Study of Influence of Carbonized Temperature on Surface Morphology of Grape Stalk

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Abstract

In this research work , the results of the SEM morphology and XRD pattern studies of charcoals and activated charcoal prepared from Grape Stalk are used to describe the effects of pyrolysis temperature and the mass ratios of KOH. In the carbonization process, Grape stalk charcoal carbonized at 300ºC to 400ºC has incomplete carbonization and the cell structure is maintained. Complete pore evolution occurred at temperatures of 500ºC. The surface image of activated carbon from Grape Stalk charcoal obtained at a pyrolysis temperature between 500ºC and 700ºC and with mass ratios between 1:3 and 1:5 showed increased porosity with increasing temperature. Increase KOH ratios slightly raised the pore size and porosity of activated charcoals. The change of pyrolysis temperature from 500ºC to700ºC for ratios ranging between 1:3 and 1:4 has a big effect on the pore size. However, the 1:5 ratio of activated charcoal suppressed the pore size. This result showed that the over KOH ratio resulted in an insulating layer, covering the particles of Grape Stalk charcoal. The XRD pattern showed that the constituents of Grape Stalk activated charcoal were probably graphite, amorphous C, amorphous SiO2, K2O, K and K2CO3.

Index Terms-Pyrolysis,Grape Stalk,Carbonization,Charcoal,

I. Introduction

Organic matter may be converted by controlled thermal decomposition into carbon. The mechanisms involved in the conversion of organic matter to carbon are: [1] desorption of adsorbed water upto 150oC, [2] splitting of matter structure water between 150oC and 260oC, [2] chain scissions, or depolymerization, and breaking of CO and C-C bonds within ring units evolving water, CO and CO2 between 260oC and 400oC,[3]- [4] aromatization forming graphitic layers above 400oC, and [5] above 800oC, the thermal induced decomposition and the rearrangement reaction are almost terminated leaving a carbon template structure. The major components of organic matter break down in a stepwise manner at 200-800Oc (hemi-cellulose), 260-350oC (cellulose) and 280-500oC (lignin).[6] Between 260oC and 400oC almost 80! of the total weight loss occurs which may vary between 40! (lignin) to about 80! (cellulose)[7] due to evolution of H2O, CO2, and volatile hydrocarbon species from fragmentation reactions of the polyaromatic constituents . Chemical activation of carbons is a very common method for obtaining activated carbons[8] with very high surface areas.[9] KOH is one of the most effective agents employed for organic materials[10]. KOH might be more selective in the activation process, causing a more localized reaction with the carbon precursor and is more effective for the highly ordeed materials[11].Thus, it can be stated that direct KOH activation of a lignocellulosic material is not necessarily an advantage [12]. The temperatures of pyrolysis and activation are considered to be the most important parameters controlling the activated carbon production[13}. There are many precursors from which activated carbons can be obtained.[14] The use of organic materials for activated carbon is common.[15] These materials are obtained as by-products of the agricultural and food industries and, hence, they are cheap and their use contributes to the conservation of the environment [16]. Grape Stalks are a solid waste from finished food products, such as chips, slices, and dried banana. They are high organic carbon (41.37%). This waste has been subjected to biomethanation [17] and biogas production [18].

The Grape Stalk charcoals have been prepared by carbonization at 300-700oC. It was found that the percentage of charcoal from Grape Stalk was decreased with the increase of carbonization temperature.[19] However, the percentage of fixed carbons was reversed. The maximum of iodine numbers of charcoal from Grape Stalks were found to be at the carbonized temperature of 500oC.[20] The charcoals of Grape Stalks with carbonization at 500oC were activated with KOH in ratios of 1:3 to 1:5 by weight. Then, these activated charcoals were recarbonized at 600o to 900oC. The iodine number of activated charcoals increased with increasing ratios of KOH, but the ethylene blue absorptions were increased a little [21]-[22]. These results suggest that activated carbons prepared from Grape Stalk using KOH activation may be developed for adsorbents.

In this study, the results of the SEM morphology and XRD pattern studies of charcoals and activated charcoals prepared from Grape Stalk are used to describe the effects of pyrolysis temperature and the mass ratios of KOH.

