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Research Article

Effect of Reaction Time and Temperature on the Properties of Carbon Black Made from Palm Kernel and Coconut Shell

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Abstract

Objective: Lignocellulosic biomass derived carbon black was thermally produced from Coconut Shell (CS) and Palm Kernel Shell (PKS). The effects of carbonization conditions on the characteristics of the produced lignocellulosic derived carbon black were studied. **Methodology:** Carbonization was carried out between 400 and 700°C for reaction ranging between 30 and 90 min. Practically, the carbonization temperature has a more prominent impact than the carbonization reaction time used in this experiment. **Results:** The result showed that high temperature carbonized carbon black had higher iodine adsorption as compared to carbon black that derived from low temperature. Prolong the reaction time resulting in structural deformation, hence less surface area for adsorption. In addition, the characteristics of carbon black from CS was fairly better than PKS carbon black in terms of iodine adsorption, surface area and fixed carbon content. The carbon black derived from PKS had lower iodine adsorption due to the poor development of porosity that contained higher ash and volatile matters. **Conclusion:** These study serves as fundamental tool to establish ideal production routes for carbon black manufactured from lignocellulosic biomass especially in the form of nut or seed shell.

Key words: Palm kernel shell, coconut shell, carbon black, carbonization temperature, carbonization reaction time

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Carbon black provides materials with excellent properties such, as well developed pore structures and high internal surface area and they have been employed in a wide number of industrial applications like purification of gases, used as an absorbent for the removal of organic pollutants from water, used as a catalyst and also one of the best electrically conducting materials^{1,2}. Generally, carbon black used as the absorbent for the removal of diverse pollutants from water as carbon black has a porous structure which analogous to activated carbon³⁻⁶. Currently, a global move toward the generation of renewable energy as the demand for non-renewable coal-based carbon has been growing interest throughout the world⁷⁻¹⁰. Palm kernel shell and coconut shell appear to be a promising raw material for this purpose. Due to high carbon content of palm kernel shell and coconut shell, both of the lignocellulosic biomass have been one of the key lignocellulosic biomass materials in order to replace the fossil fuel in the carbon black industry^{11,12}. Carbon black was the desirable material to use as applicable absorbent to eliminate the pollutants from aqueous solution with their special characteristics which are that carbon black was comprised of large specific surface area, pore structure, enriched surface functional groups and mineral components⁶. The purpose of carbonization process is to enrich the carbon content as well as create an initial porosity for the carbon black, while the activation process may helps in enhancing the pore structure¹³. Carbonization parameters play an important role in the development of initial pore structure in the carbon as the volatile matters will discharges from the carbon's matrix through the process of carbonization¹⁴. Since the pore development in the char has a great influence on the pore characteristics of subsequently produced carbon black carbonization parameters should be taken into account prior to manufacturing of carbon black. Reaction temperature and reaction time considered to be an important process variables for carbonization¹⁵. The aim for this study is to evaluate the effect of carbonization temperature and reaction time on the properties of the carbon black made from CS and PKS. Analysis of variance (ANOVA) was used to test the main effects of carbonization temperature and carbonization reaction time on mass yield, bulk density, pH value, ash content, volatile content, fixed carbon content and iodine adsorption from CS and PKS and also their interactions. Furthermore, the determination of the Brunauer, Emmett and Teller (BET) internal pore surface area and volume,

structural analysis of the carbon crystals and pore bodies from the Scanning Electron Microscope (SEM) were also taken as responses.

MATERIALS AND METHODS

Material preparation: Palm Kernel Shells (PKS) were collected from Seri Ulu Langat Palm Oil Mill, Dengkil Selangor and Coconut Shells (CS) were collected from the local market at Pasar Besar Kuantan, Pahang. Collected PKS and CS were cleaned and dried in an oven at 105 °C for 48 h. The dried PKS and CS were then crushed and sieved to 2-5 mm size range.

Carbonization process: The dried samples was placed in a furnace and carbonized under the conditions as follows: Temperature 400, 500, 600 and 700 °C for 30, 45, 60, 75 and 90 min. The carbon black yield was determined by using the following^{16,17} Eq. 1:

$$\text{Yield (\%)} = \frac{W_c}{W_o} \times 100 \quad (1)$$

where, W_c is the dry weight (g) of the sample after carbonization and W_o is the initial dry weight (g) of the sample. The carbon black preparation experiments were carried out several times to obtain enough carbon black for further analysis. Each carbonization treatment will performed in triplicate.

