PRODUCTION OF ACTIVATED CARBON FROM RICE HUSK AND IT'S CHARACTERIZATION

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ABSTRACT

In recent years, worth mentioning priority has been focused on the utilization of agricultural wastes or agricultural biomass for the production of various carbonaceous materials. This study has been carried out to demonstrate the potential of utilizing rice husk for the production of activated carbon. Activated carbon is a carbonaceous, highly porous material which is widely used in water purification, gas separation, catalysis etc. In this study, production of rice husk based activated carbon has been undertaken by chemical activation with potassium hydroxide (KOH). The raw rice husk was converted into rice husk carbon by heat treatment with 600 ^oC. The ratio of rice husk carbon and KOH solution of 1N was kept 1:5 for activation. The activated sample again processed with heat treatment of 750 ^oC to obtain the activated carbon. In this study, the characterization was done by Scanning Electron Microscopy and X-Ray Diffraction analysis. The SEM images revealed the fibrous, non-porous morphology of rice husk carbon and at the same time indicated the porous structure of activated carbon. From XRD analysis, the average crystallite size for rice husk carbon was found out 4.995 nm and for activated carbon of 9.12 nm which is about 1.8 times. The interlayer spacing for the both carbon was determined to be of 0.13 nm. The approximate percent crystallinity for rice husk carbon and activated carbon was determined 24.89% and 39.11% respectively. This study shows the porous and more crystallite morphology of produced activated carbon from agricultural by-product that will help in promoting resource recovery process for agricultural wastes.

Keywords: *Rice husk, Rice husk carbon, Activated carbon, SEM, XRD.*

1. INTRODUCTION

Activated carbon is a carbonaceous and highly porous medium which is composed of a complex structure of carbon atoms. The large surface area of activated carbon is used for adsorption of toxic chemicals, dyes, various heavy metals, removal of organic and harmful pollutants, various types of petrochemicals etc. It is widely used in filtration and purification (Baccar, Bouzid, Feki, & Montiel, 2009). The impurities from gaseous and liquid media are removed through the porous network in the lattice structure of activated carbon. This porous structure of activated carbon originates a vast surface on which adsorption occurs. Usually higher internal surface area offers higher effectiveness of activated carbon. Activated carbons are usually characterized by their large surface area, high micro porosity and adsorption capacity, enabling them to be utilized as an effective adsorbent in water treatment processes (Poinern et al., 2011).

Activated carbon is a product of good market demand for its versatile uses. However, the commercial production of activated carbon is not cost effective and together with the fact that the regeneration of used activated carbon is extremely difficult, much attention has been given to synthesizing amorphous activated carbon from renewable sources (Muniandy, Adam, Mohamed, & Ng, 2014). Now-a-days a wide variety of agricultural wastes are being used as the source of production of activated carbon. Some recent examples are coconut shells (Gratuito, Panyathanmaporn, Chumnanklang, Sirinuntawittaya, & Dutta, 2008), rubber wood saw dust (Srinivasakannan & Bakar, 2004), sugar-cane bagasse (Ahmedna, Marshall, & Rao, 2000), cassava peel (Sudaryanto, Hartono, Irawaty, Hindarso, & Ismadji, 2006), cotton stalk (Girgis & Ishak, 1999), rice husk (Suzuki, Andrade, Sousa, & Rollemberg, 2007) etc. Rice husk is an agricultural waste and major by-product of rice milling industry. It is cheap and also locally available in plenty in the whole world. Rice husk is mainly composed of various organic ligno cellulosic biomass and ash. The typical composition of rice husk is listed in Table 1.1. Most of the rice husk is used as fuel and regarded as a low value energy resource. The untreated rice husk creates a disposal problem and also unfavorable for the environment. Production of activated carbon from rice husk can increase the value of this agricultural waste, reduce the disposal cost, can be used as an adsorbent and thus provide cost effective alternative to the existing commercial carbon.

Table 1.1: Main components and contents of rice husk (Guo et al., 2002).

