Synthesis and characterization of activated carbon produced from kenaf core fiber using H₃PO₄ activation

M.S. Shamsuddin, N.R.N. Yusoff, M.A. Sulaiman

Faculty of Earth Science, University Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia

Abstract

Kenaf core fiber (KF) which is an agricultural biomass was used to produce low-cost activated carbon using acidic chemical activating agent. The aim of this study is to find out the changes occurring in kenaf core fiber during activation with phosphoric acid (H₃PO₄). The surface area of the formed phosphoric acid treated kenaf core fiber activated carbon (KFAC) was determined by physical adsorption of N₂ gas. Brunauer, Emmett and Teller (BET) surface area, and micropore volume values were 299.02 m²/g and 0.12 cm³/g, respectively. Fourier transform infrared (FT-IR) spectroscopy analysis identified the presence of carbonyls, alkenes and hydroxyls. Field Emission Scanning Electron Microscope (FESEM) image showed gradual formation of pores due to elimination of volatiles and contaminants. Powder X-ray diffraction (XRD) analysis indicated the appearance of broad diffraction background revealed predominantly amorphous structure. The proximate and ultimate analysis showed high percentage of carbon and low percentage of ash which is an indication of a good material for production of porous carbon.

Keywords: Kenaf core fiber; activated carbon; chemical activation; phosphoric acid

1. Introduction

Activated carbons (AC) are made from materials rich in carbon through carbonization and an activation process. A porous structure and its adsorption properties can be obtained in carbonaceous materials via either chemical or physical activation. Physical activation involves pyrolysis of the source material at 800°C-1000°C to produce charcoal. This is then followed by activation using steam, carbon dioxide (CO₂) or oxygen (O₂).

* Corresponding author. Tel.: +609 947 7000; Ext: 3941; fax: +609 - 947 7012.
E-mail address: nraihan@umk.edu.my
Chemical activation involves the impregnation of the precursor material with a chemical activating agent followed by activation at temperatures of 400°C-700°C under nitrogen atmosphere. Zinc chloride (ZnCl₂), potassium hydroxide (KOH) and phosphoric acid (H₃PO₄) are widely used as chemical activating agents. The activating chemical agents influence the pyrolytic decomposition and inhibiting formation of tar and volatile matter, thus enhancing the yield of AC. The dehydration and oxidation characteristics of chemical activation agent require much lower activation temperature compare to physical activation. A comparative study of chemical (H₃PO₄) and physical activation using biomass fiber as AC has been reported. The research found that the surface area recorded by physical activation was slightly higher than chemical activation but lower in term of yield production. The carbonization of biomass at high temperature would trigger the emission of higher greenhouse gaseous (GHG) such as carbon monoxide (CO) and methane (CH₄) which is an unfriendly approach.

There has been remarkable interest in the production of AC due to its adsorptive, environmental, thermal, electrical and mechanical characteristics. It is proof from previous study that AC is one of the leading industrial materials due to its well developed pore structure and adsorption properties. Recent developments in modern technologies have resulted in various novel applications of AC. Coal-based AC is the most common adsorbent used, however, it is costly and not sustainable. Abundant low cost agriculture biomass, which contain high amounts of natural polymers such as cellulose, hemicellulose, and lignin, are suitable alternative materials to produce low-cost and green adsorbents with necessary modification to enhance its efficiency. Various studies on the production of AC have been done by applying different agricultural biomass including rice husk, grape seed, rambutan peel, kenaf fiber, maize cob and date pit.

Kenaf (Hibiscus cannabinus, L) is herbaceous annual plant that belongs to the family of Malvaceae. Kenaf possess two kind of fibers that may be explored to produce AC. The long fiber contain approximately 30% of the total volume of the plant whereas the short fiber represents the remaining of 70%. The stem of kenaf plants consists of the outer bark (bast) and inner core, both contain fibrous components. Recent studies have demonstrated the capability of kenaf core and bast fibres to enhance bioremediation and adsorption process. There were earlier studies have been made to produce ACs from the inner cores of kenaf where the first study utilized KOH and CO₂ through physicochemical activation, whereas the other study utilized potassium oxalate (K₂C₂O₄) under different impregnation ratios. Both studies have significantly increased the evolution porosity in the carbon matrix. Hence, the objectives of the present study were to synthesis the AC from kenaf core fiber using H₃PO₄ as activating agent and conducted the characterization of elemental analysis, surface area, surface chemistry and morphological properties.

