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Feature Article

Studies on Pyrolysis Behaviour of Banana Stem as Precursor for Porous Carbons

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Abstract

Porous carbons have been prepared from different parts of banana stems using two different routes, viz., by pyrolysing the mass at different temperatures as well as by treating the dried mass with chemicals followed by pyrolysis. The pyrolysis behaviour of all these materials has been studied up to 1000°C. Samples treated with acids exhibit more increase in surface area as compared to those treated with alkalies or salts. Analysis of BET surface area shows that the carbon prepared at low temperature shows mixed porosity, i.e., micro and mesopores. Samples heated to high temperature above 700°C show decrease in macroporosity and increase in microporosity. Liquid adsorption studies have been made using methylene blue and heavy oil. The activated carbons so prepared exhibit higher oil adsorption mainly in the macro and mesopores.

Keywords : *Activated carbon, Pyrolysis, Surface treatment, Surface area*

1. Introduction

Activated carbons are one of the most important types of industrial carbons used in domestic as well as in a large variety of industrial sectors ranging from chemical industries and consumer products to electronic industries [1-3]. This large potential applications come from the fact that activated carbons with desired internal surface area, porosity and adsorption characteristics can be manufactured by choosing a right kind of precursor or controlling the process conditions. It can be produced virtually from any carbonaceous solid precursor both naturally occurring or synthetic [3, 4]. However, feed stock of biological origin such as wood, coconut shells, agricultural wastes, or coalified plant matter such as coals, lignites etc. is still the major raw materials for commercial activated carbon. Though new synthetic precursors such as polymeric fibers are being tried to produce activated carbon with high surface area [3, 5-7], more and more agricultural wastes are also being investigated as precursors for activated carbon. Interest in latter type of precursors is on regional basis and is primarily aimed at utilising cheap and abundantly available vegetation to produce low cost activated carbon as well as to control pollution from plants degradation which otherwise is of serious concern. Banana is a major crop grown and consumed all over the world. The complete plant including stem is highly porous with fibrous structure. This could be a good precursor for porous carbon specially for bio application and water purification. Present studies report pyrolysis behavior of banana stem and development of porous carbons therefrom.

2. Experimental

2.1. Raw Material and Treatment

Green banana stem of Mosalinn (Alusaccae) variety from Gujarat was used in the present studies. Rectangular plate-like samples of dimensions 15 cm × 10 cm × 1 cm were cut from different parts of the stem. Drying was carried out by keeping the samples in between parallel steel plates. These dried pieces of banana stem were then used as precursor for obtaining char and activated carbon. Fig. 1 shows overall scheme of pyrolysis and chemical treatment. Samples of dried banana stem were weighed and treated with activating chemicals. Phosphoric acid, nitric acid, zinc chloride and potassium hydroxide were used as activating chemicals. All the chemicals were of AR grade. The samples were immersed in activating agents at room temperature for 24 hrs. After the treatment the samples were dried at 100°C. Pyrolysis of the samples was carried out in Muffle furnace. In all series, the samples were heated at rate of 30°C/hr up to desired end temperature and held at maximum temperature for 2 hrs. Cooling was done at 60°C/hr. Before surface area analysis, the char samples were grounded and sieved through 100 mesh sieve to have samples of same size.

2.2. Characterization of samples

Density of the samples was measured by Pycnometer method using kerosene as the liquid medium. Thermogravimetric analysis of the samples was carried out using Mettler TA 4000 Thermal analysis system at heating rate of 10°C/min.

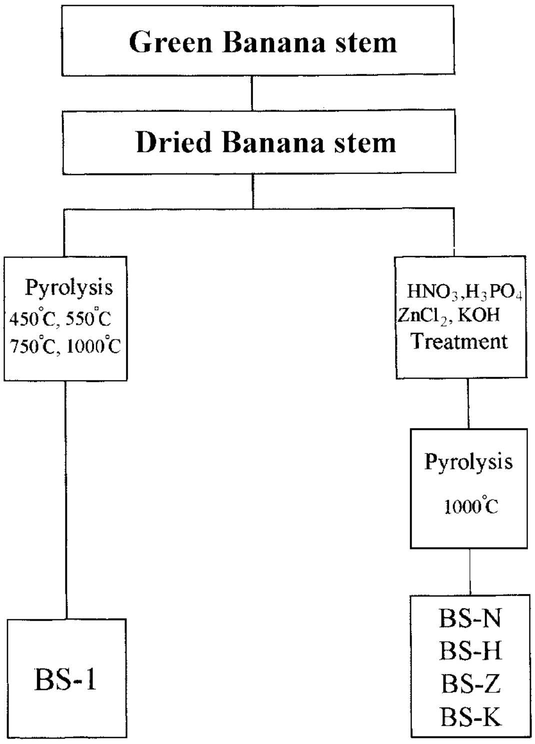

Fig. 1. Schematic representation of experimental procedure.