II. Preparation of Activated Charcoal

Grape Stalk as the precursor material was obtained from the banana vendor, Pune, India. It was well washed with H_2O several times and used after oven drying at 110ºC for 3 h. The dried sample was used for charcoal and activated charcoal preparation. The charcoal was prepared by a carbonized temperature of 300ºC to 600ºC for 1 h under a closed system in a porcelain crucible and then cooled to room temperature. The charcoal was then subjected to

KOH activation. The charcoal was agitated in KOH (CARLO ERBA Reagent) at a ratio of 1:3, 1:4 (charcoal : KOH) weight by weight basis. After the agitation was finished, the pre-carbonized charcoal slurry was left overnight at room temperature and, then, dried at 110ºC for 24 h. The samples were then activated in a closed system. Consequently, the samples were heated to optimize temperatures of 500ºC, 600ºC and 700ºC and maintained at a constant temperature for 1 h before cooling. After cooling down, the activated charcoal was washed successively several times with 0.2 N HCl (AR Merck), then with hot water until the pH became neutral, and finally with cold water to remove the excess KOH compounds. The washed samples were dried at 110ºC to get the final product. The charcoal and activated charcoal were characterized by SEM and XRD.

A Surface Morphology

Scanning electron microscopy was used to visualise the surface morphology of the charcoal and activated charcoal samples. A LEO 1455 VP scanning electron microscope was used. The samples were coated with gold by a gold sputtering device for a clear visibility of the surface morphology.

B .XRD Analysis

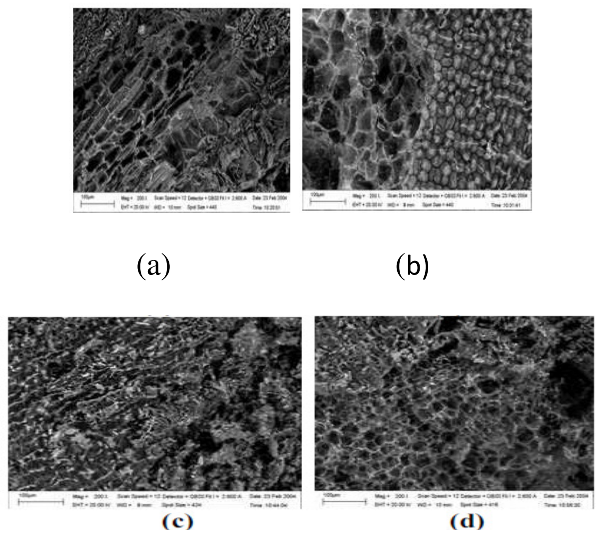
X-ray diffraction (XRD) was measured on a PW 3040/60, X. Pert Pro MPD X-ray diffract meter to determine the crystalline phases formed in Grape Stalk activated charcoal.

III. Results And Discussion

A. Influence of Carbonized Temperature on the Development of Porosity of Charcoal:

In the carbonization process, the development of porosity of Grape Stalk charcoal starts at 300^{o}C and increases with increasing carbonized temperature (figures 1.1 (a) - (d)).

Figures 1.1 (a) and (b) show a pore and a cellular structure of Grape Stalk charcoals which was carbonized at 300^{o}C to 400^{o}C.



(a) (b) (c) (d)

Figure 1.1 Surface images of Grape Stalk charcoal with carbonized temperature at (a) 300^{o}C (b) 400^{o}C (c) 500^{o}Cand (d) 600^{o}C.