2. Experimental methodology

2.1. Raw materials

The raw kenaf core fiber (KF) sample was obtained from Lembaga Kenaf dan Tembakau Negara. Phosphoric acid (H₃PO₄) (~85% acid) and Sodium Hydroxide (NaOH) were obtained from Merck (M) Sdn, Bhd, Malaysia. All chemicals used in the investigation were of analytical grade.

2.2. Sample preparation

Preliminary washing of the raw materials with hot distilled water were conducted and dried in an oven at 105°C for 24 h to remove all moisture. The dried samples were cut into small pieces, sieved to the size of 500-600 μm and stored in air-tight containers to prevent moisture build up and fungi infections. Chemical activation was carried out by initially carbonizing the precursor in muffle furnace under inert atmosphere from room temperature to carbonization temperature of 400°C for 1 hour under a closed system. The resulting char was labelled as KFC. The KFC was subsequently impregnated with 30% ortho-phosphoric acid (H₃PO₄) with impregnation ratios of 1:4 (w/w) for 24 h of soaking duration. Next, the sample was filtered using a vacuum pump and dehydrated overnight in an oven at 105°C. The dried sample was then pyrolysed for activation at temperatures of 500°C. After the activation
period of 1 hour the sample was allowed to cool down to the room temperature. The resultant activated carbon was labelled as KFAC. KFAC then washed with 1.0 M NaOH and successively rinsed with hot distilled water followed by cold distilled water until the filtrate reached a stable pH of 6 - 7. The samples were then dried in an oven at 110°C for 24 h. The produced ACs were further crushed and sieved to get the particles size of 200-300 µm and were kept in an airtight container prior to analysis.

2.3. Physical and chemical characterization

2.3.1 Proximate and ultimate analysis

Proximate analysis to determine the moisture content, volatile matters, fixed carbon, and ash residues of the precursor (KF) was carried out using Thermogravimetric Analyzer (Perkin Elmer TGA7, US). Approximately 30 mg activated carbon were placed in a platinum crucible on the pan of a microbalance and then heated between 22°C and 900°C at a heating rate of 10°C/min, with constantly weighed. Ultimate analysis was done using the Elemental Analyzer (Perkin Elmer, Series II 2400) to evaluate the percentage of carbon, hydrogen, and oxygen value was determined by difference.24

2.3.2 Fesem analysis

Morphological study of raw KF, KFC and KFAC was done using a Zeiss Supra 35VP Field Emission Scanning Electron Microscope. The samples were mounted onto a FESEM holder with double-sided electrically conducting carbon-adhesive tabs to prevent the surface of the specimens when exposed to the electron beam. The samples were then coated with a 20 nm thick layer of gold using a Polaron Equipment Limited model E500, set at a voltage of 1.2 kV (10 mA) and a vacuum 20 Pa for 10 min.

2.3.3 Powder X-ray diffraction study

X-ray diffraction analysis (XRD) was performed on KFAC in order to determine the crystallinity or amorphous nature. The analysis was performed by Brukers D2 Phaser X-ray diffractometer using Cu-Ka (λ=0.15406 Å) radiation source operating under a voltage of 40 kV and a current of 25 mA. The diffraction angle (2θ) was varied from 10° to 90°. The X-ray diffraction patterns were collected with a scan rate of 4.2°C/min.

2.3.4 FTIR spectrum study

The surface chemistry of the samples were analysed by identifying the surface functional groups of the samples using Fourier transform infrared spectroscope (FTIR-2000, Perkin Elmer). The spectra were recorded from 4000 to 500 cm⁻¹ resolution in the mid-infrared region.

2.3.5 Surface area analysis

Nitrogen adsorption at 77 K (liquid nitrogen) was conducted using a Micromeritics ASAP 2020 V3.04H (Micromeritics®) instrument to obtain the adsorption isotherm of the sample. The Brunauer-Emmett Teller (BET) method was used to calculate specific surface area of the activated carbon from the isotherms. All samples were degassed at 350°C for 6 h prior analysis.
3. Results and discussion

3.1. Raw material characterization

The proximate analysis involves the determination of moisture content, volatile matter, fixed carbon and ash content of the raw KF. The results of the proximate and ultimate analyses values are shown in Table 1. In view of the data of proximate analysis, KF shows low moisture content (5.6%), high percentage of volatile matter (77.3%), average content of fixed carbon (11.0%) and low ash content (6.9%). High volatile matter content usually reduces the solid yield in the carbonization stage while a low inorganic content is vital due to their abilities to produce a low ash and high fixed carbon content. Ultimate analysis showed that raw KF has 50.5% of carbon and 8.47% of oxygen. Experimental conditions of the carbonization and activation steps are not the only major contribution towards porous structure of AC but also being influenced by the original nature and structure of the starting material. High phenolic content in lignin compound of biomass make it important in AC preparation as it leading to higher carbon yields than those obtained from the two other main macromolecular compounds of biomass: cellulose and hemicellulose.

