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Synthesis and Characterization of Green Porous Carbons with Large Surface Area by Two Step Chemical Activation with KOH

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Graphical abstract
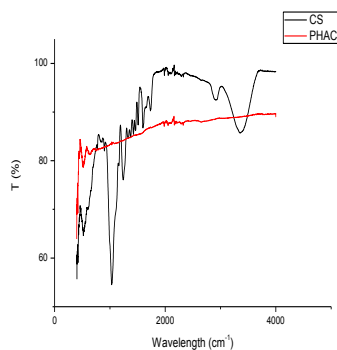
Abstract

Porous carbons were synthesized from coconut shell using chemical activation by potassium hydroxide (KOH). N_2 adsorption isotherm analysis for BET surface area and pore volume of the synthesized porous carbon were carried out. The Langmuir surface area, BET surface area and pore volume are 1646 m^2/g, 1353 m^2/g and 0.6 cm^3/g, respectively. From the FTIR analysis, hydroxyls, alkenes, carbonyls and aromatics functional groups were identified. The proximate and ultimate analysis shows high percentage of carbon and less ash content which indicates a good precursor material for porous carbon. The carbonization temperature and time were also varied to observe their effect on the yield of char, with carbonization at 700^0C for 2 h having highest yield of 32%.

Keywords: Adsorbent; coconut shell; micropores; synthesis; chemical activation; potassium hydroxide

■1.0 INTRODUCTION

Conventionally, coal and agricultural byproducts with lignin and celluloses materials are the major sources for the synthesis of commercial activated carbons [1]. Due to the elevated cost and non-renewable nature of coal as a precursor for commercial activated carbon (AC) and enormous world demand for it, agricultural wastes are potential substitute materials for the synthesis of AC [2-3], because they are abundant, inexpensive, demonstrate good properties such as; low content of inorganic material, as the presence of inorganic materials in the precursor is capable of influencing the adsorption capacities of the resulting adsorbents, while on the other hand, high content of volatiles (usually above 50%) helps to create basic pore structure during carbonization [4].

The production of AC is achievable by either physical or chemical activation. These two processes involves two stages namely; carbonization and activation. In each stage, heat treatment is required; although the temperature range for physical activation is higher due to the absence of chemical impregnation. However, effectiveness of activated carbon is dependent on modification of its properties to enhance its affinity towards specific contaminant [5-6]. The surface functional groups are derived from the precursor, heat treatment, chemical treatment and methods of activation [7].

Hence, this work is aimed at the synthesis of high surface area and porous granular activated carbon from coconut shell using KOH chemical activation for properties tailored towards organic contaminants removal from water.

■2.0 EXPERIMENTAL

2.1 Materials

Coconut shells employed in this study were acquired from a vendor in Skudai, Johor, Malaysia. The shells were cleaned properly in deionized water, and further dried in an oven at 105ºC

for 24h. Then, they were crushed and separated using sieves and shakers to the size range of 1.18–2.36 mm.

2.2 Sample Preparation Methods

Chemical activation was done by initially carbonizing the precursor under a flow of nitrogen (150 cm^3/min) from ambient temperature to carbonization temperature of 700°C, 2 h (10°C/min) heating rate. Then, the carbonized sample was impregnated with KOH and the mixture was mixed properly before loaded into the reactor and subsequently heated to a temperature of 800°C in the presence of Nitrogen gas at the rate of 10°C /min and 100 cm^3/min flow rate. Then, activated by heat treatment under a CO_2 flow of 150 cm^3/min at 800°C (at 10°C/min) for two hours. After activation, the samples were allowed to cool down to 50°C under N_2 flow after which they were removed from the furnace. The activated carbon were then washed with deionized water and dried in the oven at 105°C for 24 hours [7]. All samples were stored in the desiccators [5]. Each sample was stored in sealed flasks and labeled.

2.3 Characterization

Pore structural analysis was characterized with Micromeritics ASAP 2020 for full isotherm analysis. Scanning electron microscopy (SEM) analysis with Karl Zeiss (EVO50 XVPSEM, Germany) was carried out for precursor (CS) and potassium hydroxide activated carbon (PHAC) to study the development of porosity and surface morphology cum elemental composition. The surface organic structures of the raw material and AC were chemically and structurally studied by Fourier Transform Infra-red Spectroscopy (FT-IR) spectra recorded at 4 cm^{-1} of resolution and 16 scans min^{-1} between 4000 and 370 cm^{-1} using a Perkin Elmer Spectrum one series model instrumental Analysis with the KBr disc method.