A temperature of 300^{o}C to 400^{o}C led to incomplete carbonization of Grape Stalk and the cell structure is maintained. There are some rudimentary pores due to the release of volatiles. Evident pore evolution occurred in carbonization temperatures of 500^{o}C. Raising the temperatures from 500^{o}C to 600^{o}C has a good influence on the Grape Stalk with the generation moderately developed for charcoal production and shows characteristics open cellular structure in the original Grape Stalk (figures 1.1 (c) and (d)). It can also be seen that the distribution of the open pores is uniform and forms a honeycomb structure. The scanning electron micrograph of charcoal (figures 1.1 (c) and (d)) clearly showed its complete porous structure and the opening of cell pores on the surface. The study of Mendez et al. showed that the main important weight change of sewage sludge had been produced due to the light compounds volatilization and pyrolysis transformations at 450ºC. This stage is primary pyrolysis (in the 300ºC to 500ºC range) with evolution of most gases and tars with formation of the basic structure of the char. A temperature of 500ºC was found sufficient for Grape Stalk charcoal production. Therefore, considering economical and manufacturing factors, it was recommended the use of 500ºC carbonization temperature for banana charcoal production. Thus, we selected banana charcoal carbonized at 500ºC for subsequent KOH activation and characterization.

B. Influence of Activation Pyrolysed Temperature and Ratios of KOH on the Development of Porosity of Activated Charcoal:

Figures 1.2-1.4 shows the surface images of activated carbon from Grape Stalk charcoal obtained at pyrolysis temperature between 500ºC and 700ºC and mass ratios between 1:3 and 1:4. In this study it was established that the activated charcoal activated by KOH lost its original cellular structure and looked broken, therefore it was more fragmented during activation pyrolysis than carbonized charcoal. Generally, with the increase of activation temperature and the ratio of KOH, pore widening should occur. An increase in KOH ratio slightly raises the pore size and porosity of activated charcoals which is due to the aggressive action on the cellular structure, indicating that carbon gasification was enhanced by the increased KOH ratios. By increasing the temperature from 500ºC to 700ºC and ratios of KOH from 1:3 to 1:4, the amount and size of porosity of activated charcoal increased. Increasing of the temperature raised the C-KOH reaction rate, resulting in an increased carbon burn-off. Concurrently, the volatiles from the charcoal continue to evolve with increasing activation temperature, whereas the C-KOH reaction enhances the existing pores and creates new porosities. The pore size depends on the banana charcoal: KOH ratios. Because the KOH reagent is a strong base, it is able to interact with carbon atoms and thus catalyze the dehydrogenation and oxidation reaction, leading to the increment of tar evolution and development of porosity. The change of pyrolysis temperature from 500-700ºC for ratios ranges between1:3 and 1:4 has a big effect on pore size. However, the 1:5 ratio of activated charcoal suppressed pore size. It is seen that the white sphere and some fluffy materials appear in the pores of activated charcoal (figures 2-4). The white spheres and fluffy materials may be due to the presence of K_2O, K_2CO_3 or K residues and increase with increasing ratios of KOH. It could be supposed that during the KOH activation process, various reactions can be considered with such products as H_2, K, K_2CO_3, and K_2O. At higher temperature, the formation of K_2O is thermodynamically the most stable. The increase of KOH ratios on samples containing a large amount of potassium suggests that the high ratio KOH may give more K_2CO_3 and K_2O during pyrolysis. They were analyzed to be possibly either K_2CO_3 or K_2O from the corresponding EDS spectra. Elemental analysis on the white point of activated charcoal shows that large amounts of K and O. The K_2CO_3 formation may not only occur on the outermost carbon surface, whereby K_2CO_3 forms a shell around the carbon and has no effect on the carbon structure, but also in the pores and cavities of the carbon where molten KOH could be located. K_2CO_3 formed here would cause carbon lamellae separation, deformation and structure crumbling. In the impregnated samples, increasing pyrolysis temperature at a constant impregnation ratio gives rise to an enhancement of the pore size. The same behaviour was observed in activated carbon which ratios of KOH 1:3 to1:4 (figures 8.2-8.4). It appears that a larger amount of K_2CO_3 formed causes a larger pores size and the structural deformation. However, the surface image of Grape Stalk activated charcoal with KOH activation of ratio 1:5 has smaller pore size than activated charcoal with ratios of KOH 1:3 to 1:4. It might be explained that the larger ratio of KOH probably forms an insulating layer, covering the particles, thus reducing the activation process and the contact with the surrounding atmosphere.