BET surface area of the samples was measured on Micromeritics Gemini 2375 Surface area analyser. The samples were cleaned prior to measurement by heating the sample at 250°C for 24 hrs.under continuous flow of Argon.

Methylene blue adsorption studies were carried out as per standard technique. Accurately weighed 0.5 gm carbon sample was placed in stoppered bottles. 10 ml of methylene blue solution of different concentration was added to the samples taken in different bottles. The bottles with the samples were kept at 60°C for one hr. On cooling to room temperature, the solutions were filtered. The filtrate was taken in quartz cuvette and absorbance was measured using Shimadzu UV-VIS spectrophotometer 1601.

For adsorption of heavy oil, a water-oil mixture was prepared. 10 gm of rotary pump oil was taken in a beaker. To this, 40 ml of hot distilled water was added and the mixture was agitated to produce homogeneous emulsifier. To this mixture, 0.2 gm of specific char sample was added with constant stirring of the solution. After treatment, the sample was filtered and dried. The dried sample was weighed again and the adsorption of oil was calculated.

3. Results and Discussion

3.1. Anisotropic structure of banana stem

Fig. 2 shows structure of green banana stem. It consists of a major outer part having soft mesh and channel like structure and inner hard part having longitudinal fibrous structure. In order to study the effect of this differential structure on the ultimate product, the two parts were separated and dried. Rectangular pieces of different parts of banana stem were kept in between the two steel plates and dried in order to avoid shape distortion. It was found that during drying both the parts though exhibit similar weight loss of about 93-95%, show different dimensional changes characteristic of the portion of the stem. Fig. 3 shows dimensional changes of the two parts on drying. As seen from the figure, maximum shrinkage takes place in the thickness direction. Moreover, inner part of the stem exhibit much higher shrinkage (about 20%) along the length of the stem as compared to outer part. This may be due to compact fibrous structure in former part as compared to mesh type structure of the outer soft part.


Fig. 2. Photograph of green banana stem.

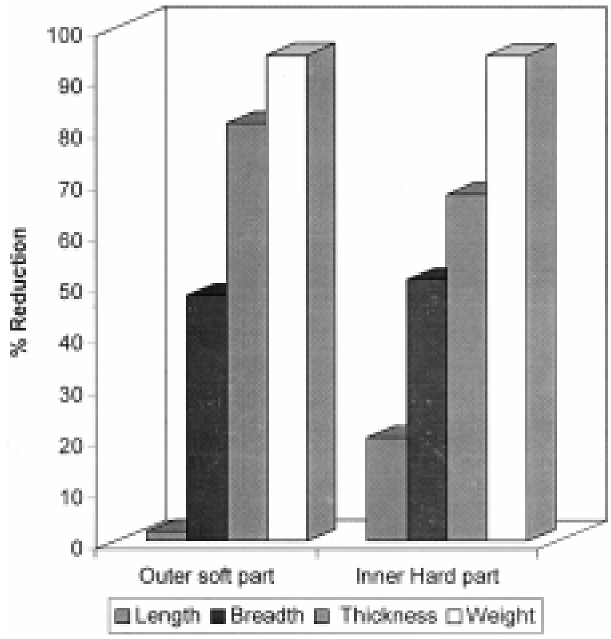

Fig. 3. Dimension reduction of banana stem during drying.

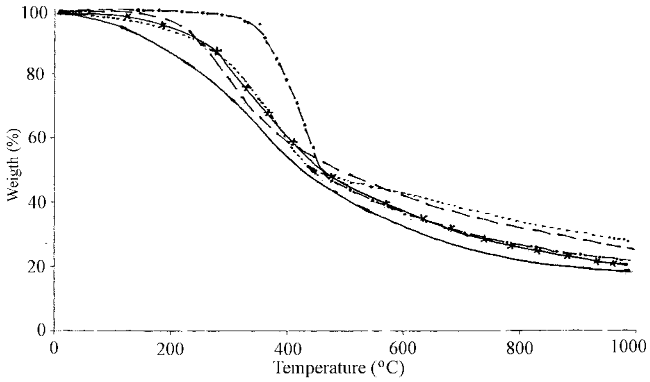

Fig. 4. TGA plots of dried banana stem as such and chemically treated banana stem.
— BS-1, --- BS-H, -·-·- BS-N, ······ BS-Z, –×– BS-K

Mesh type structure hinders the gross shrinkage due to presence of transverse interconnecting channel type structure. Therefore outer portion results in fluffy carbon and inner portion gives compacted carbon mass.

