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ACTIVATED CARBON FROM WASTE BIOMASS OF PSYLLIUM HUSK: EFFECT OF STEAM ACTIVATION ON SURFACE CHARACTERISTICS

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ABSTRACT

Psyllium Husk, commonly known as Sat-Isabgol is a biomass of medicinal value from Plantago ovate plant. Clean Psyllium husk is produced through winnowing process. Khakha powder is generated as a waste material from winnowing process. It is a cellulosic mass and hence can be used as carbon precursor. Khakha powder was pyrolyzed and subjected to steam activation. The carbonization and steam activation were done in N_2 atmosphere at 800 ^{0}C with different steam flow rate from 0.2 to 0.5 ml/min. The maximum BET surface area was obtained at a steam flow rate 0.3 ml/min. The SEM micrographs showed that with increase in steam flow rate, volume of pores increase and pores were uniformly distributed. It was found that the single step carbonization-activation process produced high surface area and good surface properties than that of two step carbonization and activation process.

Key words*: activated carbon, carbonization, steam activation, surface area, khakha Powder*

INTRODUCTION

Every country worldwide has a large amount of low commercial value, humid (~50% water content) agro forestry residues. Most of these do not find economic utilisation and market. To obtain energy through combustion of these waste materials without pollution is difficult and expensive. However, since these are carbonaceous materials are good source of carbons and activated carbons. With development of several new, efficient, low pollution technologies, the techno-economical viable concept to produce activated carbon from these precursors can be explored. The application of activated carbon mainly depends on the size and distribution of pores.

Activated carbon, a widely used adsorbent, is mainly composed of carbonaceous material with high surface area and porous structure [1]. Raw materials for its production are chosen depending on their price, purity, potential extent of activation and stability of supply [2]. For adsorption from gas phase mainly microporous carbon is used whereas, mesoporous carbon is advantageous for liquid phase application. Numerous studies have been devoted to preparation of low-cost high quality carbon adsorbents for treatment and purification of water, air as well as various chemical and natural products [1, 3]. The raw materials being used are usually carbonaceous materials like wood [4], coal [5], nut shells [6], husks [7] and most agricultural by-products materials [1, 3, 8]. In the present study, Khakha powder, a bio waste obtained through winnowing of Psyllium Husks was used which was derived from the seeds of plant called '*Plantago ovata*'. In India it is known as Sat-ISABGOL and in international market it is known as Ispaghula. The upper layer is called Psyllium Husks. It is cleaned by winnowing system. Psyllium Husk or Sat Isabgol has medicinal value while the powder obtained through winnowing is a waste biomass. Since this is a carbonaceous material, results in porous carbon on pyrolysis under inert atmosphere. Activation of cellulosic derived carbon is carried out to enhance the diameter and volume of the clogged pores which are created during carbonization process and to create some new porosity and readily assessable pore structure and very large internal surface area. The nature of precursor and method of activation, both have strong influence on the pore structure and adsorption capacity of resulting activated carbon.

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Apart from the raw materials, the characteristics of activated carbon largely depend on the activation method employed. The physical activation by the action of steam results in the development of porous structure and the extensive internal surface area [3]. Steam is preferred for activation because the water molecule has smaller dimensions than carbon dioxide molecule, and consequently the use of steam leads to:

- Faster diffusion into the porous network;
- Easier access into the micropores;
- A faster reaction rate, i.e. approximately three times faster than carbon-carbon dioxide reaction at a temperature of 800^{0}C and a pressure of 10 kPa [9].

In the present work, studies were performed on pyrolysis of Khakha powder, a waste biomass from winnowing of Psyllium Husk, and activation of the resulting carbon mass. Activation has been carried out in two ways, i.e. single step, carbonization at 800°C followed by steam activation and in two steps, i.e. carbonized samples were stem activated at 800°C.