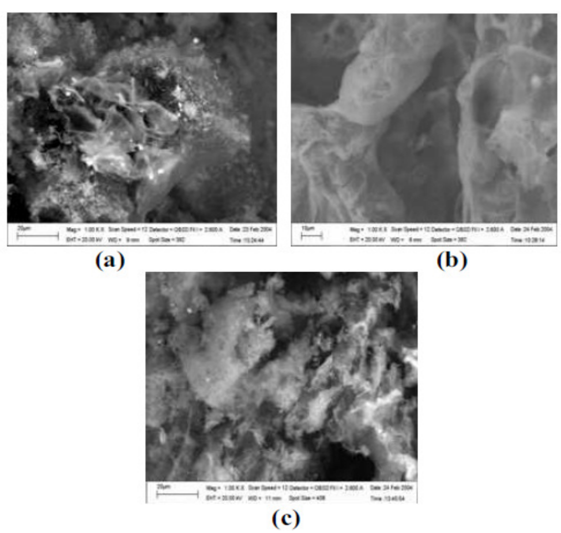


Fig. 1.2 Surface images of Grape Stalk activated charcoal with KOH activation of ratio 1:3 and Pyrolysed temperature at (a) 500ºC (b) 600ºC and (c) 700ºC.

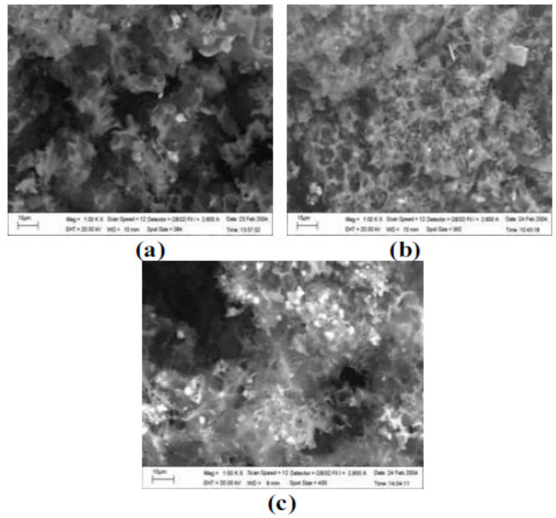


Fig.1.3 Surface images of Grape Stalk activated charcoal with KOH activation of ratio 1:3 and Pyrolysed temperature at (a) 500ºC (b) 600ºC and (c) 700ºC.

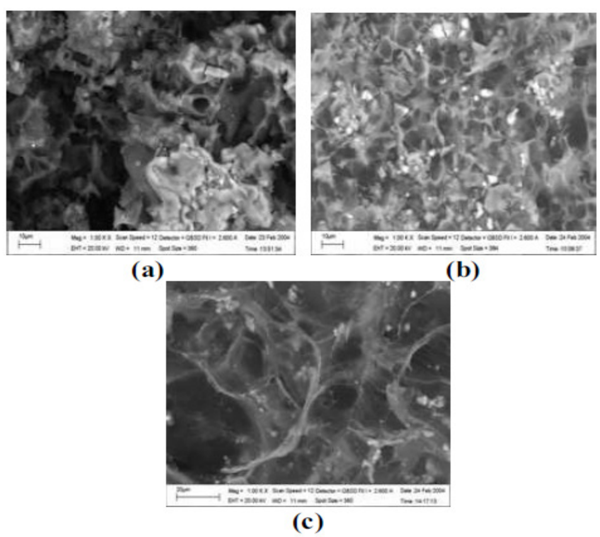


Fig. 1.4 Surface images of Grape Stalk activated charcoal with KOH activation of ratio 1:4 and Pyrolysed temperature at (a) 500ºC (b) 600ºC and (c) 700ºC.