3.2. Pyrolysis behaviour of dried banana stem

3.2.1. TGA studies on dried banana stem

Pyrolysis behaviour of dried banana stem as such as well as after chemical treatment was studied using thermogravimetric analysis. Fig. 4 shows TGA plots of these samples in nitrogen. All samples show four domains of weight loss in almost similar temperature ranges but differing in peak temperatures. The first weight loss occurs around 150°C due to desorption and evolution of water molecules. It is more pronounced in as such dried stem and is less in samples treated with chemicals. This shows that chemical treatment of banana stem further dehydrates it. It is known that chemicals affect the lateral bonding much more than the longitudinal bonding in cellulosic structure, making the material more porous in transverse direction [8]. Next steep weight loss is observed between 250-350°C. This, as proposed by Tang & Becon [9], is due to splitting of cellulosic structure and chain scission and breaking of some carboxyl, carbonyl bonds etc. in the ring structure evolving water, CO & CO_2. The chemical treatment affects the weight loss in this temperature range too. Since the common feature of chemical activating agents is their ability to act as dehydrating agents which influence the pyrolytic decomposition of cellulosic materials and prevents the formation of non-carbonaceous degradation products like tars below 500°C, the carbon yield in chemically treated samples will be high. This is what is observed in the TGA graphs. Further, samples treated with acids exhibit weight loss in narrow temperature range as compared to those treated with alkali. This may be due to the preferential reaction of the chemicals with hydroxyl groups during chemical treatment. Whereas 50-80% of the precursor may be volatalized by pyrolysis below 500°C, further heating to 900°C results in only additional 4-10% volatilization. Weight

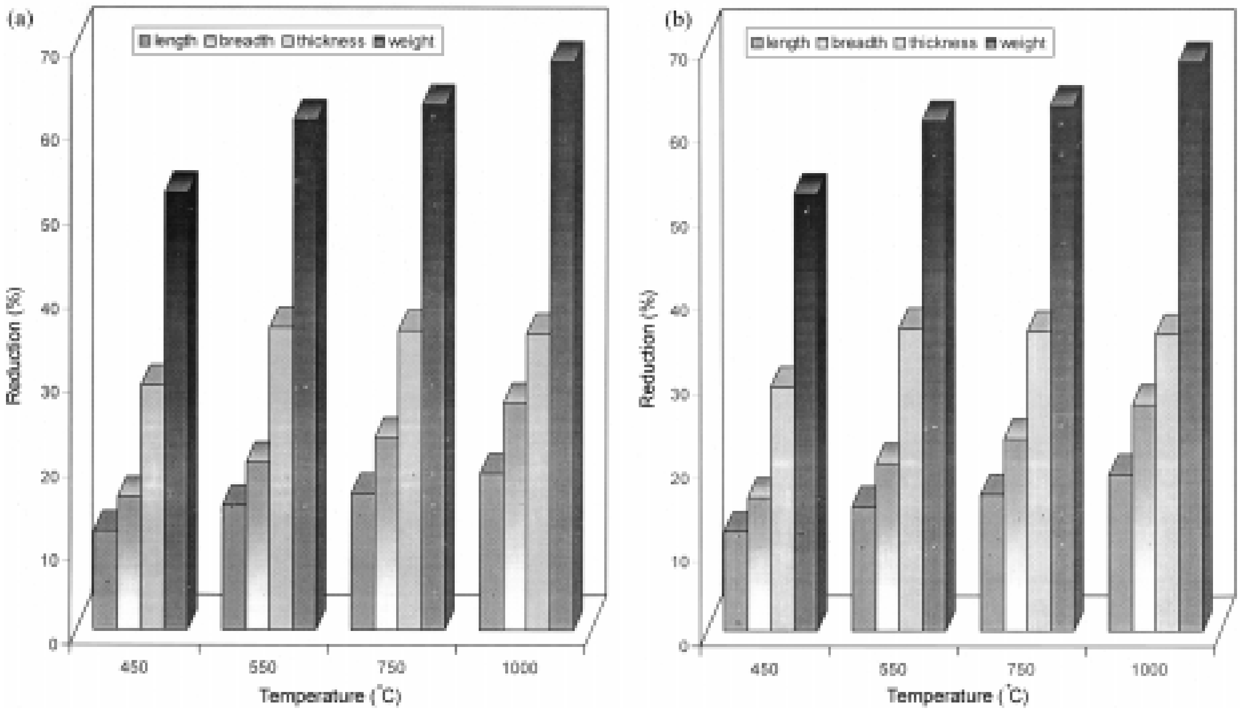

Fig. 5. (a) Dimensional changes in outer hard part of banana stem during pyrolysis, (b) Dimensional changes in outer soft part of banana stem during pyrolysis.

