

Synthesis and Characterization of Bio-Based Porous Carbons by Two Step Physical Activation with CO₂

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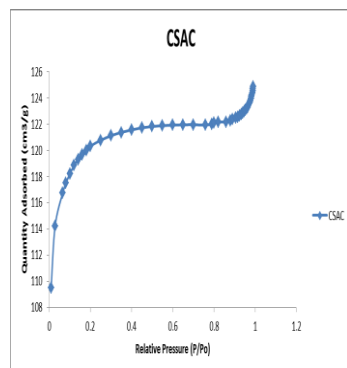
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Graphical abstract



Abstract

Porous carbons were synthesized from coconut shell using two step CO₂ activation and their characteristics were investigated. Nitrogen adsorption test for Brunauer-Emmett-Teller (BET) specific surface area and pore volume of the adsorbent produced were carried out. The Langmuir surface area, BET surface area and pore volume of the synthesized carbon are 533 m²/g, 361 m²/g and 0.19 cm³/g respectively. Micropores are predominant constituting 88% of the total surface area. From the Fourier Transform Infrared Spectroscopy (FTIR) analysis, hydroxyls, alkenes, carbonyls and aromatics functional groups were identified. Thermogravimetric analysis (TGA) results gives thermal analysis whereby moisture pyrolysis occurred at 105°C, the pyrolysis of hemicellulose and cellulose occurred at 160–390°C. However, lignin decomposition occurred in a wider temperature range (390–650°C). The proximate and ultimate analysis shows high percentage of carbon and less ash content which indicates a good precursor material for porous carbon.

Keywords: Adsorbent; coconut shell; micropores; physical activation

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1.0 INTRODUCTION

The rapid growth of agricultural sector in Malaysia constitutes over 2 million tons of agricultural waste annually and causing environmental menace. Amongst these wastes are coconut shells, oil palm shell [1].

Coconut shell is the endocarp of the coconut fruit and constitutes approximately 35 percent of the total fruit mass. In 2001, about 151,000 ha of land were cultivated for coconut plantation which generates about 5300 kg waste of coconut shells per hectare per year to the environment [2, 3]. Conversion of these wastes will serve dual purpose by disposing the wastes and at the same time adding value to them in form of adsorbents.

Activated carbons finds applications in various areas such as gas and liquid phases; CO₂ capture, removal of colour (methylene blue), portable water treatment, air purification, organic and

inorganic contaminants removal from industrial effluents and gas storage [4-5].

Previous studies have shown that precursor material and activation conditions are responsible for the properties of the resulting AC for specific applications [2, 6]. Hence, this study aims at the synthesis of well-developed porosity in granular activated carbon using coconut shell as the bio based material and two step CO₂ physical 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 deionised water, and further dried in an oven at 105°C for 24 h. 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

Two step physical activation with CO₂ was done by initially carbonizing the precursor in a furnace under a nitrogen flow (150 cm³/minute) from ambient temperature until carbonization temperature of 700°C for 2 h at heating rate of 100°C/minute. The resultant char was then activated under a CO₂ flow of 150 cm³/minute at 800°C (100°C/min) for two hours. The activated samples were cooled under inert and removed. The activated carbon were then washed with deionised water and dried in the oven at 105°C for 24 h [7]. All samples were stored in the desiccators.

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), char (A27) and activated samples (CSAC) to study the development of porosity and surface morphology. The Elemental analysis was done for elemental composition using an Elemental Analyzer. The surface chemistry of the samples were chemically and structurally analysed using FT-IR spectra observed at 4 cm⁻¹ 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. Mettler Toledo TGA/DSC1 thermogravimetric analyzer was employed for the determination of thermal decomposition of the samples.