C. Yield of Grape Stalk at 500^oC

Sample Ratio (On weight basis)	% Yield (Wt %)
1:3	9.2
1:4	10.8

D Yield of Grape Stalk at 700^oC

Sample Ratio (On weight basis)	% Yield (Wt %)
1:3	9.6
1:4	11.89

E Methylene blue numberof Grape Stalk at 500^oC

Sample Ratio	Wt of Sample (gm)	Reading in ml	Decolorizing Power
1:3	0.1	5.7	85.5
1:4	0.1	6.7	100.4

F Methylene blue numberof Grape Stalk at 700^oC

Sample Ratio	Wt of Sample (gm)	Reading in ml	Decolorizing Power
1:3	0.1	2.5	37.5
1:4	0.1	2.7	40.5

G. Phenol Number of Grape Stalk at 500^oC

Sr. No	Sample Ratio	Phenol Number
1	1:3	110
2	1:4	124

H. Phenol Number of Grape Stalk at 700^oC

Sr. No	Sample Ratio	Phenol Number
1	1:3	115
2	1:4	132

I. Tannic Acid Number of Grape Stalk at 500^oC

Sr. No	Sample Ratio	Tannic Acid Number
1	1:3	18.4
2	1:4	22

J. Tannic Acid Number of Grape Stalk at 700^oC

Sr. No	Sample Ratio	Tannic Acid Number
1	1:3	22
2	1:4	24

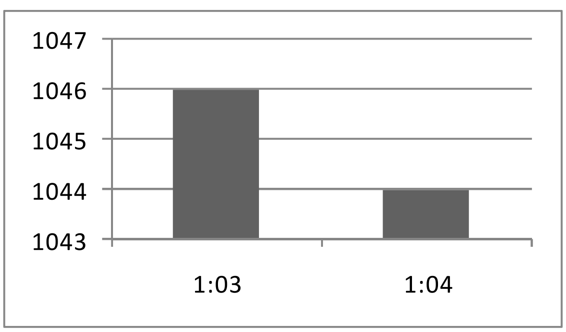
K. Iodine Number of Grape Stalk at 500^{o}C

Sample Ratio	B.R.	F Factor	Iodine Number
1:3	8	1.04	1046
1:4	8.8	1.02	1044

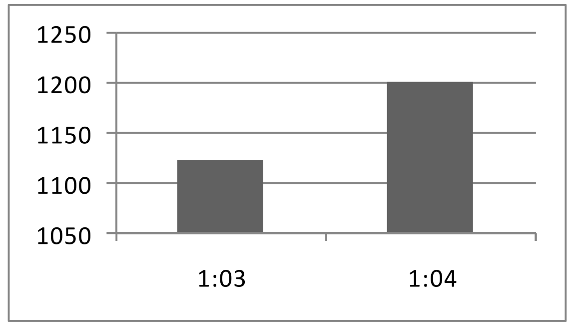
L. Iodine Number of Grape Stalk at 700^{o}C

Sample Ratio	**B.R.**	**F Factor**	**Iodine Number**
1:3	7.5	1.06	1124
1:4	6	1.09	1201

M. Effect of Iodine Number using Sample Ratio of Grape Stalk at 500^{o}C



N. Effect of Iodine Number using Sample Ratio of Grape Stalk at 500^{o}C



IV. Conclusion

Adsorbent from different raw materials such as Grape Stalk, are prepared using activating agent potassium hydroxide and phosphoric acid. Chemical characterization of adsorbents was carried by using proximate and analysis method followed by methylene blue number, phenol number, iodine number and tannic acid number.

From Grape Stalk SEM study

Conclusions are –

1 As the carbonization temperature increases, the resulting Grape Stalk charcoal is better in clearly structure and ordering.

2 Raising the temperatures from 500ºC to 600ºC has a good influence on the Grape Stalk with generation of moderately developed charcoal production and shows characteristic due to open cellular structure in the original Grape Stalk.

3 Increased KOH ratios slightly raises the pore size and porosity of activated charcoals which is due to aggressive action on the cellular structure, indicating that carbon gasification was enhanced by the KOH ratios increase to widen the pores.

4 The change of pyrolysis temperature from 500ºC to 700ºC for ratio ranges between 1:3 and 1:4 has a large effect on the pore size.

5 It is seen that the white sphere and some fluffy materials appear in the pores of activated charcoal.

6 The white spheres and fluffy materials may be due to the presence of K_2O, K_2CO_3 or K residues and increase with increasing ratios of KOH. K_2CO_3 formed would cause carbon lamellae separation, deformation and structure crumbling.

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