Main composition	**Content (Wt. %)**
SiO_2	18.8-22.3
Lignin	9.0-20.0
Cellulose	28.0-38.0
Protein	1.9-3.0
Fat	0.3-0.8
Nutrients after full digestion	9.3-9.5

Activated carbons can be synthesized by two different processes: the “physical” activation process and the “chemical” activation process. In physical activation process, the carbonized materials are activated at high temperature in accordance with the presence of steam or carbon dioxide. In chemical activation process, the carbonized material is mixed with various activating agent such as phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), zinc chloride ($ZnCl_2$) etc. and undergoes with a proper heat treatment. A comparison of chemical activation with physical activation shows that chemical activation provides a lower reaction temperature, and its global yield tends to be greater (Mohanty, Naidu, Meikap, & Biswas, 2006).

Many studies have been undertaken for the production of activated carbon by using a wide variety of materials. Here use of rice husk for the production of activated carbon by chemical activation process is proposed. One of the main purposes of this study is to discuss the SEM images for attaining better conception about the morphology of rice husk carbon before and after activation treatment. XRD analysis is also carried out to characterize rice husk based activated carbon.

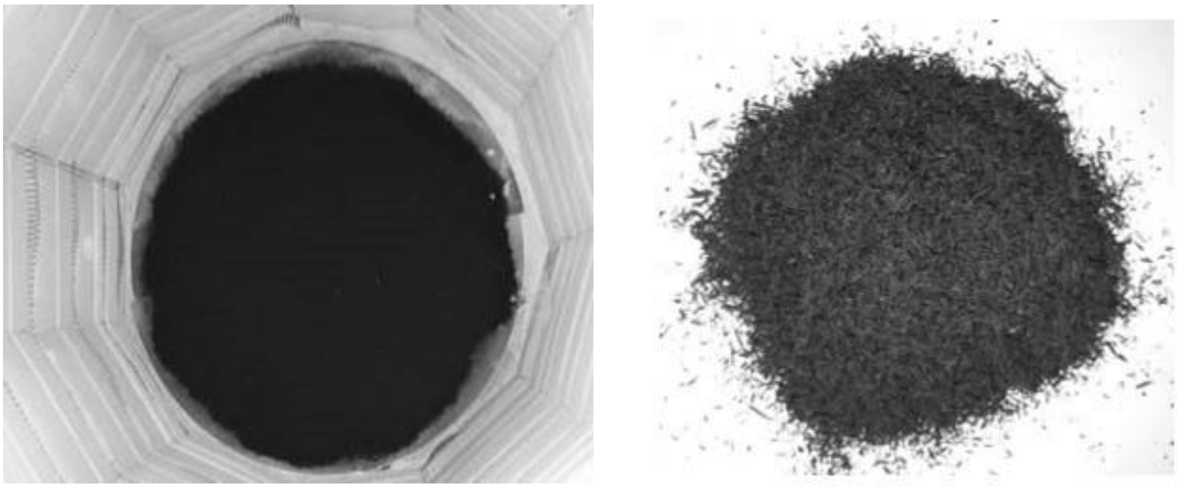
2. METHODOLOGY

2.1 Collection of Sample

Rice husk is a locally available material and is mostly available in various rice mills. The amount of this by-product is increasing every year with the increasing population. The rice husk used in this study was collected from a rice mill of Rajshahi, Bangladesh.

2.2 Preparation of Rice Husk Carbon

Raw rice husk was washed with water several times so that there was no dirt and other substances in the rice husk. It was then kept under sun shine till it was completely dried. This washed and dried rice husk was used for the preparation of rice husk carbon. This rice husk was put into the electric furnace (Model: SHTL-233) and kept for about 2 hours. The temperature was fixed at 600 ^oC. After burning at 600 ^oC for about 2 hours, the rice husk carbon was obtained. The prepared carbon is shown in Figure 1.



