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SYNTHESIS AND CHARACTERIZATION OF POROUS CARBON FROM BIOMASS USING KOH AND K₂CO₃ CHEMICAL ACTIVATION

Abdurrahman Garba[1], Hatijah Basri[1], Noor Shawal Nasri[2] and Razali Isma'il[3]

[1]Department of Science, Faculty of Science, Technology and Human Development, University Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia

[2]UTM-PMRC Institute of Oil and Gas, Energy Research Alliance, Research University, Universiti Teknologi Malaysia, Skudai, Johor Bahru, Malaysia

[3]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Skudai, Johor Bahru, Malaysia

E-Mail: agarba2008@yahoo.com

ABSTRACT

Synthesis of activated carbon (AC) from agricultural waste is a research area that has gained high interest recently because of its double-faced potential in dealing with disposal challenges and also in converting such waste to useful products. Activated carbons were prepared from oil palm shell by chemical activation using both KOH and K_2CO_3 as chemical activants. The precursor was first carbonized at a temperature of 800°C under a nitrogen flow of 150cm^3/min for 2 hours at 10°C/min.It was then impregnated with KOH or K_2CO_3 in the ratio 1:2. The mixture of both KOH or K_2CO_3 impregnated material were then loaded at different times into the reactor for subsequent heating. It was then pre-heated to a temperature of 800°C for 1 hour in the presence of nitrogen gas. The carbonized sample was then activated by heat treatment under the CO_2 flow of 150cm^3/min at 800°C for 1hr. Nitrogen adsorption analysis from BET surface area and pore volume were studied. The BET surface area and pore volume of the potassium hydroxide treated (PHAC) and potassium carbonate treated (PCAC) carbons were (305 m^2/g and 0.16 cm^3/g) and (708 m^2/g and 0.31 cm^3/g), respectively. The proximate analysis shows a high percentage of fixed carbon and low ash content which is an indication of good precursor for AC production. The FTIR spectra of both carbons showed hydroxyls, alkenes, alkynes, carbonyls and aromatics functional groups. The SEM micrographs showed that both carbons developed pores that are good enough for adsorption of contaminants. However, the results indicate that choice of chemical activant and other activation parameters enable tailoring the porosity of the carbons for a particular environment application.

Keywords: activated carbon, chemical activation, oil palm shell, potassium hydroxide (KOH), potassium carbonate (K_2CO_3).

INTRODUCTION

Water being of paramount importance to humans for both domestic and industrial use needs preservation from the point and non-point sources of contamination. The quality of our water resources is declining daily due to indiscriminate disposal of pollutants into the water bodies through industrialization, environmental changes, civilization and agriculture (Ali *et al.*, 2012). The agricultural industry had been known for its contribution towards rapid economic development and growth. Also, it has contributed to environmental pollution due to the production of abundant fractions of agricultural waste into the environment that poses disposal challenge (Evbuomwan *et al.*, 2013). Malaysia is the leading palm oil exporter in the world with over 5 million hectares of cultivated land and an average production capacity of 19.69 tonnes/ hectare (Garba *et al.*, 2015). However, Chong *et al*. (2013), asserts that over 6.89 million tonnes of oil palm shell as waste is produced per annum in Malaysia and the figure is on the inrease (Chong *et al.*, 2013). Other fractions that pose such challenges include oil palm fronds, empty fruit bunches and palm pressed fibres all from the oil palm industry. Conversion of this waste products to useful materials like activated carbon (AC) could solve their disposal problems and prevent them from ending up in the landfills. Recently, AC has

been prepared from several other biomass among which include corn cob, rice husk, coconut shell, cotton stalk, fish bone, palm oil shell etc. (Ebrahimi *et al*., 2013; Rafatullah *et al.*, 2012; Hesas *et al.*, 2013). AC is one of the porous and versatile adsorbent material commonly used in industries. The characteristics that made AC a suitable adsorbent for some applications is its high surface area and favourable pore size distribution that translate into a surface with high capacity for contaminants adsorption. It is applied for separation and purification of gases, catalyst support and adsorption of contaminants from solutions (Deng *et al*., 2010). Activated carbon as an amorphous form of carbon is a specially treated material that possess a highly developed internal pores with a large surface area. It is reasonably cheap and was used as an excellent adsorbent for the removal of a broad range of organic and inorganic contaminants. Recently, about 275 000 tons of AC are consumed per annum worldwide (Deng *et al*., 2010; Alslaibi *et al*., 2013). Commercially, the most commonly used precursors for AC preparation were coal and some other agricultural by-products. Due to its high demand, high cost of production and non-renewable nature of commercial AC, this made scientist to search for alternative materials that are cheap, renewable and sustainable. There are two standard methods to produce AC namely; physical and chemical activation. In