MATERIALS AND METHODS

The activated carbons were prepared by using the commercially available Khakha powder. The powder was dried and pyrolyzed. Activated carbons were prepared by using two different routes. In first method, the weighed amount of raw materials was carbonised at 800°C in a furnace in nitrogen atmosphere for one hour. The char obtained was activated with steam at 800°C with varying flow rate of steam, i.e. 0.3, 0.5 and 1.0 ml/min. In second method, the weighed amount of raw materials was carbonised at 800°C in nitrogen atmosphere. After one hour hold time, the steam was passed with varying flow rates, i.e. 0.3, 0.5 and 1.0 ml/min. This way both carbonization and activation were performed in single step. The activation was carried out with steam. The flow rate of steam was controlled.

Characterization

The activated carbon prepared were characterized for moisture contents of Khakha powder, ash content, carbon content, silica content etc using chemical methods and surface area of the activated carbon using nitrogen adsorption isotherms.

Moisture Content

The green samples were accurately weighed and kept in oven at 100^0C for 24 hour. The % moisture content was calculated using following formula:

$$\text{Moisture content (\%)} = \frac{\text{Weight loss (gm)}}{\text{Original Weight of green sample (gm)}} \times 100$$

Carbon Content and Volatile Content

Known amount of samples were taken in silica crucible. The crucibles containing the samples were kept in furnace for carbonization up to 850^0C in N_2 atmosphere. The % carbon content and % volatile content were calculated using following formula:

$$\text{Carbon content (\%)} = \frac{\text{Weight after carbonization (gm)}}{\text{Weight before carbonization (gm)}} \times 100$$

$$\text{Volatile content (\%)} = 100 - \text{Carbon content (\%)}$$

Ash Content and Silica Content

The weighed amount of carbon sample was heated in the furnace at 800^0C in air to oxidise the carbon to carbon dioxide, leaving behind inorganic content as ash in the sample.

$$\text{Ash content \%} = \frac{\text{Weight after oxidation of carbon sample (gm)}}{\text{Weight before oxidation of carbon sample (gm)}} \times 100$$

$$\text{Silica Content \%} = \frac{\text{Weight after HF treatment of carbon sample (gm)}}{\text{Weight before HF treatment of carbon sample (gm)}} \times 100$$

The ash residue obtained after oxidation was dissolved in HF (Hydrofluoric acid) for overnight to find out the silica content.

Surface Characteristics

The surface characteristics i.e., surface area, pore size, pore size distribution were determined by BET, Micromeritics Gemini-2375 Instruments. The samples were cleaned at 100^0C in presence of Ar gas for 1 hour and at 250^0C for 12 hours. The N_2 adsorption was studied al liquid nitrogen temperature (-196^0C). The surface morphology was studied by using HITACHI S - 3000N Scanning Electron Microscope.

The % micro pores were determined with the help of BET apparatus results and calculated using following formula:

$$\text{\% Micro pore} = \frac{\text{Micro pore area}}{\text{BET surface area}} \times 100$$

RESULTS AND DISCUSSION

The moisture content in Khakha powder was found to be in the range of 8 - 10 %.

On pyrolysis of Khakha powder (CKP) a wt loss of 65% was observed. The volatile content, carbon content, ash content and silica content in Khakha powder is shown in Fig. 1. The ash content in CKP was 15%, yielding about 12 % carbon content. The result showed that the total inorganic material in CKP is about 23%.

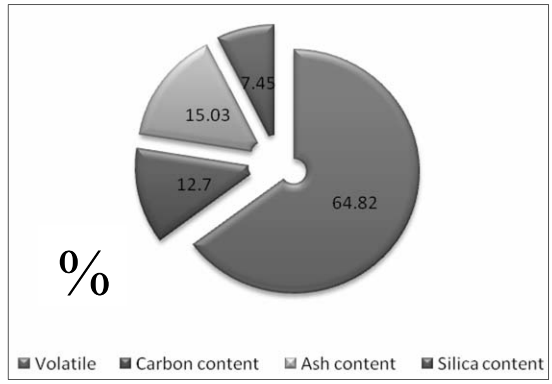


Fig. 1 Constituents of Khakha powder in %

The carbonized CKP was activated with steam at 800°C at varying flow rate of steam. The percentage carbon yield in two step steam activation process (i.e. activation followed by carbonization) at different flow rate of steam is shown in Fig. 2.