(a) Rice husk carbon in electric furnace (b) Rice husk carbon

Figure 1: Rice husk carbon produced in electric furnace at 600 ^oC

2.3 Preparation of Activating Agent

Sodium hydroxide, potassium hydroxide, zinc chloride, phosphoric acid etc. can be used as activating agent. Activating agent plays the most important role for the production of activated carbon. In this experiment, potassium hydroxide (KOH) solution was used as activating agent. For the preparation of potassium hydroxide (KOH) solution, 40g of potassium hydroxide was mixed with distilled water until the total volume became 100 ml.

2.4 Activation of Rice Husk Carbon

A 20g of rice husk carbon was taken in a beaker and mixed with 100 ml KOH solution thoroughly. The ratio of rice husk carbon and activating agent was maintained 1:5 (Rice husk carbon: Activating agent = 1:5 w/v). It was stirred for about 45-60 minutes. After activation, it was oven dried at 120 ^oC for 48 hours. The activation process is shown in Figure 2.

(a) KOH solution (b) Mixing with KOH solution (c) Oven dried activated sample

Figure 2: Activation of rice husk carbon with KOH

2.5 Production of Activated Carbon

The oven dried activated sample was put into the muffle furnace (Barnstead Thermolyne 47900 Furnace). It was kept at 750 ºC for about 1 hour. This process is shown in Figure 2.6 and 2.7. After burning it was washed with distilled water several times. It was then oven dried at 110 ºC for 24 hours. Thus, the activated carbon was obtained. The flow diagram of activated carbon production is presented in Figure 3.

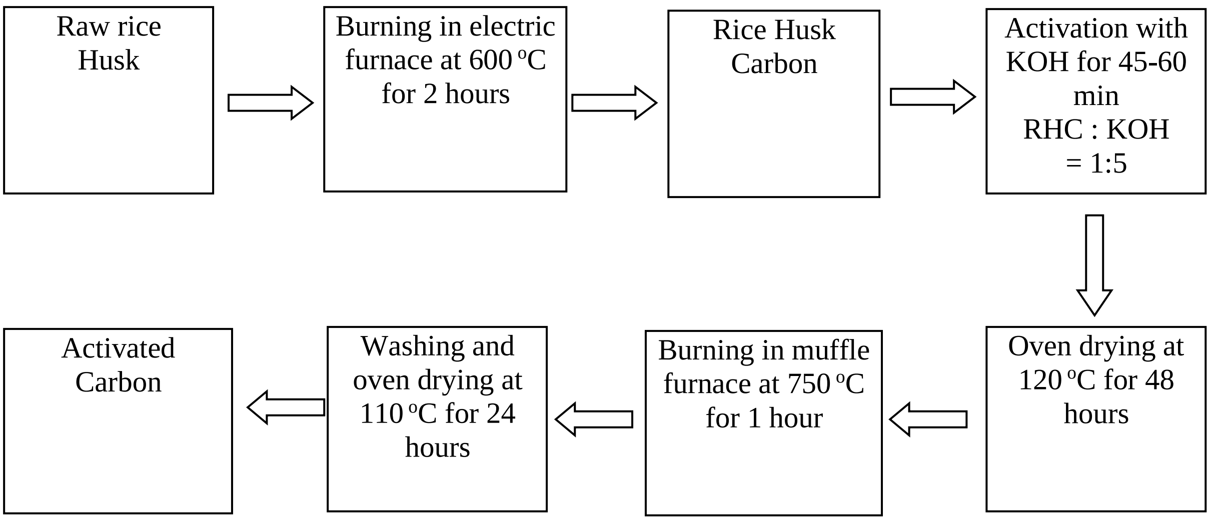


Figure 3: Flow diagram of activated carbon production process from rice husk

3. RESULTS AND DISCUSSION

Activated carbon produced from rice husk is characterized for the evaluation of morphology with scanning electron microscopy (SEM) analysis and X-ray detraction (XRD) analysis. Rice husk carbon without activated is also analyzed for comparing the change in morphology. The results are discussed in the following sections.