Table 1. Proximate and ultimate analysis values of raw KF.

<table>
<thead>
<tr>
<th>Proximate analysis (%)</th>
<th>Ultimate analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon</td>
<td>C</td>
</tr>
<tr>
<td>Moisture content</td>
<td>H</td>
</tr>
<tr>
<td>Ash content</td>
<td>N</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>O</td>
</tr>
</tbody>
</table>

3.2. Surface morphology

FESEM micrographs of raw KF, KFC and KFAC produced are depicted in Fig. 1(a), 1(b) and 1(c) respectively. The surface of raw KF as shown in Fig. 1(a) was curly form, highly packed, porousless, and having no cavities. An early work has been conducted on various concentration of H₃PO₄ activation using frond waste of Saudi Arabian date trees (R-PDF). The finding found that the surface of R-PDF was curly form resulted from the presence of cellulose, hemicelluloses and lignin in the raw material without any cracks. However, the surface of KFC as shown in Fig. 1(b) became rough and some irregular pores started to form due to removal of volatile matter after carbonization at 400°C. Some anonymous fragments with small pores at early stage of formation were observed as well on the surface of KFC, which might indicate the residues of tarry substances formed during the carbonization stage. This was agreed by previous study where the surface porosity of the char products were increased after carbonization process, resulting in large surface area with small voids on the surface. Furthermore, these voids formation assisted on the decomposition of volatile matter from biomass. Activation at 500°C with H₃PO₄ resulted in the creation of more pores and a substantial removal of volatiles matter. This has been approved by the well-developed pores which clearly observed on the surface of the KFAC as shown in Fig. 1 (c). Pore development in the KFC during pyrolysis was also important as this would enhance the surface area and pore volume of the KFAC by promoting the diffusion of H₃PO₄ molecule into the pores and thereby increasing the H₃PO₄–carbon reaction via acid hydrolysis processes which would then create more pores. The glycosidic linkage in hemicellulose and cellulose will be hydrolyzed by H₃PO₄ along with the cleavage of aryl bond in lignin.
3.3. Phase analysis

Fig. 2 illustrates the X-ray diffraction (XRD) pattern of the KFAC. Appearance of broad diffraction background and the absence of a sharp peak reveals a predominantly amorphous structure\(^{33}\). There are two broad diffraction background corresponding to \(2\theta = 25^\circ\) and \(2\theta = 43^\circ\) in the spectrum. The crystallinity recorded by KFAC is 8.5\% with 91.5\% amorphous. This value recorded was closed to previous study which used different lignocellulosic raw materials\(^{34}\). The study applied oil palm empty fruit brunch (EFBAC), bamboo stem (BSAC) and coconut shell (CSAC) as activated carbon and their XRD analyses revealed all the synthesized AC in the form of amorphous state with low crystallinity. Table 2 showed the crystallinity and amorphous percentage in the KFAC with comparing with AC derived from other lignocellulosic raw materials.

![X-ray diffraction of the KFAC.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallinity %</th>
<th>Amorphous %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>KFAC</td>
<td>8.50</td>
<td>91.50</td>
<td>Recent study</td>
</tr>
<tr>
<td>CSAC</td>
<td>8.19</td>
<td>91.81</td>
<td>(^{34})</td>
</tr>
<tr>
<td>EFBAC</td>
<td>1.68</td>
<td>98.32</td>
<td>(^{34})</td>
</tr>
<tr>
<td>BSAC</td>
<td>13.25</td>
<td>86.75</td>
<td>(^{34})</td>
</tr>
</tbody>
</table>

Table 2. Crystallinity and amorphous percentage of KFAC and other AC derived from lignocellulosic raw material
3.4. Fourier transform infrared analysis