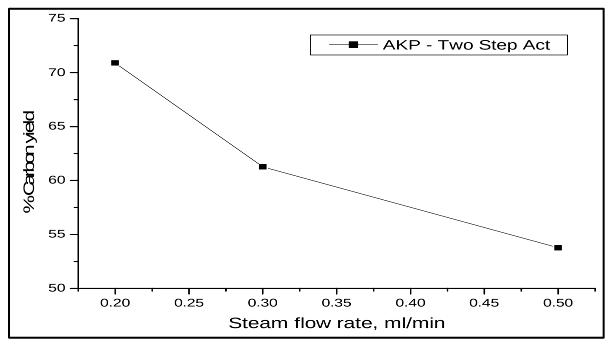


Fig. 2 % carbon yield after steam activation at different steam flow rate of Khakha powder

On activation, some carbon atoms get oxidised to carbon dioxide and get removed leaving behind highly porous structure. When activation is carried out with steam at high flow rate, bunt off is higher and carbon percentage obtained get reduced. The activation process can also be accelerated by impurities present in the char as such, resulting in a more macroporous carbon. Therefore, as the steam flow rate increases at high temperature, the carbon yield decreases. The surface characteristics of activated carbon were studies by BET method. The nitrogen adsorption isotherms are given in Fig 3.

Though, samples are invariably microporous, these adsorption isotherms shows very interesting results. Fig. 3 shows that as the steam flow rate is increased from 0.1 to 0.3ml/min, the volume of nitrogen adsorbed is increased and shape of isotherm changes to type I with characteristic H4 hysteresis loop. This is an indication of the start of the development of mesopores in the sample. The adsorption in the macropores is insignificant while the micropores have large internal surface area and contribute significantly to adsorption. Since average micropore area increases due to activation process, adsorption capacity of carbon also gets increased.

On further increase in flow rate from 0.3 to 0.5ml/min, the oxidation is fast and also diffusion, it appears that inorganic

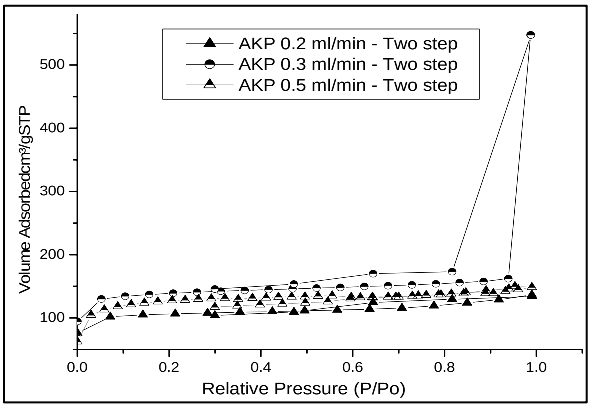


Fig. 3 Nitrogen adsorption isotherm of Activated Khakha powder, (at -196^{0}C)

impurities present act as catalyst and at higher steam flow rate the pores are created and destroyed owing to coalescence and transition of larger pores into small new pores.

Fig. 4 shows the variation in surface area and micropore area with steam flow rate using single step activation of AKP (activated Khakha powder), the BET surface area i.e. 537.03 m^2/g was almost similar than that of two step activation.