3.1 Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscope image provides idea about the surface texture and topography of the sample. The surface of the prepared samples was investigated using Curl Zeiss (Model: EVO-18) Scanning Electron Microscope. Figure 4 represents the fibrous texture of rice husk carbon. Figure 5 indicates surface topography of rice husk carbon having only some cracks and curves. It is clear from this SEM image that, rice husk carbon is non-porous. Here only carbonization of rice husk occurs without creating any porous structure. It is due to the insufficient heat treatment and absence of any activating agent. On the contrary, surface texture of activated carbon is non-fibrous (Figure 6). Figure 7 indicates surface topography of activated carbon having some number of pores. This porous structure is formed because most of the organic volatiles are developed gradually leaving behind the ruptured surface topography of activated carbon with few numbers of pores. This transformation occurs due to the decomposition of the volatiles. The activation process in accordance with the presence of potassium hydroxide (KOH) and the high temperature is mainly responsible for this. The equation for this transformation can be written as,

$$6KOH = 2K + 3H_2 + 2K_2CO_3 \quad (1)$$

The potassium carbonate (K_2CO_3) becomes decomposed at the time of activation. At this time CO_2 gas is released. The volatile organic compounds are evolved when the reaction between the potassium hydroxide (KOH) and the carbon precursor takes place. Sufficient heat treatment plays the most important role. So, for the formation of pores, not only proper activating agent but also sufficient heat treatment is necessary. The creation of pores increases both the surface area and the pore volume and affects the efficiency of adsorption.