3.0 RESULTS AND DISCUSSION

3.1 Proximate and Ultimate Analysis

The raw material contains minimal ash content, as presented in Table 1, which is an advantage for a precursor material in the synthesis of activated carbons. The fixed carbon composition (23.38%) from the proximate analysis when compared with other studies can be said to be quite high with 18.7, 18.6 and 21.6% [6, 8, 9]. 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% [8, 9]. The high composition of carbon in the coconut shell as presented from the elemental analysis indicates a good precursor for porous carbon.

3.2 Scanning Electron Micrograph

The SEM analysis of the raw coconut shell (CS), char of sample carbonized at 700°C for two hours (A27) and coconut shell activated carbon (CSAC) are presented in Figure 1. The surface morphology varies significantly with CS showing no pore formation due to the presence of volatiles and other contaminants on the surface, while A27 shows some rudimentary pores formed as a result of the space created by the volatilization of the moisture,

hemicellulose, cellulose and lignin content of the raw coconut shell after carbonization.

However, CSAC shows pore widening as a result of the activation process, leading to more developed pore structures. This pore widening mechanism is the result of the reaction of CO₂ with the walls of the pores during the physical activation process.

Table 1 Proximate and ultimate analysis of raw coconut shell used in this study

Proximate analysis (%)	
Carbon	23.38
Moisture	5.62
Ash	1.11
Volatiles	71.37
Ultimate analysis (%)	
C	48.66
H	6.34
N	1.52
S	0.038
O	43.43

3.3 Surface Area and Pore Volume

The surface area of activated carbon is very important and translates its adsorption capacity [6]. The carbonization process leads to the development of rudimentary pore structure of the char, while the activation process enhances the widening of the rudimentary pores rendering it more easily accessible. The BET surface area is 368 m²/g of which 88% are predominantly micropores and the pore volume is 0.19cm³/g.

This result compares well with the result achieved by Daud and Ali [8], Aworn *et al.*, [10], Singh *et al.*, [11], and Nasri *et al.*, [12], where BET surface area of 183 m²/g, 383 m²/g, 378 m²/g and 167 m²/g were reported from various carbonaceous precursors. The detailed comparison of the results obtained from this work and other studies is presented in Table 2. The isotherm plot is a type I curve as presented in Figure 2.

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 CSAC) as presented in Figure 3. The intensity of the spectra varies slightly from the precursor to the activated carbon. The spectrum shows the existence of some representative peaks of lignocellulosic materials of coconut shell similar to hydroxyl, alkenes, aromatics and carbonyls functional groups [3]. The wide band at 3438 to 3387 cm⁻¹ is evident of (O–H) peaks in the hydroxyl groups. However, this peak is more pronounced in the activated carbon (CSAC) which suggests the presence of more phenolic groups after activation with CO₂.