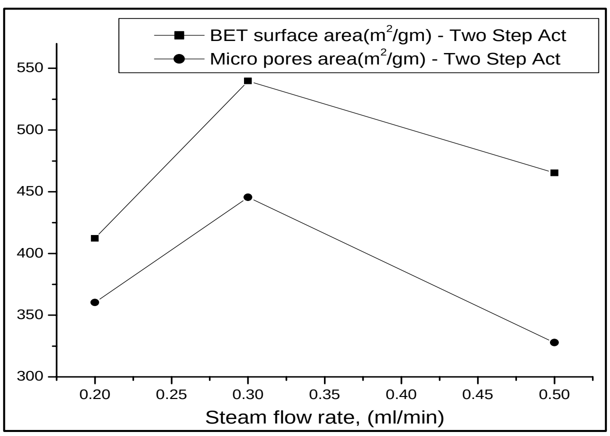


Fig. 4 Effect of steam flow rate on BET surface area

The BET surface area and percentage micropore decreases with increase in steam flow rate after 0.3 ml/min as shown in the Fig. 3 and Fig. 4 respectively. This shows that the steam flow rate has direct effect on surface area and micropore area.

Table 1: change in average pore diameter with different steam rate for AKP

Act step, Khakha Powder	Steam flow rate, ml/min	Ave. Pore diameter, by BET, nm
Two step	0.2	2.01
Two step	0.3	6.45
Two step	0.5	1.97

The Table 1 shows that average pore diameter lies in the range of 1.9 to 6.4 nm at different steam rate. It clearly shows that with increasing the steam rate i.e. 0.2 to 0.5 ml/min, some of the micropores get converted to mesopores. Because the amount of inorganic matter present in khakha powder is higher this increases the kinetic reactivity of steam. But as the steam rate increases from 0.3 to 0.5 ml/min, more meso pores get converted into micropore because at higher steam rate the pores are created and destroyed owing to coalescence and transition of larger pores in to small new pores.

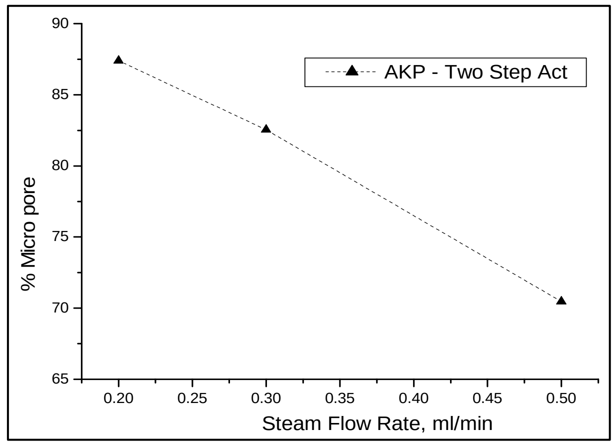


Fig. 5 Effect of steam flow rate on % micropore.

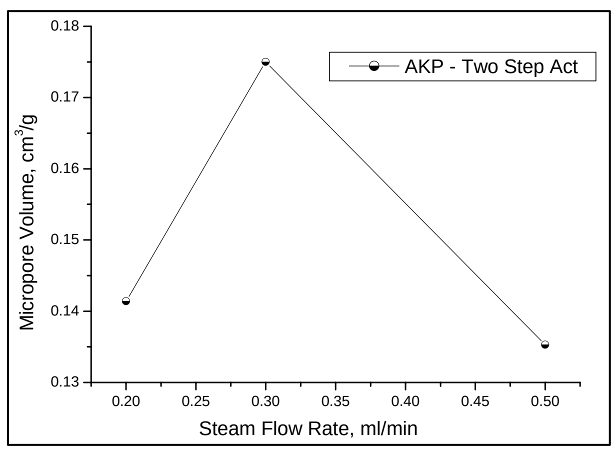
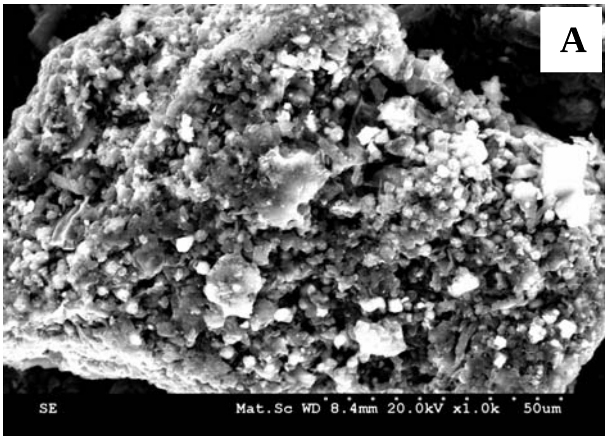