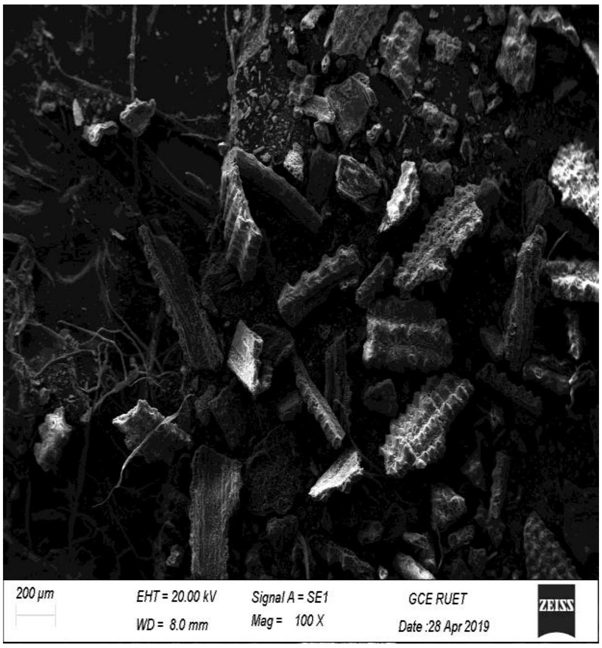


Figure 4: Fibrous texture of rice husk carbon

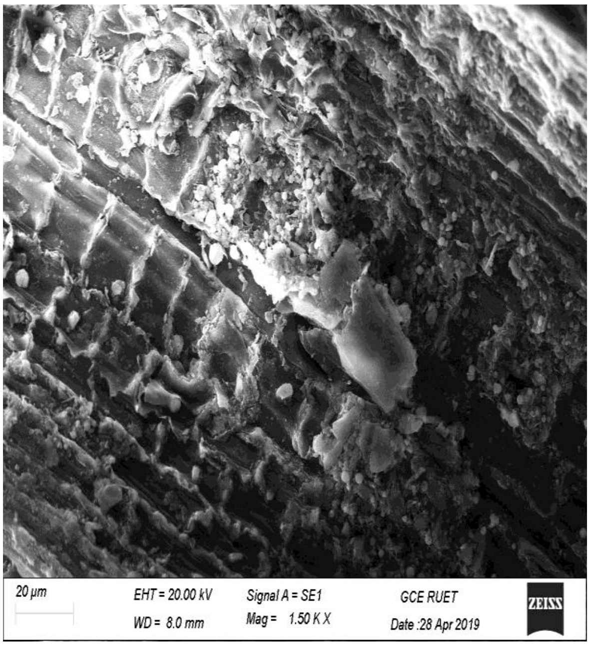


Figure 5: Non-porous surface of rice husk carbon

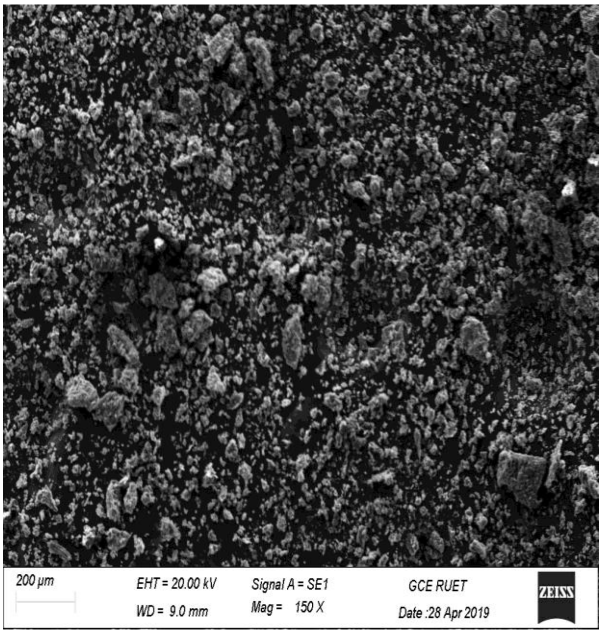


Figure 6: Non-fibrous texture of activated carbon

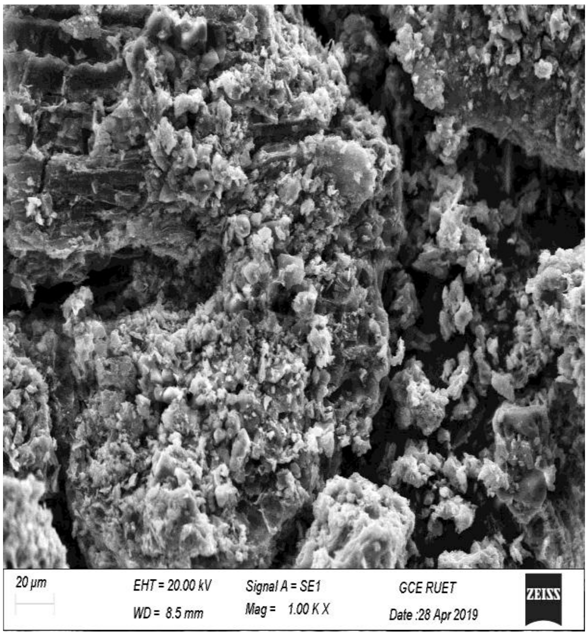


Figure 7: Porous surface of activated carbon

3.2 X-Ray Diffraction (XRD) Analysis

The X-ray diffraction method is suitable for characterization and identification. From XRD pattern, interlayer spacing, crystallite size, percent crystallinity etc. can be determined. This test was performed by BRUKER D8 ADVANCE XRD Machine. The XRD pattern of rice husk carbon and activated carbon is given below in Figure 8 and 9.