Characterization of the manufactured carbon black

Determination of iodine number: The iodine number is determined according to the ASTM D4607-94 method. The iodine number is defined as the milligrams of iodine adsorbed by 1 g of carbon. The experiment consists of treating the sample with 10 mL of 5% HCL. This mixture is boiled for 30 sec and then cooled. About 100 mL of 0.1 N (0.1 mol L⁻¹) iodine solution was then added to the mixture and stirred for 30 sec. The resulting solution is filtered and 50 mL of the filtrate is titrated with 0.1 N (0.1 mol L⁻¹) sodium thiosulfate, using starch as indicator. The iodine amount adsorbed per gram of carbon (X/M) was calculated by the Eq. 2:

$$\frac{X}{M} = \frac{\left(N_1 \times 126.93 \times V_1 - \left(\frac{V_1 + V_{HCl}}{V_F} \right) \times (N_{Na_2S_2O_3} \times 126.93) \times V_{Na_2S_2O_3} \right)}{M_c} \quad (2)$$

where, N_i is the iodine solution normality, V_i is the added volume of iodine solution, V_{HCl} is the added volume of 5% HCl, V_f is the filtrate $N_{Na_2S_2O_3}$ volume used in titration, is the sodium thiosulfate solution normality, $N_{Na_2S_2O_3}$ is the consumed volume of sodium thiosulfate solution and M_c is the mass of activated carbon¹⁸.

Determination of surface area: The Brunauer-Emmett-Teller (BET) surface areas were determined by nitrogen adsorption at 77 K. The nitrogen gas adsorption measurements were done after the carbon was degassed at 300°C in an inert condition for 24 h. A relative pressure of between 10⁻⁵ and 0.995 of nitrogen gas was used to obtain the N₂ adsorption isotherm. The BET surface area, mesopore volume and micropore surface area of the activated carbon were determined by the application of the Brunauer-Emmett-Teller (BET).

Determination of porous: A scanning electron microscope was used for obtaining micrographs of the prepared carbon black. Scanning Electron Microscopy (SEM) analysis was carried out on the carbon black which prepared under optimum conditions to study its surface texture and the development of porosity.

Determination of volatile content: To determine the volatile content, oven-dry samples are placed in a ceramic crucible and the weight of each crucible and the biomass is noted. The crucibles are then placed and in the furnace at a temperature of 900°C for 7 min. After cooling, the volatile content is calculated according to Eq. 3:

$$\text{Volatiles (\%)} = \frac{100 \times m_3}{m_2} \quad (3)$$

where, m_2 is the mass of oven-dry sample and m_3 is the mass of sample after heating.

Determination of ash content: The ash content was determined by burning (dry oxidation) the oven-dried sample (2 g) in a muffle furnace model at 575 ± 25°C for 4 h as per the TAPPI standard method, T211 om-85. This test method was used to determine the amount of ash, remaining after dry oxidation of the sample.

Determination of moisture content: The moisture content was determined using the "oven drying method" described in

ASTM D2867-09. A clean empty porcelain capsule was oven dried at 105°C, then cooled in a desiccator and then 1-2 g of the sample were weighed. The content was then oven dried at 110°C to a constant weight for 3 h. The percentage moisture content was calculated using the Eq. 4:

$$\text{Moisture (\%)} = \frac{\text{Initial weight} - \text{Oven dry weight}}{\text{Oven dry weight}} \times 100 \quad (4)$$

Determination of fixed carbon content: The fixed carbon was determined using the Eq. 5:

$$\text{FC (\%)} = 100 - (\text{VM\%} + \text{AC\%} + \text{MC\%}) \quad (5)$$

where, VM is the volatile matter of carbon black, AC is the ash content and MC is the moisture content of the sample.

Determination of bulk density: Bulk density (g cm⁻³) is defined as the mass of a unit volume of the sample in air, including both the pore system and the voids among the particles¹⁹. In this test, 10 mL measuring cylinder was dried in oven at 110°C for 30 min. Sample was filled into cylinder with three layers and tapped about 300 times for each layer until its fully compacted and reweighed described in ASTM²⁰ D2854-70 as in Eq. 6:

$$\text{Bulk density} = \frac{W_{bc} - W_c}{W_{bc}} \quad (6)$$

where, W_{bc} is the mass of the sample and the container, W_c is the mass of the container and W_{bc} is the volume occupied by the biomass.

Determination of pH: The standard test method for determination of carbon black pH ASTM D 3838-80 was used^{21,22}. One gram of sample was weighed and transferred into a beaker. About 100 mL of distilled water was measured and added and stirred for 1 h. The samples were allowed to stabilize before the pH was measured using a pH meter. Samples were run in triplicates.

Data analysis: The data of physical and chemical properties of carbon black were analyzed using Statistical Package for the Social Science (SPSS) produced for the analysis of variance (ANOVA) at 95% confident level ($p \leq 0.05$). Differences of the treatment effects were determined using Tukey-Kramer

multiple comparison test when significance was observed. The effects were considered to be not statistically significant when the p-value was higher than 0.05 at the 95% confidence level.