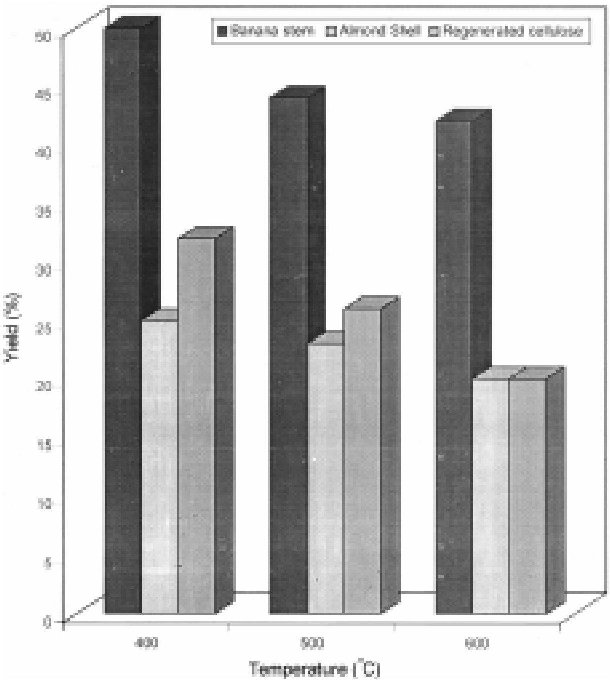

Fig. 6. Yield of different chars prepared at different HTT from different cellulosic materials.

loss in the higher temperature region (500-900°C) is due to polycondensation, molecular rearrangement and formation of carbon structure [8-10].

3.2.2. Physical changes during pyrolysis

Samples of dried banana stem were pyrolysed to different temperatures under flowing nitrogen. The changes occuring in dimensions and mass were measured and are plotted in Fig. 5. The anisotropic character of pyrolysis is seen in Figs. 5a and b. During pyrolysis also, inner hard part exhibited higher longitudinal shrinkage (Fig. 5a) as compared to outer mesh type soft structure (Fig. 5b) However, both the parts maintained their morphology during pyrolysis. The char yield of banana stem was compared with those obtained from other conventional cellulosic materials such as almond shell and coconut shell. These are compared in Fig. 6. As seen from this fig., char yield from banana stem is substantially higher as compared to that from other sources.

Further, the effect of chemical treatment on the yield had been studied. It has been found that banana stem treated with any particular chemical (acid or base) and then pyrolysed to a particular temperature exhibited higher yield than obtained from the stem as such pyrolysed to the same temperature followed by chemical treatment. This shows that by chemical treatment of banana stem the chemistry of pyrolysis gets changed. Due to dehydration, different macromolecular networks are formed which result in promotion of cross linking of structure and suppression of tar formation during pyrolysis.

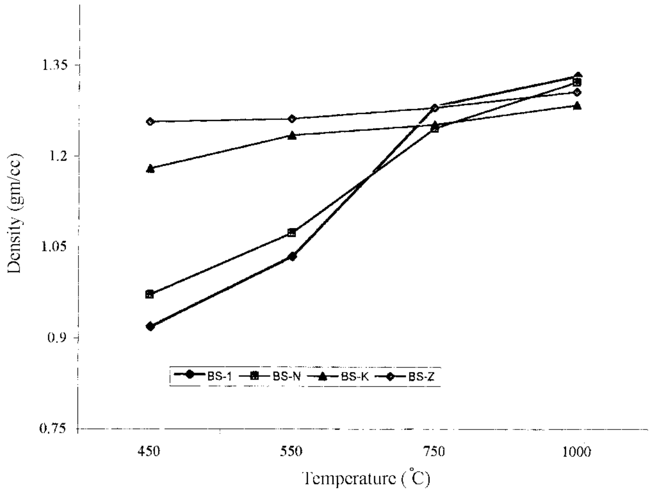

Fig. 7. Density of chars after heat treatment at different temperature.