■3.0 RESULTS AND DISCUSSION

3.1 Proximate Analysis

The proximate analysis of the raw material and samples used in this study are presented in Table 1, where the activated sample (PHAC) had the highest percentage of fixed carbon (70%) due to the removal of volatiles as indicated by higher percentage of volatiles in the precursor (71%).

3.2 Effect of Pyrolysis conditions on Carbon Yield

The activated carbon yield was defined as the final weight of product after activation, washing, and drying. Carbonization conditions have effect on the yield as presented in Table 2, with 2 hours carbonization at 700°C having the highest yield (32%). The percent yield was determined from the relation; Yield (%) = W_f / W_i * 100%, where, W_f and W_i are the final activated carbon dry weight (g) and the precursor dry weight (g), respectively.

3.2 Scanning Electron Micrograph

The SEM analysis of the raw coconut shell (CS) and potassium hydroxide activated carbon (PHAC) are presented in (Figure 1a-b). The surface morphology varies significantly with CS showing no pore formation due to the presence of volatiles and other contaminants on the surface. However, PHAC shows pore widening as a result of the activation process, leading to more

developed pore structures, formed as a result of the space created by the volatilization of the moisture, hemicellulose, cellulose and lignin content of the raw coconut shell.

3.3 Surface Area and Pore Volume

The most important property of the activated carbon is its adsorptive capacity, which in general is proportional to the surface area [8]. The BET surface area and pore volume are 1345m^2/g and 0.6cm^3/g respectively which compares well with the result achieved by Daud *et al.,* [9], where BET surface area of 183m^2/g was reported from coconut shell precursor. The higher the burn-off, the more rounded the ''knee'' becomes due to the continuous widening of the pore size distribution as shown in the type I isotherm as presented in (Figure 2). In addition, the linear branch of the isotherms becomes no longer parallel to the pressure axis and a hysteresis loop appears; the changes observed in this region of the isotherm indicate a gradual development of mesopores.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrum analysis allows the identification of different functional groups on the surface of the samples (CS and PHAC) as presented in (Figure 3). The intensity of the spectra varies slightly from the precursor to the activated carbon. The spectrum shows the presence of some typical bands of lignocellulosic materials of coconut shell belonging to functional groups such as hydroxyl, alkenes, aromatics and carbonyls [4]. The wide band at 3438cm^{-1} to 3387cm^{-1} is ascribable to (O–H) vibrations in the hydroxyl groups. However, this peak is more pronounced in the activated carbon (PHAC) which suggests the presence of more phenolic groups after activation with CO_2. The bands between 1700cm^{-1} and 1580cm^{-1} could be assigned to alkenes conjugation moves (C=C) which are characteristics of cellulose and hemicelluloses [11] with the precursor (CS) having the highest intensity probably due to the carbonization temperature of 700°C. Some features of carbonyl group (C=O) is also observed at around 1700cm^{-1} for the precursor (CS) but absent in the activated sample (PHAC) which may be attributed to the carbonization and activation process. The band at 1170 and 1164cm^{-1} can be as a result of C-O stretching vibrations in tertiary, secondary and primary alcohol, this is more evident in the case of the precursor (CS) [12-13].

3.5 Elemental Analysis

The precursor has low ash content, as presented in Table 3, which can be considered as an advantage for the production of activated carbons. Also, the fixed carbon composition (23.38%) from the proximate analysis when compared with other studies can be said to be quite high as presented in Table 3 with 18.7, 18.6 and 21.6% [8, 9-10]. The same trend was observed from the ultimate analysis with the carbon content of the precursor (CS) from this study having 48.66% which equally compares well with 48.63 and 53.4% [9-10]. The high composition of carbon in the coconut shell as presented from the elemental analysis indicates a good precursor material for porous carbon [14].

Table 1 Proximate analysis showing percentage composition of the samples raw (CS), carbonized (A27) and activated (PHAC) coconut shell

| Sample	Moisture / %	Volatiles / %	Ash /%	Fixed carbon / %
CS	5.62	71.37	1.11	23.38
A27	3.52	66.48	1.80	28.22
PHAC	4.50	15.48	10.00	70.02

Table 2 Effect of carbonization temperature and time on yield

| Sample Code	Carbonization Time / hr	Carbonization Temp. / ^{0}C	Yield / %
A26	2	600	29.00
A27	2	700	32.00
A46	4	600	29.24
A47	4	700	29.24

Table 3 Proximate and ultimate analysis showing percentage decomposition of coconut shell in this study compared with other studies

