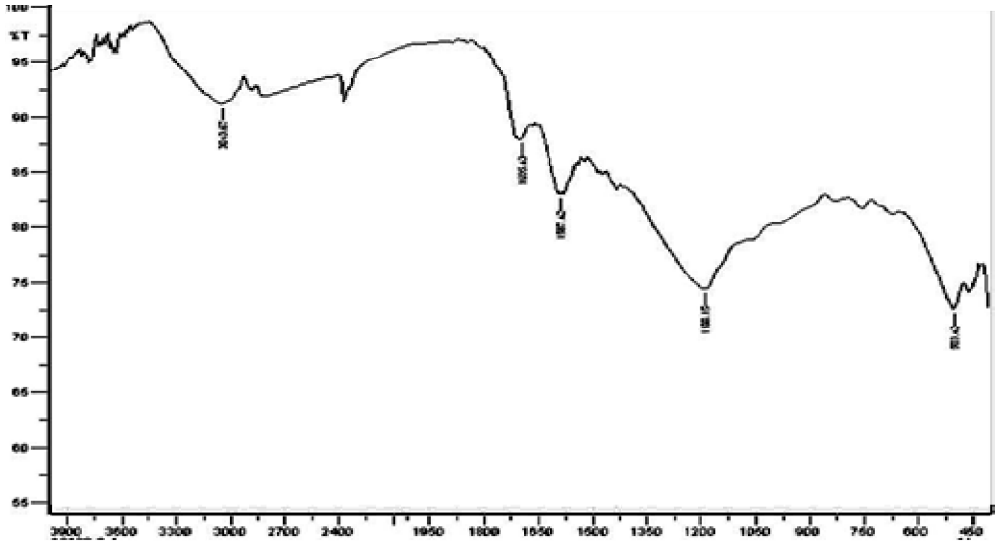
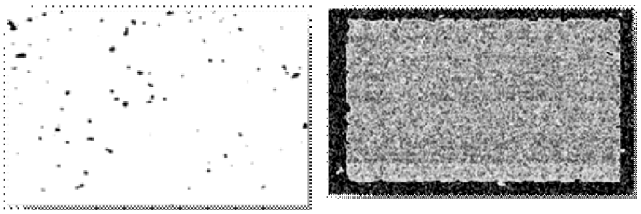


Fig. 8. Fourier transform infra red spectra for *Arecanut shell* activated carbon at activation temperature 400°C.

tional groups[8]. There is also a presence of broadband between 1300 and 1000 cm^{-1} with the strong band around 1200 cm^{-1} and a shoulder around 1080 cm^{-1}. According to Puziy *et al*., the peak at 1220–1180 cm^{-1} may be ascribed to the stretching mode of hydrogen bonded P O, O C stretching vibrations in P-O-C linkage, and P OOH; and the shoulder at 1080–1070 cm^{-1} can be ascribed to ionized linkage P+-O^{-} in acid phosphate esters. Surface images of *Arecanut shell* captured by research microscope. Fig. 9a shows the original microscopic image of overall distribution of particles and Fig. 9b shows the section view of particle distribution. distribution of Arecanut.

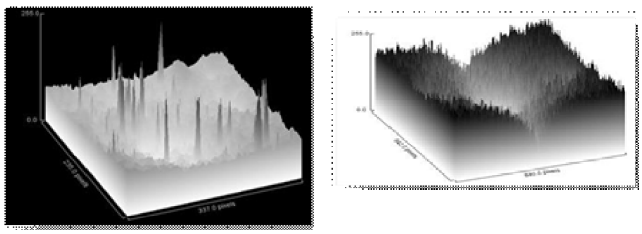


(a) Original microscopic of particles distribution of Arecanut (b) Section view of particle

Fig. 9. Microscopic images of Arecanut particle distribution.

Ferets diameter:

After performing all above analysis of particle size distribution it became the necessity to calculate the Ferrate diameter. From Cauchy's theorem it follows that for a 2D convex body, the Feret diameter averaged over all direction ⟨F⟩ is equal to the ratio of the object perimeter (P) and pi, i.e. ⟨F⟩ = P/π. Perimeter of particle is calculated as = 2.24E + 03. Therefore, Ferets diameter is 8.00E + 02 from Fig. 10.