3.3. Characterization of pyrolysed banana stems

3.3.1. Density of Chars

Fig. 7 shows density of chars at different heat treatment temperatures of banana stems as such as well as chemically treated ones. The density of all chars is found to increase with heat treatment temperature due to attainment of perfection of carbon structure. At lower heat treatment temperature (450°C), the density of chars from as such stem is much lower than of those obtained from chemically treated ones. This may be partly due to the increased carbon yield as result of chemical treatment and partly due to retention of residues of the incorporated salts and chemicals within the porous structure. However, at higher heat treatment temperature, the trend reverses. The density of chars from chemically treated stems is lower than that of from pure stem. Chemical compounds act in two ways. These dehydrate the precursor at lower temperature and suppress tar formation. At the same time, these get intercalated in the structure. In heating to temperature above 600°C, these intercalated species might result in exfoliation and fluffiness of the chars resulting in decreased bulk density. This shows that chemicals, though supposed to act as stabilizers resulting in high char yield, affect the development of carbon structure during pyrolysis resulting in more porous structure with lower density. The density of chars of acid or salts treated stems is found to be higher than that of alkali treated samples.

3.3.2. SEM studies

The SEM micrographs of banana stem char made at 1000°C from different portion of banana stem are shown in Fig. 8. A general view of the pyrolysed samples (Figs. 8a and 8b) show that the longitudinal fibrous structure of inner part and segmented mesh type structure of the outer part of banana stem is maintained during pyrolysis of banana stem.

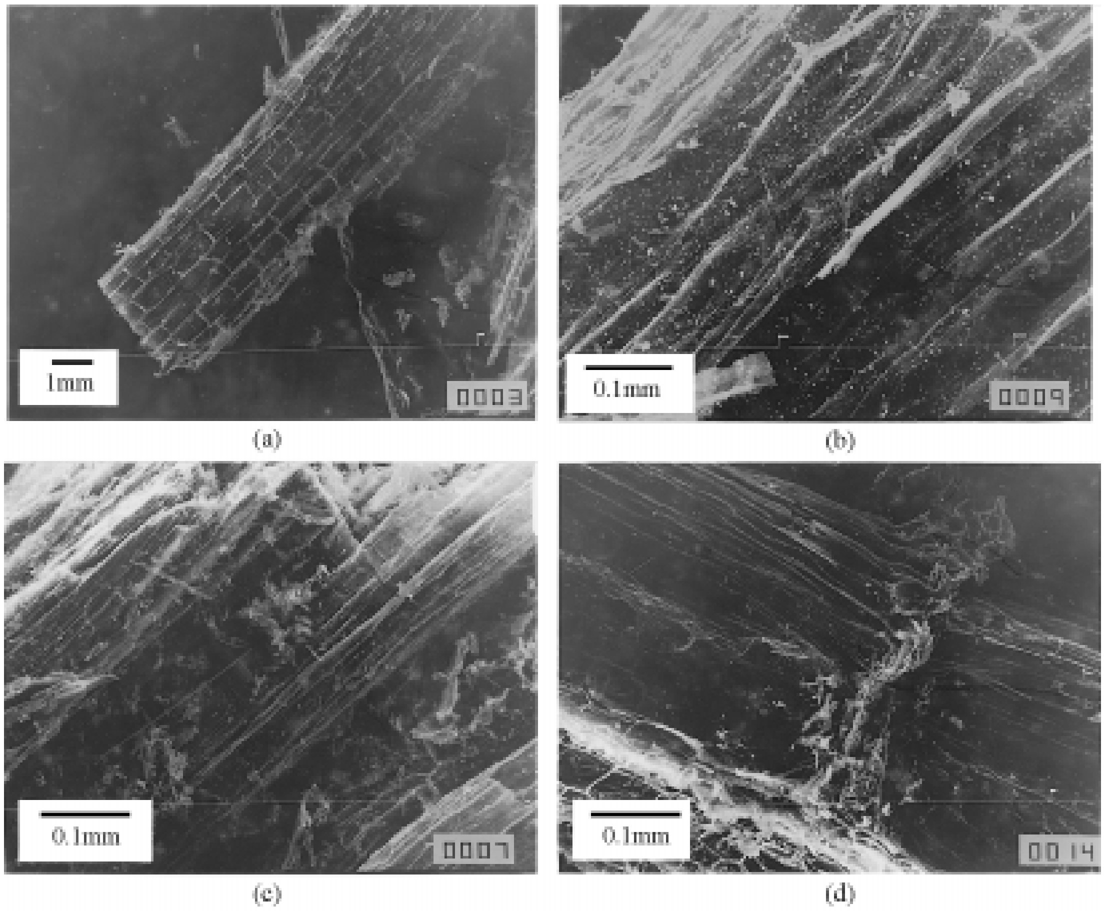

Fig. 8. SEM micrographs of banana stem based porous carbons (a) and (c) outer part, (b) inner part, (d) pyrolysed chemically treated stem.