Proximate / %	Daud and Ali, 2004	Yang *et al*., 2010	Cazetta *et al*., 2011	This Study
Moisture	8.21	10.5	3.52	5.62
Volatiles	73.09	70.06	74.60	71.37
Ash	0.1	0.66	1.28	1.11
Fixed carbon	18.6	18.75	20.60	23.38

Ultimate / %	Daud and Ali, 2004	Demiral *et al*, 2011	This Study
Carbon	48.63	53.4	48.66
Hydrogen	6.51	7.5	6.34
Nitrogen	0.14	1.7	1.52
Sulphur	0.08	0.0	0.038
Oxygen	44.64	37.4	43.43
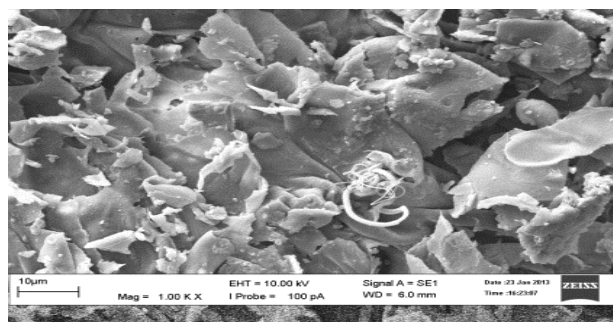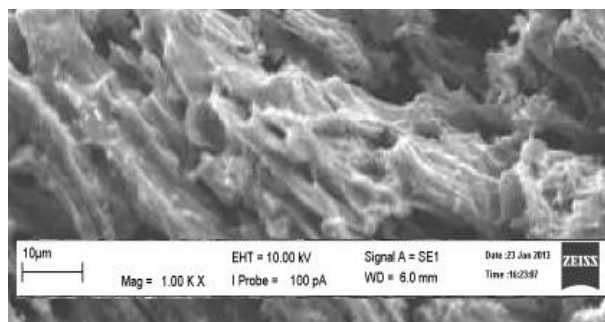
(a)   (b)

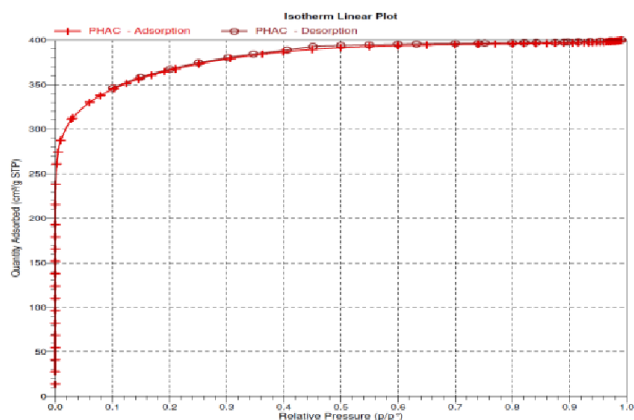**Figure 1** SEM images of (a) CS and (b) PHAC

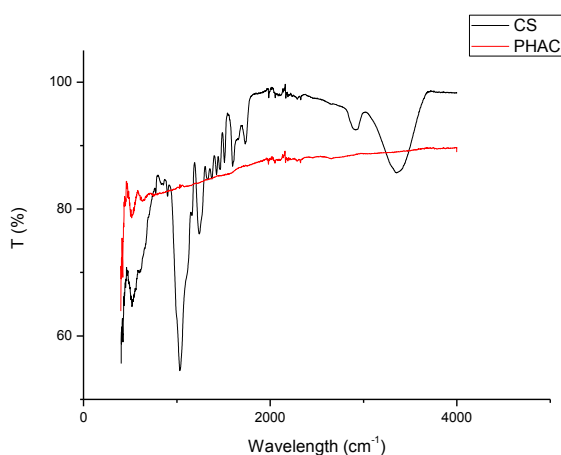**Figure 2** Type I isotherm linear plot from N_2 adsorption analysis

Figure 3 FTIR Spectra of raw (CS) and activated (PHAC) coconut shell samples

■4.0　CONCLUSION

This study establishes that coconut shell based granular activated carbons with large surface area and well developed porosity can be prepared using chemical activation with KOH. Moreso, the process leads to materials with specific properties, so that the procedure to be employed has always to be chosen according to the final application the carbon is intended for. The large surface area translates to high adsorption capacity while the porosity permits to tailor the pore size distribution more accurately, making it possible to obtain carbons with narrower pore size distributions. The chemical activation also permits to tailor the synthesized carbons towards hydrophobic organic contaminants due to the functional groups in the surface chemistry.

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