(a) Surface area plot of overall particle (b) Surface area plot of individual particle

Fig. 10. Surface area plot images of overall and individual particle.

From Table 3 minimum Ferets diameter is 1 μm and Feret diameter is measured from 2–6 μm and circularity is measured from 0.6–1, circularity 1 defines particle is circular, less than 1 defines irregular shape. These circularity of particle help to increase the porosity and hence the adsorption rate of particle, which defines the solidity of the particle. Thus Feret diameter influences the surface area of the particle.

Table 3. Feret diameter of average particles

Perim.	Circ.	Feret	Feret angle	Min feret	Solidity
11.899	1	5.385	21.801	3	0.889
5.657	1	2.828	45	2	0.857
7.657	1	3.606	146.31	2	1
5.657	1	2.828	135	2	1
10.485	1	4.472	153.435	3	0.857
5.657	1	2.828	45	2	0.857
12.485	1	5	126.87	4	0.897
7.657	1	3.606	123.69	2	1
18.728	1	7.616	156.801	5	0.889
5.657	1	2.828	45	2	0.857
18.728	0.967	7.28	105.945	5	0.885
7.657	1	3.606	146.31	2	1
22.971	0.476	9.849	23.962	3.905	0.656
9.899	1	4.472	26.565	3	0.8
12.485	0.887	5.385	68.199	3	0.846
5.657	1	2.828	135	2	1
4.243	1	2.236	153.435	1	1
28.385	0.577	10	126.87	7	0.747
9.071	1	4.243	45	3	0.875
9.899	0.898	4.123	165.964	3	0.737
9.071	1	4.243	45	3	0.941
9.657	1	4.243	135	3	1
5.657	1	2.828	45	2	0.857
9.899	1	4.472	26.565	3	0.857
13.899	1	5.831	120.964	4	0.889
10.485	1	4.472	153.435	3	0.909
13.314	1	5.385	158.199	4	0.889
46.527	0.72	16.553	115.017	11.586	0.805
16.728	1	6.708	63.435	5	0.885
4.243	1	2.236	153.435	1	1
17.314	0.545	7.28	74.055	3	0.722
18.728	0.86	6.708	116.565	6	0.857
7.071	1	3.162	161.565	2	0.8
5.657	1	2.828	135	2	1
14.728	1	5.831	120.964	4.921	0.864
16.142	0.868	6.708	153.435	4.243	0.818
10.485	1	4.472	116.565	3	0.857
4.243	1	2.236	153.435	1	1
7.657	1	3.606	146.31	2	1
19.556	0.92	8.602	144.462	4.95	0.889

Conclusion

Activated carbons were prepared from *Arecanut shell* using phosphoric acid as chemical activating agent. The effect of impregnation ratio and activation temperature on pore structure and surface chemistry of resulting carbons were also studied. Optimized impregnation ratio for yield, methylene number, iodine number, acid adsorption value is 3:1. The pore structure of the carbons was studied by nitrogen adsorption, *Arecanut shell* has the highest N_2 adsorption characteristics SEM, and its surface chemistry was determined by Boehm titration method and FTIR to know the dominance of acid group. Thus it can be concluded that carbon with well-developed pores are produced at activation temperature of 400°C. At constant activation temperature (at the different impregnation ratio) the amount of acidic functional groups decreases while the basic surface groups of the carbon are increase. This happens due to increase of yield uptill impregnation ratio 3:1 and decease from impregnation from 3:1 to 4:1. Thus impregnation ratio 3:1 is considered as optimized ratio. Iodine adsorption number comprises the measurement of iodine amount in the adsorption layer of an activated carbon sample (in mg iodine/g adsorbent) Methylene number value is below 400, depicts that *Arecanut shell* derived activated carbon is not suitable for removal of dye particle. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes, Ferets diameter helps enhances the all characterization values and provides information about the adsorption application. Fast fourier transform (FFT) images helped to know particle applicability to reach the nanoscale.

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