On examination at higher magnification (Fig. 8c), it is found that the material within a segment from outer part also posses fibrous structure, similar to the one from inner portion. On treatment of the stem with chemicals, the long fibrous structure is seemed to have been destroyed (Fig. 8d). Latter material is more fluffy while the char from banana stem as such is more compact and dense.

3.3.3. Ash content

In comparison to commercially used woods for activated carbons, the banana stem chars have been found to contain much higher ash. The ash content in the samples pyrolysed at 450°C is found to be in the range of 38%. This may be due to the retention capacity of porous structure of stem which acts as carrier of minerals from earth to the stem. In the chars obtained at 1000°C, the ash content is in the range of 20-28%, being lower in chemically treated samples. It further supports that the chemicals are reacting with the structure during pyrolysis. Silica makes about 75-80% of the total ash content.

3.3.4. BET surface area

BET surface area of all carbon samples (chars and activated carbon) prepared at different heat treatment temperatures and activated with different agents were measured by N_2 adsorption at liquid nitrogen temperature. Surface area of these carbons are shown in Table 1. As seen from the table, the surface area increases and average pore diameter decreases with heat treatment temperature. The chars obtained up to 550°C heat treatment temperature mainly contain macropores. On raising the heat treatment temperature either the walls of macropores collapse or unpyrolysed blocked pores get opened up creating micro porosity. In general, substantial micropore volume is developed around 550°C. The micropore volume may approach minimum around 900°C as has also been observed for general cellulosic materials, coals and polymers [11].

Surface area of chemically treated chars (1000°C) is also given in Table 1. As seen from the table most of the chemicals do not have any significant effect on the ultimate surface area and pores of the chars. As stated above, inorganic materials act as catalyst for dehydration at lower temperature but on heat treatment to higher temperature when the pores are getting reorganized, inorganic materials may fill or block

Table 1. Surface area of char prepared at different HTT

Types of carbon	Heat treatment temp. (°C)	BET surface area (m^2/gm)	Miropore area (m^2/gm)	Micropore vol. (cm^2/gm)	Avg. pore diameter (Å)
BS-1	450	2.9477			446.7583
	550	27.1186	16.6429	0.010514	94.6488
	750	73.7096	24.7267	0.012178	20.3296
	1000	227.7116	123.2735	0.056280	17.8785

some portion of the macropores. Nitric acid treatment show positive effect. The surface area of the char is found to get enhanced to almost double on treatment with nitric acid. This is because nitric acid does not leave behind any inorganic materials. Though nitric acid treatment shows significant improvement in micropore area and micropore volume as well, the average pore diameter is found to remain the same.

3.3.5. Adsorption studies on heat treated chars

Porous carbons are effective adsorbents for many special applications [12, 13]. The physio-chemical nature of the carbon is an important factor in adsorption process. Measurement of BET surface area by nitrogen adsorption showed that the banana stem chars mainly contain macropores and mesopores at lower temperature while micropores are formed at higher heat treatment temperature. In order to further analyse these pores liquid adsorption studies were performed on selected samples.

– Methylene Blue Adsorption : The decolorizing property of the chars was studied using methylene blue adsorption. The adsorption isotherms of as such banana stem chars are given in Fig. 9a. The adsorption isotherm belong to type VI. Adsorption takes place in steps due to the presence of pores of different sizes viz micro, meso and macropores. Maximum adsorption takes place for samples heat treated to temperature between 750°C and 1000°C. This correspond to appropriate pore diameter in chars prepared at that temperature. Fig. 9b shows methylene blue adsorption by chemically treated samples. In contrast to as such banana stem char, chemically treated samples (except treated with $ZnCl_2$) show a steady state adsorption. The adsorption capacity of chemically treated samples is higher than that of as such banana stem chars.