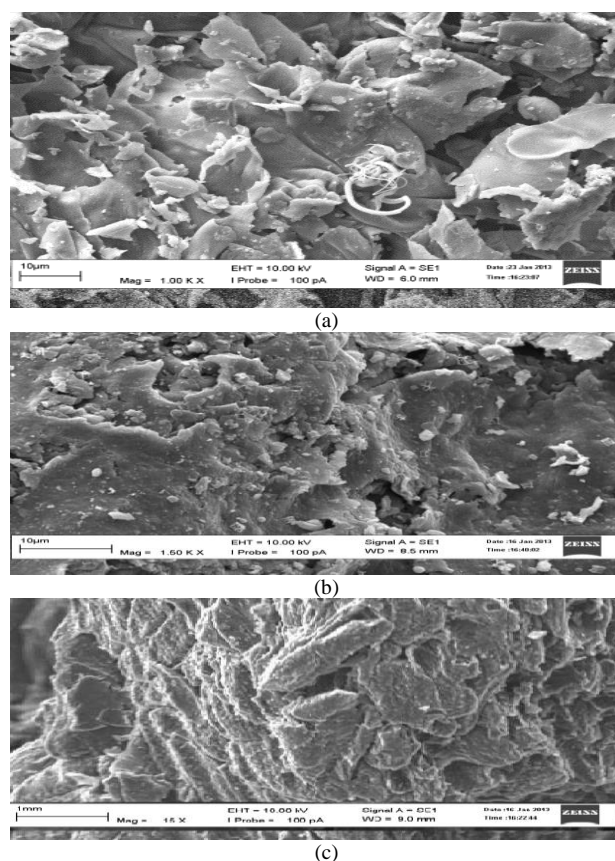


Figure 1 SEM images of (a) CS, (b) A27, and (c) CSAC

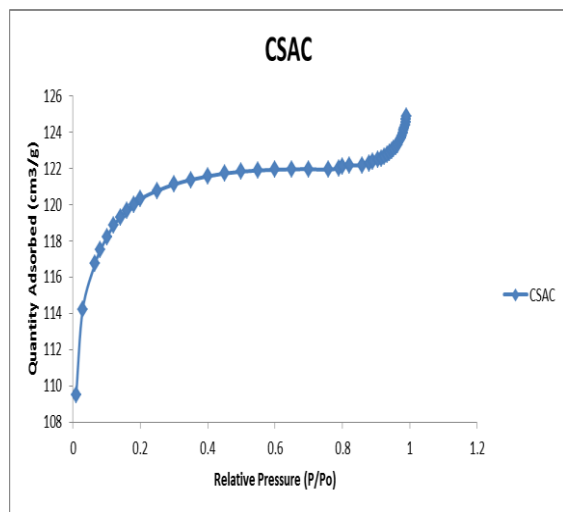


Figure 2 Type I Isotherm linear plot from N_2 adsorption analysis

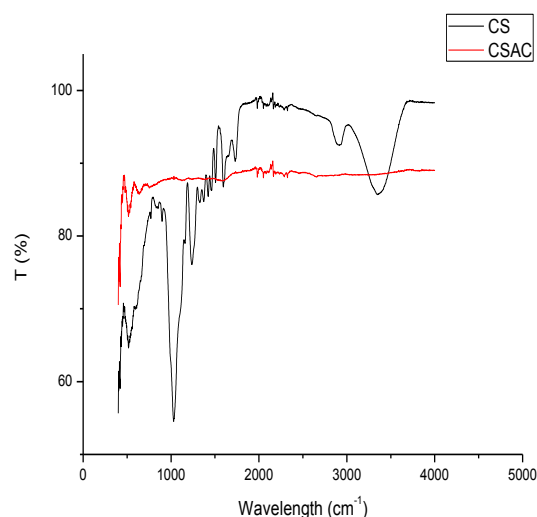


Figure 3 FTIR Spectra of raw (CS) and activated (CSAC) coconut shell samples

The bands between 1700 and 1580 cm^{-1} could be allotted to alkenes conjugation moves ($C=C$) which are characteristics of cellulose and hemicelluloses [13], 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 detected at around 1700 cm^{-1} for the precursor (CS) but absent in the activated sample (CSAC) which may be attributed to the carbonization and activation process. The band at 1170 and 1164 cm^{-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) [14-15].

3.5 Thermogravimetric Analysis

Thermograms reveals weight loss during the TG analysis of samples and it is divided into onset temperature, peak derivative temperature and stable or constant temperature region. The first stage occurs around 50°C up till 120°C for both samples showing the beginning of thermal decomposition with moistures being the major component eliminated at this stage as presented in Figure 4, the percentage moisture removal are 5.62% and 4.5% for CS and CSAC respectively. Afterwards, there is a noticeable gradient at 250°C indicating the beginning of the elimination of volatile components like hemicellulose, cellulose and lignin. This trend continues up till about 650°C . Within the temperature range of 250 to 650°C , the peak derivative temperature was achieved indicating the maximum weight loss (370°C for CS and 650°C for CSAC). It is also noteworthy that above 650°C , all the decomposition has been completed due to a stable temperature region which corresponds to end of the thermal decomposition process. Hence the sample has been carbonized at this temperature and any further heating may destroy the porous structure of the sample.