physical activation, the process consist of two steps: the carbonaceous material is first pyrolyzed at high temperature and in an inert environment to remove most of its hydrogen and oxygen contents followed by activation at high temperature and in the presence of oxidizing gases like steam or carbon dioxide. On the other hand, chemical activation process involves the impregnation of the precursor material with a dehydrating agent which influences the pyrolytic decomposition of the precursor, followed by conventional heat treatment. At the pyrolysis stage, tars are formed combined with the chemical activant in the cavities of the AC that can be removed by washing the AC to generate the porosity of the AC (Arami-Niya *et al.*, 2010; Cecen and Aktas, 2012). The most frequently used chemicals employed as activating agents include H_3PO_4, $ZnCl_2$, NaOH, KOH and K_2CO_3 among others (Ali *et al.*, 2012; Jibril *et al.*, 2013). Alkali hydroxides such as KOH are expensive, corrosive and hazardous which create disposal problems. However, K_2CO_3 is not dangerous as it is often added to foods as an additive.

The primary aim of this study was focused on comparison for production of sustainable high surface area and porous activated carbon (AC) using two chemical activants (KOH and K_2CO_3) with basic properties tailored towards removal of organic contaminants in aqueous solutions. For the above reason, the AC's were prepared under the same experimental conditions and were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), proximate analysis, ultimate analysis and Nitrogen adsorption analysis.

MATERIALS AND METHODS

Materials

The precursor material was oil palm shell obtained from a local market in Batu Pahat, Malaysia. The oil palm shells were thoroughly washed with distilled water several times and were dried in the oven for 24 hours to remove dust. Then, the shells were ground and separated using sieves and shakers into sizes between 0.6mm - 1.18mm as the starting materials.

Sample preparation

The precursor was first carbonized from ambient temperature to carbonization temperature of 800°C under a nitrogen flow of 150cm³/min for 2 hours at 10°C/min. Then, the carbonized material was impregnated with KOH or K_2CO_3 in the ratio of 1:2 and their slurries were heated at 70°C for two hours. The mixture of KOH or K_2CO_3 impregnated material were then loaded into the reactor for subsequent heating to activation temperature of 800°C for 1 hour at 10°C/min heating rate in the presence of nitrogen gas. The material was then activated by heat treatment under the CO_2 flow of 150cm³/min at 800°C for 1hr. After activation, samples were then allowed to cool down to 50°C under nitrogen flow after which they were removed from the furnace. The activated carbon produced were then washed with 0.1 M HCl, hot distilled water and then cold distilled water to remove residual salts and organic matters until the pH of the washings was between 6 to 7 (Deng et al., 2010; Nasri et al., 2014). Finally, the samples were dried at 105°C for 24 hours. The activated carbon (AC) obtained from chemical activation with KOH and K_2CO_3 were levelled PHAC and PCAC respectively.

Characterization

The AC produced was characterized by BET surface area and pore volume analysis using Micromeritics ASAP 2020 for full isotherm analysis determined from the adsorption isotherms of N_2 at -196°C after degassing about 10mg of the samples under vacuum at 350°C and pressure of 10^{-5} Torr for 4 hours. The surface morphology of the samples was identified by scanning electron microscopy (SEM) model JSM-7600F (JEOL Ltd, Japan) for the raw precursor (RPS), KOH treated AC (PHAC) and K_2CO_3 treated AC (PCAC). The FTIR was used to identify the functional groups present in the prepared carbons from the precursor material. FTIR spectra were recorded at 4cm⁻¹ resolution and 16 scans min⁻¹ between 4000 and 400cm⁻¹ by using a Perkin Elmer spectrum-Two model.

RESULTS AND DISCUSSIONS

As shown in Table-1, the precursor material has low ash content (2.38%) which is considered as an advantage for activated carbon synthesis (Nasri et al., 2014). The fixed carbon for both PHAC and PCAC are similar and high when compared with other studies as presented in Table 2 (Daud and Ali, 2004; Guo et al., 2005; Lim et al., 2010). This indicates a good precursor material for activated carbon production (Rafatullah et al., 2012).