The FT-IR spectra of raw KF and KFAC are depicted in Fig. 3. The raw KF and KFAC all displayed bands at 3350-3200 cm\(^{-1}\) representing stretching vibration of O-H in hydroxyl groups. The present of this group in raw and AC was reported in the previous literature\(^1,35\). The raw KF characteristic band at 2907 cm\(^{-1}\) assigned to C-H stretching indicate the methyl and methylene groups\(^2\) and band at 1737 cm\(^{-1}\) correspond to the C=O stretching of the acetyl group in hemicellulose\(^35\). In addition, bands at 1595 cm\(^{-1}\) and 1423 cm\(^{-1}\) of raw KF are indicative of aromatic compounds (C-C) stretching in the aromatic ring. Bands at 1325 cm\(^{-1}\) and 1235 cm\(^{-1}\) attributed to N-O and C-O stretching vibration respectively. Other important absorption bands at 1036 cm\(^{-1}\) represent C-O stretching\(^36\) and 1235 cm\(^{-1}\) associated to the C-O stretching of the aryl group in lignin\(^35\). It can be suggested from the spectrum that the main oxygen groups present in the raw KF are carbonyl, ethers and alcohols group which are normally present in plant cellulose\(^37\). The spectra of the KFAC are different from that of the raw material where many bands disappeared during the AC preparation including the carbonization and the activation. The band intensities were found to be dependent on the activation temperature. Elimination of peaks at 2907 cm\(^{-1}\), 1737 cm\(^{-1}\), 1423 cm\(^{-1}\) and 1325 cm\(^{-1}\) indicates decomposition of functional groups present in oxygenated hydrocarbons, reflecting the carbohydrate structure of cellulose and hemicellulose\(^38,39\). The reduction of intensity of band 1235 cm\(^{-1}\) in raw KF to 1218 cm\(^{-1}\) in KFAC was believed to be due to the alteration of lignin structure containing the ester and ether linkage after the chemical treatment\(^40\). The band at 1737 cm\(^{-1}\) which correspond to C=O stretch in aldehydes, saturated aliphatic which present only in raw KF is due to thermal instability of aldehyde and ketone groups at high temperature\(^41\). However, introduction of peaks at 766 cm\(^{-1}\) shows formation bending vibration from \(-\text{C} (\text{triple bond}), \text{C-H from alkynes which corresponds to C–O–C stretching (ester, ether and phenol) and out-of-plane bending in benzene derivatives.}"

![Fig. 3. FT-IR spectra of raw (KF) and activated (KFAC) kenaf core fiber.](image-url)
3.5. Surface area and porosity study

Surface area analysis by BET showed that the carbon synthesized after activation with H₃PO₄ (KFAC) had better surface properties in terms of surface area and micropore area compared to the carbonized sample (KFC). An early research has been done on the efficiency of H₃PO₄ as an activating agent in producing activated carbon with surface area up to 1720 m²/g with impregnation ratio as its significant influence. It is clearly shown that the dehydration process by chemical activating agent increases the surface area and porosity. This could be a good indication of the H₃PO₄ impregnation as a catalyst of porosity development. It is supported by previous study that pore structure was started to be organized on the surface after H₃PO₄ activation of precursor due to the release of tars from cross-linked framework. Table 3 showed the surface properties values of KFC and KFAC. It demonstrated that KFAC provided better properties of carbon with BET surface area (299.02 m²/g), micropore area (229.20 m²/g) and micropore volume (0.12 cm³/g). KFC recorded lower surface properties with BET surface area (13.68 m²/g), micropore area (7.16 m²/g) and micropore volume (0.004 cm³/g).

<table>
<thead>
<tr>
<th>Table 3. Surface properties of KFC and KFAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical properties</td>
</tr>
<tr>
<td>Surface area cm²/g</td>
</tr>
<tr>
<td>Micropore area m²/g</td>
</tr>
<tr>
<td>Micropore volume cm³/g</td>
</tr>
</tbody>
</table>

4. Conclusion

This study discussed the preparation of activated carbon using H₃PO₄ as an activating agent. Pore structure and surface chemistry of the raw KF are altered after being carbonized and activated with dehydration agent. Clear FESEM image on the changes of surface morphology from raw KF to KFAC indicate the increase of surface area and pore development after carbonization and activation. The FTIR spectroscopy showed presence of significantly different peak frequencies of functional groups before and after activation. The XRD results confirmed that KFAC showed less crystallinity with broadness peak due to amorphous nature. BET surface area and porosity increase from after carbonization and activation.

References


16. Cuerda-correa EM, Maca A, Ortiz AL. Author’s personal copy Textural and morphological study of activated carbon fibers prepared from kenaf Author’ s personal copy. 2008;111:523-529.