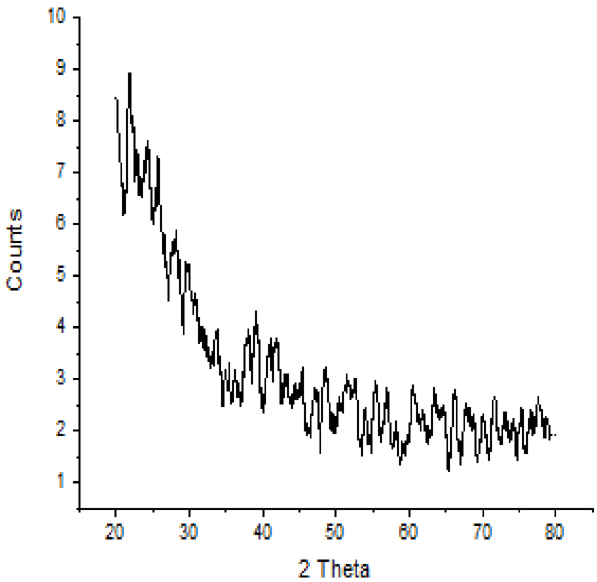


Figure 8: XRD pattern of rice husk carbon

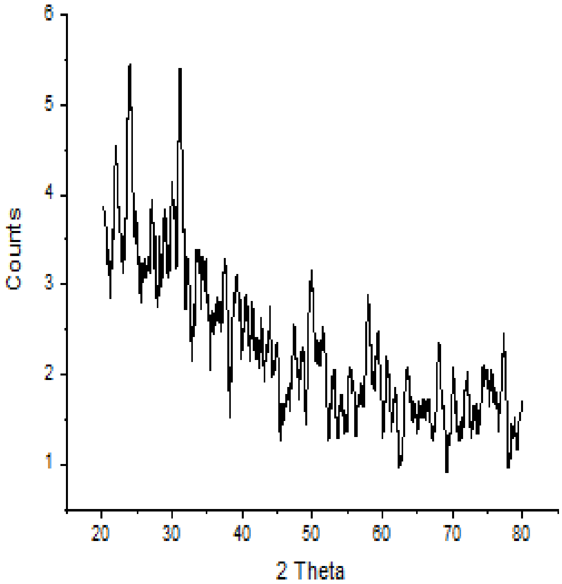


Figure 9: XRD pattern of activated carbon

Figure 8 and 9 represents the XRD pattern of rice husk carbon and activated carbon which was activated with potassium hydroxide (KOH) at a fixed activation temperature. Generally, for all XRD pattern the intensity at lowest Bragg angle is higher than the intensity at highest Bragg angle. It occurs because of structure factor. With increasing Bragg angle the interlayer spacing (d value) becomes smaller. Both the XRD patterns of rice husk carbon and activated carbon represent the amorphous nature of carbon. They represent a structure of disordered carbon materials. Their components (atoms, molecules or ions) are poorly stacked up without any regular, periodic manner. From these XRD patterns crystallite size, interlayer spacing, approximate percent crystallinity can be determined by analysis.

3.2.1 Determination of Crystallite Size from XRD Pattern

Crystallize sizes can be determined from XRD pattern by using Scherrer equation. From Scherrer equation,

$$L = (K\lambda)/(\beta \cos\theta) \quad (2)$$

Here, L= crystallite size (nm), K= Shape factor (0.9), λ= wavelength of X-Ray (0.154 nm), β= Full Width at half maximum (FWHM) (radian), θ= Bragg angle (degree).

Table 1 and 2 shows the crystallite sizes of rice husk carbon and activated carbon at various Bragg angle and finally the average crystallite size was determined. The crystallites are quite small for both samples. Usually smaller crystallites have greater ratios of surface area to volume. Smaller crystallites also improve the formability of a material. The average crystallite size of activated carbon (9.12 nm) is greater than that of the rice husk carbon (4.995 nm). The difference of this average crystallite size is not much as it was calculated in nano-meter. Again, from the SEM images, the surface morphology of activated carbon is highly porous while the rice husk carbon is non porous. So, the efficiency of activated carbon as adsorbent must be higher than that of the rice husk carbon.