Table-1. Proximate analysis of RPS, PHAC and PCAC.

Sample	Moisture (%)	Volatiles (%)	Ash (%)	Fixed carbon (%)
RPS	5.60	68.75	2.38	23.27
PHAC	4.42	5.40	7.50	82.68
PCAC	4.50	6.40	7.50	81.60

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Table-2. Proximate analysis of raw precursor in this study compared with other studies.

Proximate analysis (%)	Lim *et al*., 2010	Daud *et al*., 2004	Guo *et al*., 2005	This study
Moisture	-	7.96	-	5.60
Volatiles	76.7	72.47	77.6	68.75
Ash	2.1	1.10	2.60	2.38
Fixed Carbon	21.2	18.70	19.80	23.27

Scanning electron microscopy

The SEM images of raw oil palm shell (RPS), potassium hydroxide treated activated carbon (PHAC) and potassium carbonate treated activated carbon were presented in (Figure-1a-c). The surface morphology shows a significant difference between the raw material and the other AC's produced. It indicates RPS has no pores due to the presence of volatiles and other contaminants that blocked the pores. However, both AC's showed the development of pores due to the activation process that lead to formation and widening of the existing small pores formed as a result of spaces created by vapourized moisture, hemicellulose, cellulose and lignin contents of the raw precursor. In addition, the pores widened since in KOH and K_2CO_3 activation, the chemical compounds and other related contaminants occupied the cavities formed after pyrolysis process. These salts were blown out of the cavities by washing the product with 0.1M HCl to create micropores within the carbon matrix (Wu *et al*., 2005). It could also be seen from Figure-1, the micrograph of PHAC and PCAC were similar but the PCAC has bigger cavities diameter compared to PHAC. However, this difference suggests that the surface morphology of the AC's prepared from the raw precursor was dependent on the type of activating agent used.
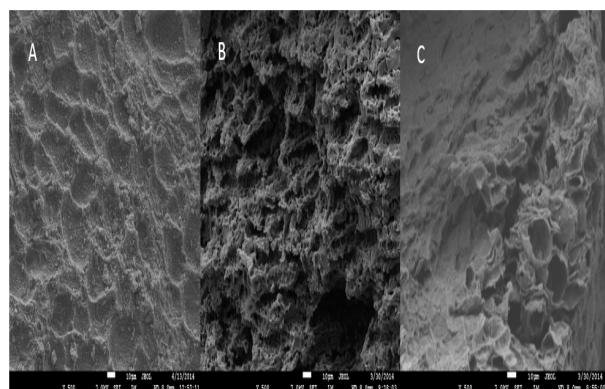
Figure-1. Showing SEM images of (a) RPS, (b) PHAC and (c) PCAC.