– Heavy Oil Adsorption by Banana Stem Chars : As stated above, banana stem chars contain predominantly macropores and mesopores at lower heat treatment temperatures. This was evident from methylene blue adsorption. The studies

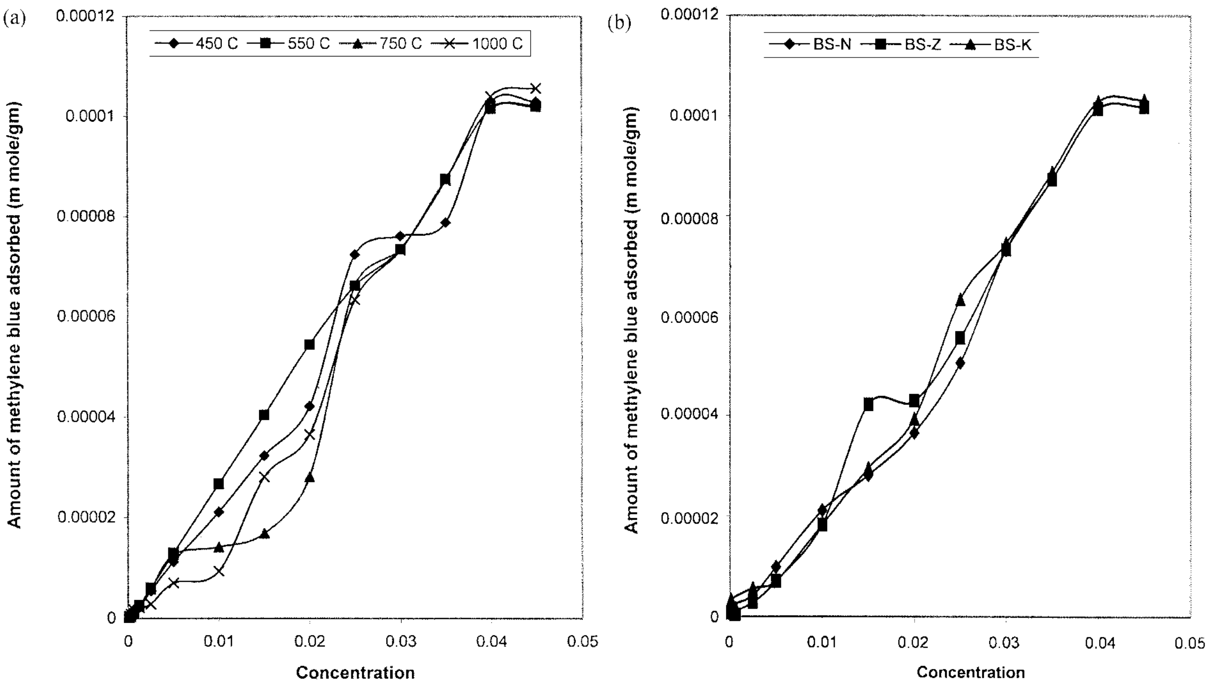

Fig. 9. (a) Methylene blue adsorption isotherms of chars prepared at various temperatures, (b) Methylene blue adsorption isotherms of chemically treated carbons prepared at 1000°C.

Table 2. Surface area of the chemical treated carbon

Sample	BET surface area (m^2/gm)	Micropore area (m^2/gm)	Micropore vol. (cm^2/gm)	Avg. pore diameter (Å)
BS-N	342.0935	212.3466	0.097198	18.9517
BS-Z	184.2440	123.7141	0.056587	18.9324
BS-K	140.8426	71.0056	0.032272	17.9137

were extended to adsorption of heavy oil (Rotary Vacuum Pump oil) mixed with water. Fig. 10 shows adsorption of heavy oils by as such stem chars prepared at different heat treatment temperatures. The oil adsorption is maximum for chars prepared at lower temperatures. This is because the chars prepared at lower temperature consist of macropores good enough to adsorb bigger molecules of oils. The adsorption capacity of chemically treated chars is compiled in Table 2. As seen from the table, the heavy oil adsorption capacity increases in chars treated with phosphoric acid but is lower in other chemically treated chars. These results show that the size of pores of carbon is very important for the specific adsorption in addition to the chemical nature of surface. The porosity on the carbon of appropriate dimension has to be generated for the adsorption to take place with respect to the size of adsorbate.