Fig. 6 Effect of steam flow rate on percentage micropore volume

Fig. 5 and 6 show that as the steam rate increases in activation process, the overall percentage micropores decreases and the micropore volume increases. These results indicate that widening of micropores start on activation and these get converted into mesopores. In other words the microporosity is very sensitive to the change in steam activation rate. From Fig. 4, 5 and 6 it is concluded that the steam flow rate during activation process play an important role in controlling the BET surface area, percentage micropore and micropore volume of activated carbons.

Fig. 7 shows the SEM micrograph of AKP. As seen from the Fig., the activation process removes the disorganized carbon, exposing the aromatic sheets to activation agents and leads to development of microporous structure.



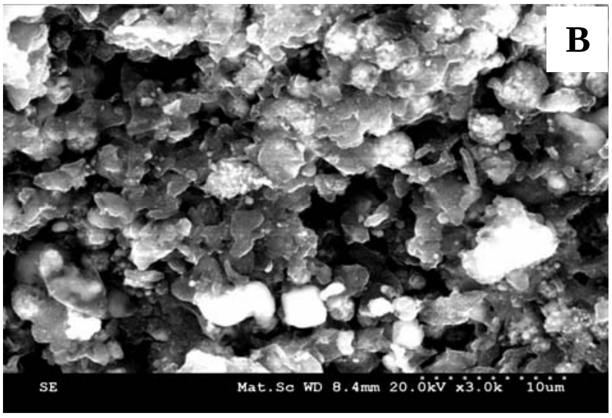


Fig. 7 SEM image of carbonized and steam activated Khakha powder at (A) 50 µm and (B) 10 µm

With increase in steam flow rate, volume of pores increases and pores are finely distributed on the surface of activated carbon. The cell structures in both the samples are found to be quite different. There is presence of solid mass within the pores and this solid mass reacts with steam during activation process and acts centre for creation of pores with them. These also contribute to the mesoporosity generation in the samples during activation process.

In the early stage of activation, less than 10 % burn-off take place. The disordered carbon is removed and the aromatic sheet gets exposed and creates a reaction with the activation agent, leading to the development of microporous structure. The blocked pores formed during the carbonization step are opened in this stage. For the next stage, the reaction widens the existing pores or formation of the large size pores by the complete burnout of the walls between the adjacent pores, leading to the transition of the microporosity to mesoporosity or macroporosity and hence the lowering in the micropore volume and surface area. Although the precise mechanism of the activation process is not fully understood, the major mechanism involved may be viewed as the gasification reaction between carbon atoms contained in the carbonized product and the activating agent. Each carbon atom in the char has different reactivity depending on their arrangement and position. The carbon atom located at the edge and boundary of aromatic sheet or at defect positions and dislocations or discontinuities will have higher reactivity.

CONCLUSION

In present studies it is seen that the activation burn off depends on steam flow rate at same temperature. The activation burn off occurred due to oxidation of carbon by steam. This reaction takes place on the outer surface as well as in the micro-meso surface. The reaction on the surface generated new pores and the reaction inside results in the widening of the size of the pore.

Thus by optimizing the activation conditions such as temperature, flow rate of steam and type of reaction, sample with controlled surface area and pore size can be produced. In case of AKP, the maximum BET surface area was found about 539.77 m^2/g with activation burn off about 38.73 % for two step activation.

Finally it is concluded that for the production of activated carbon from Psyllium Husks derived waste biomass i.e. Khakha powder, the one step activation process is cost affective, less time consuming and mainly energy saving process. It also increases surface properties as compared to multi step activation.

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