4.0 CONCLUSION

The present work demonstrates that coconut shell based granular porous carbons with well-developed porosity can be synthesized using physical activation with CO_2 . Nevertheless, the resultant properties and application of the activated carbon has to be determined through the procedure, activation conditions and precursor materials. However, the resulting materials from this

study can be applied for the removal of contaminants from gaseous and liquid phases. This is due to the presence of high porosity created by the reaction of the gas with the walls of the pores which originates from the conductor vessels present in the botanical structure of the precursor. In addition, the two step activation

procedure employed in this study is not common but highly effective in porosity development.

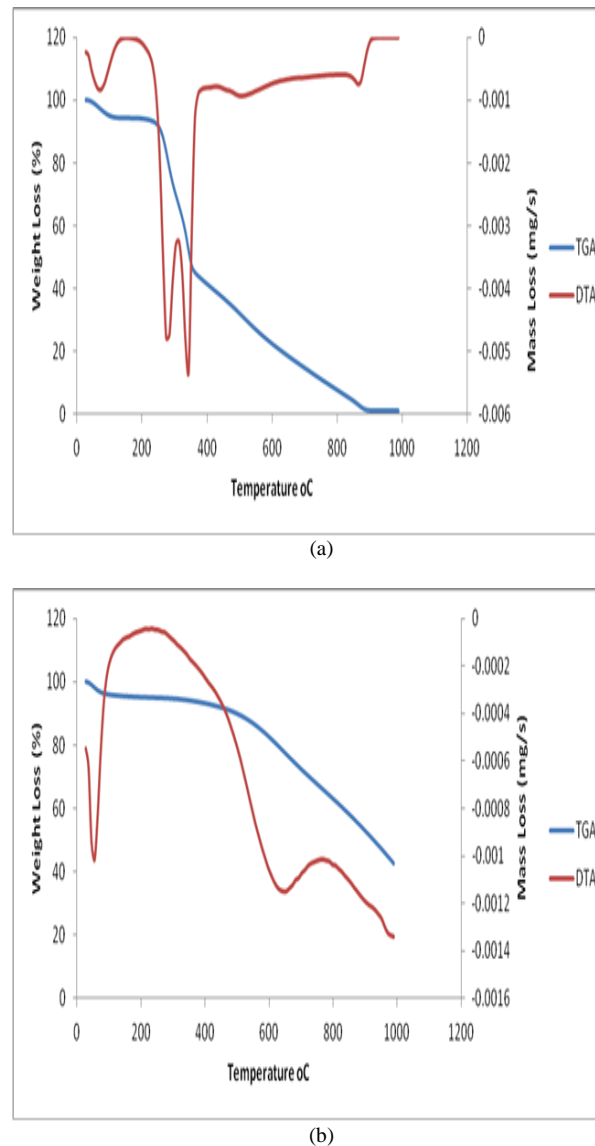


Figure 4 TGA-DTG curve for (a) CS and (b) CSAC showing the thermal decomposition

Table 2 Comparison of the characteristics of porosity in activated carbons of present work with other literature

Sample	Activation method	S_{BET} (m^2/g)	V_p (cm^3/g)	V_{micro} (cm^3/g)	Microporosity (%)	References
CS	Two step physical activation by CO_2	368	0.192	0.167	88.9	This Study
CS	Physical activation with CO_2	183	-	0.15	-	[8]
PKS	Physical activation with CO_2	260	-	0.22	-	[8]
MCA	Physical activation with CO_2	467	0.202	0.218	92.9	[10]
CS	Physical activation	378	0.260	0.120	89.0	[11]
PKS	Two step Physical activation by CO_2	167	0.091	0.080	91.0	[12]

V_p : pore volume, V_{micro} : micropore volume, S_{BET} : BET Surface area, CS: coconut shell, MCA: macadamia nut shell, PKS: palm kernel shell

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