Table 1: Crystallite size of rice husk carbon

Bragg angle θ (degree)	**Shape factor K**	**Wavelength λ (nm)**	**FWHM β (radian)**	**Crystallite size, L (nm)**
(23.90/2) =11.95	0.9	0.154	0.17	0.83
(24.46/2) =12.23	0.9	0.154	0.14	1.01
(40.28/2) =20.14	0.9	0.154	0.30	0.49
(46.21/2) =23.11	0.9	0.154	0.02	7.53
(62.73/2) =31.37	0.9	0.154	0.07	2.32
(77.64/2) =38.82	0.9	0.154	0.01	17.79

So, the average crystallite size of rice husk carbon = 4.995 nm.

Table 2: Crystallite size of activated carbon

Bragg angle θ (degree)	**Shape factor K**	**Wavelength λ (nm)**	**FWHM β (radian)**	**Crystallite size, L (nm)**
11.08	0.9	0.154	0.54	0.26
11.96	0.9	0.154	0.01	14.17
15.57	0.9	0.154	0.01	14.39
20.43	0.9	0.154	0.08	1.85
25.12	0.9	0.154	0.04	3.83
29.21	0.9	0.154	0.04	3.97
34.05	0.9	0.154	0.01	16.73
38.66	0.9	0.154	0.21	17.75

So, the average crystallite size of activated carbon = 9.12 nm.

3.2.1 Determination of Interlayer Spacing from XRD Pattern

Interlayer spacing is generally defined as an inter atomic spacing value. It can be determined from XRD pattern by using Bragg's law. From Braggs's law,

$$d = \lambda / 2\sin\theta \quad (3)$$

Here, *d*= interlayer spacing (nm), θ = incident angle (degree), λ= wave length of X-Ray (0.154 nm)

Table 3 and 4 shows the interlayer spacing of rice husk carbon and activated carbon at various Bragg angle and then the average interlayer spacing was determined. From Table 3 and 4 it is clear that, with increasing Bragg angle the interlayer spacing is decreasing. This gradual decrease of interlayer spacing occurs so that the variation of the electron density perpendicular to the diffracted plane becomes smaller as it is an important factor for the intensity formation.

Table 3: Interlayer spacing of rice husk carbon

Incident angle at peak position (degree)	Wave length λ (nm)	Interlayer spacing d (nm)
23.90	0.154	0.19
24.46	0.154	0.19
40.28	0.154	0.12
46.21	0.154	0.11
62.73	0.154	0.09
77.64	0.154	0.08

Average d= 0.13 nm

Table 4: Interlayer spacing of activated carbon

Incident angle at peak position (degree)	Wave length λ (nm)	Interlayer spacing d (nm)
22.16	0.154	0.20
23.92	0.154	0.19
31.14	0.154	0.15
40.86	0.154	0.12
50.23	0.154	0.10
58.41	0.154	0.09
68.09	0.154	0.08
77.32	0.154	0.08

Average d= 0.13 nm

3.2.2 Determination of Percent Crystallinity (Approximate)

Crystallinity is the degree of structural order in a material. An approximate calculation was done to find out the crystalline percentage from the XRD patterns by analysis. Following equation can be used to calculate the approximate crystalline percentage,

*% Crystallinity= {(Area of crystalline peaks) / (Area of all peaks)} * 100* (4)

Approximate percent crystallinity for rice husk carbon was found out 18.9% and the rest 81.1% was amorphous and for activated carbon crystallinity was 21.63% and the rest 78.37% was amorphous. So, both rice husk carbon and activated carbon exhibit mainly amorphous nature. The atoms or molecules in these carbon materials are in an irregular and unorganized state. They are disorderly stacked up due to lacking of structural characteristics. Generally, any carbon material produced from agricultural waste exhibits amorphous nature.

4. CONCLUSION

The porous surface topography of activated carbon was identified by SEM images. This porous structure clearly indicates the good adsorption capacity of activated carbon that was produced in this study. The surface morphology between rice husk carbon and activated rice husk carbon was also differentiated by the SEM images. The nature of both rice husk carbon and activated carbon was found out amorphous from XRD patterns. The crystallites of both the sample were small that represents greater ratio of surface area. This greater surface area can be used more efficiently in case of activated carbon for its porous structure.

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