The active carbons prepared by pyrolysis or chemical treatment from an organic source have pores of all different sizes, micropores, mesopores and macropores. The proportion of a particular porosity generated in the active carbon depends on the preparation conditions, nature and chemical composition of the precursor. The conversion of cellulosic material to solid carbon yields porous carbon based on the original anatomy of solid mass of the precursor. The comparison of the surface area of untreated carbon and chemically treated carbon shows that as the heat treatment temperature is raised, more and more microporosity is generated and number of macropores become small. The activation treatment given either by heat treatment or by chemicals results in the formation of surface oxygen complexes. This also results in the increase in the aromaticity of carbon surface due to crosslinking and polymerization of organic molecules, removal of volatiles and opening of blocked pores as the heat treatment temperature is raised. During the process of activation the spaces between the elementary crystallites become cleared of various carbonaceous compounds and nonorganized carbon. Carbon is also removed partially from the graphitic layers of elementary crystallites. The resulting voids are termed pores. Large pores or macropores open up directly on the external surface of the particles, mesopores branch off the macropores and micropores branch off the mesopores. Macropores enable the molecule of adsorbate to pass rapidly to smaller pores situated deeper within. The adsorption in the macropores is insignificant for small adsorbate molecules while micropores have large internal surface area and contribute significantly to the adsorption. Since the

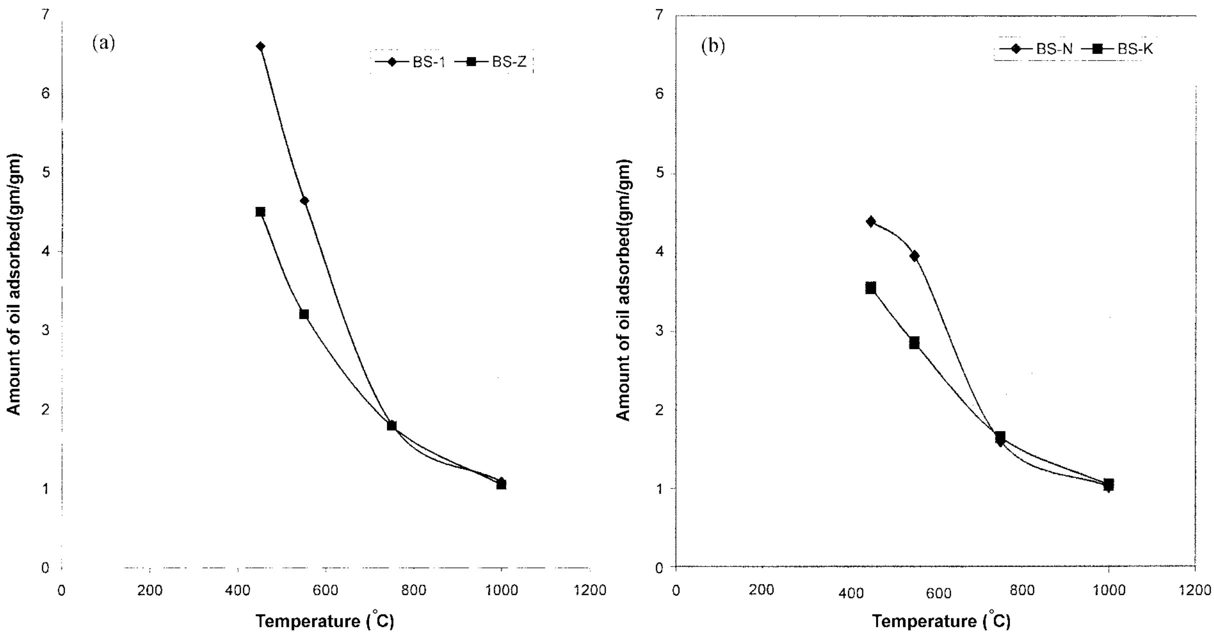

Fig. 10. (a) Amount of oil adsorbed by BS-1 & BS-Z prepared at different HTT. (b) Amount of oil adsorbed by BS-N & BS-K prepared at different HTT.

average micropore area increases due to heat treatment or chemical treatment, the adsorption capacity of carbon also increases. The increase in the adsorption capacity is more in the nitric acid treated carbon. It may be due to its capacity to generate more microporosity. On the other hand heavy oil is composed of large molecular units. These studies show that the presence of macropores on carbon contribute to the adsorption of heavy oil. The macroporous carbon ir-respective of heat treatment or chemical treatment adsorbed oil. However, as the macroporosity of carbon decreased with high heat treatment, the extent of adsorption of heavy oil gets lowered.

4. Conclusion

The surface properties as well as adsorption capacity of carbon prepared either by heat treatment as such or by chemical treatment followed by heat treatment depend on the morphology of the precursor. Banana stems, on carbonization, give higher yield as compared to other active carbon precursors. Pyrolysis of banana stem due to its fibrous structure results in porous carbons consisting of predominantly meso and macro-pores at low temperature pyrolysis (600-700^{o}C). Chemical treated banana stems yield better porous carbons. These studies reveal that banana stem is a potential material for making activated carbon of desired porosity and pore structure for liquid adsorption specially of large molecules.

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