Surface area and pore volume

The most important aspect of activated carbon is its adsorption capacity which is directly proportional to its surface area (Nasri *et al.*, 2014). The BET surface area and pore volume of PCAC and PHAC were 707.8 m^2/g and 305.1 m^2/g while the pore volumes were 0.31 cm^3/g and 0.16 cm^3/g, respectively. The results showed that PCAC has a higher surface area as well as pore volume, so it is expected to have more adsorptive capacity than PHAC. In addition, PHAC may have higher adsorption capacity depending on the size of the contaminant to be adsorbed, that is a small sized contaminant prefer adsorbent with smaller pore volume. The results of N_2 adsorption using both activants compare well with those obtained by Adinata et al. (Adinata *et al*., 2007). They reported surface area and pore volume of 1170 m^2/g and 0.57 cm^3/g from palm oil shell precursor. They showed that specific surface area increases from 600-800°C, decreases above 800°C and the maximum surface area was obtained around 800°C. Therefore, it was deduced that both KOH and K_2CO_3 were good activants below 800°C. Therefore, as carbonization temperature increases, the C–KOH/K_2CO_3 reaction rate also increases which leads to increased carbon burn-off (Nasri et al., 2014). The higher the burn-off, the more the knee becomes rounded due to continuous widening of the pore size distribution as shown in type I linear isotherm plot from Figure 2 and 3. Also, the linear branch of the isotherms becomes no longer parallel to the pressure axis in both cases and a loop which indicate a region of the gradual development of mesopores appears (Rafatullah *et al.*, 2012).
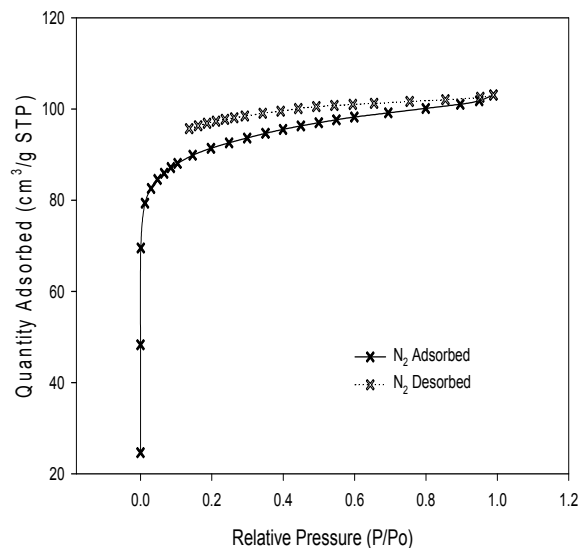
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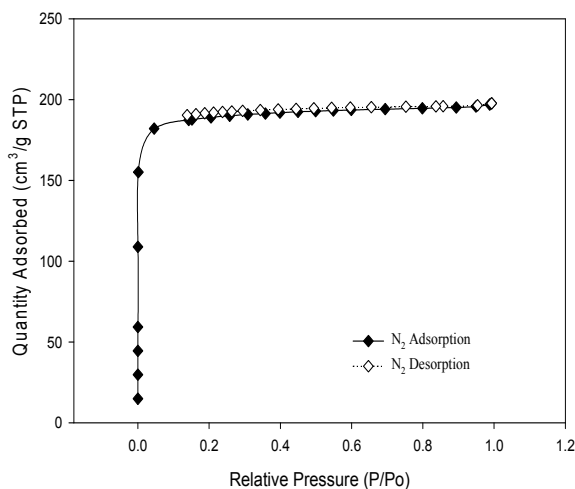**Figure-2.** Linear plot for N_2 adsorption and desorption of PCAC.

Figure-3. Linear plot for N_2 adsorption and desorption of PHAC.

Fourier Transform Infrared Spectroscopy

The spectra of RPS in Figure-4, indicates bands at 3330, 1594, 1033, 875 and 621 cm^{-1} which shows the presence of OH stretching vibration in OH functional groups, C=C stretching in aromatic rings, C–O stretching vibration in ethers, C–O–C stretching vibration (ester, ether and phenol) and out-of-plane bending vibration in benzene derivatives respectively (Guo & Lua, 2003; Koay et al., 2014). The spectra also showed elimination of vibration peaks at 3330, 1594 and 875 cm^{-1} in both PHAC and PCAC which is due to decomposition of functional groups and liberation of volatiles through carbonization process (Foo & Hameed, 2012). However, the introduction of bands at 3882 and 620 in both AC's shows formation of

OH stretching from free alcohols or phenols and bending vibration of carbon (triple bond) or C-H from alkynes
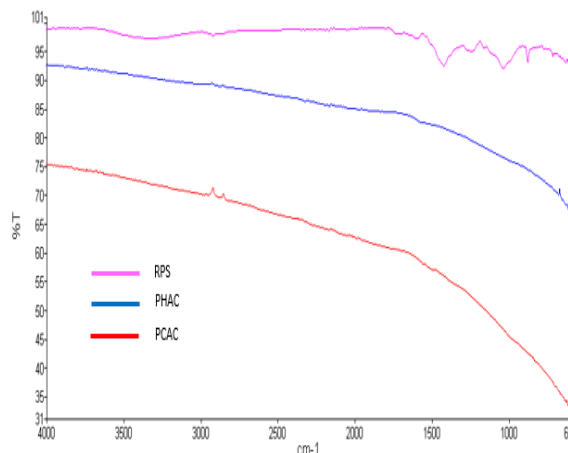

Figure-4. Showing FTIR spectra of RPS, PHAC and PCAC.

CONCLUSIONS

This study discussed the production of green and porous activated carbons using KOH and K_2CO_3 as the activating agents. The activated carbons produced under the same experimental conditions were characterized by the formation of functional groups and cavities on the surfaces due to chemical activation processes as compared to the raw precursor. When KOH was employed as activant, there is the formation of a microporous carbon as noticed from the SEM images and BET analysis. On the other hand, if K_2CO_3 is used, more mesopores are distributed on the surface of the carbon. Summarily, the choice of chemical activant and activation processes allows tailoring the porosity of AC produced for a particular purpose.

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