RESULTS AND DISCUSSION

Final mass yield, bulk density and pH value: Analysis of variance revealed statistically significant differences ($p < 0.01$) in mass yield and bulk density for different levels of carbonization temperature and carbonization reaction time for CS and PKS. Significant interaction at $p < 0.05$ of both independent variables was also observed on the bulk density for carbonization of CS and PKS. However, no significant differences ($p > 0.05$) in pH for different levels of both independent variables and in mass yield for interaction of both independent variables.

Mass yield: Table 1 summarizes carbonization treatments at temperatures 400-700°C for CS and PKS. The carbonized biomass mass yield varies from 20-34% of its original weight. The mass yield of carbon black significantly decreased with higher carbonization temperature and longer reaction time for both of the lignocellulosic biomass. At 400°C, the highest weight loss was observed in CS (72%) compared to PKS with 66% weight loss. However, further increasing the temperature from 400-700°C only reduced the mass yield on average by 8% for both biomass. The reduction of mass yield most likely due not only to a more complete carbonization and volatilization but also to some burning occurring at the higher temperatures as a result of the presence of air²³. Highest mass loss was obtained using carbonization temperature 700°C regardless of the reaction time. This indicates that the carbonization reaction time used in this study has a lesser effect than the carbonization temperature.

Bulk density: Bulk density is important if the produced carbon is used in a filtration system because it determines the volume that can be contained in a filter casing²⁴. Lower bulk density indicates a good absorbent²⁰. As the carbonized temperature increased, the bulk density slightly decreased. The lowest bulk density for CS and PKS were achieved when carbonized using temperature 700°C and reaction time of 90 min. Hence, higher temperature and longer reaction time were favoured to improve the adsorption value of carbon black.

Table 1: Analysis variance (ANOVA) for the mass yield, bulk density, pH value of CS and PKS carbon black

Carbonization temperature (°C)	Reaction time (min)	Yield (%)	Bulk density (g cm ⁻³)	pH
Coconut shell				
Untreated		-	0.542	6.4
400	30	28.158 ^a	0.557 ^f	7.0
400	45	27.720 ^a	0.527 ^{def}	6.5
400	60	27.433 ^{ab}	0.526 ^{def}	6.4
400	75	27.093 ^{ab}	0.513 ^{cde}	6.2
400	90	26.551 ^{bc}	0.510 ^{cde}	6.1
500	30	25.516 ^{cd}	0.541 ^{ef}	7.0
500	45	24.728 ^{de}	0.513 ^{cde}	6.7
500	60	24.535 ^{def}	0.513 ^{cde}	6.5
500	75	24.314 ^{ef}	0.500 ^{bcd}	6.4
500	90	24.170 ^{ef}	0.501 ^{bcd}	6.3
600	30	24.305 ^{ef}	0.527 ^{def}	7.0
600	45	23.660 ^{ef}	0.501 ^{bcd}	6.7
600	60	23.604 ^{efg}	0.501 ^{bcd}	6.7
600	75	23.569 ^{fg}	0.500 ^{bcd}	6.6
600	90	22.183 ^h	0.476 ^{ab}	6.5
700	30	22.508 ^{gh}	0.527 ^{def}	7.0
700	45	21.511 ^{hi}	0.501 ^{bcd}	7.0
700	60	21.027 ⁱ	0.490 ^{abc}	6.8
700	75	20.953 ⁱ	0.476 ^{ab}	6.7
700	90	20.426 ^j	0.465 ^a	6.7
Palm kernel shell				
Untreated			0.667	6.3
400	30	33.701 ^a	0.590 ^f	7.6
400	45	33.101 ^a	0.572 ^e	7.5
400	60	32.598 ^{ab}	0.557 ^{cde}	7.2
400	75	31.800 ^{abc}	0.556 ^{cde}	7.1
400	90	30.955 ^{bc}	0.556 ^{cde}	7.0
500	30	30.430 ^{cd}	0.572 ^e	7.6
500	45	28.651 ^{de}	0.556 ^{cde}	7.5
500	60	28.617 ^{de}	0.541 ^{bcd}	7.4
500	75	28.371 ^e	0.527 ^b	7.3
500	90	28.223 ^e	0.500 ^a	7.2
600	30	27.760 ^{ef}	0.562 ^e	8.2
600	45	27.296 ^{efg}	0.559 ^{de}	8.0
600	60	26.937 ^{efg}	0.556 ^{cde}	7.9
600	75	26.837 ^{efg}	0.527 ^b	7.7
600	90	26.148 ^{fgh}	0.500 ^a	7.7
700	30	25.981 ^{fgh}	0.556 ^{cde}	8.4
700	45	25.886 ^{fgh}	0.541 ^{bc}	8.3
700	60	25.509 ^{gh}	0.527 ^b	8.1
700	75	24.573 ^h	0.526 ^b	7.9
700	90	24.506 ^h	0.501 ^a	7.9

Means followed by the same letter in the same column are not significantly different at $p \leq 0.05$ according to Tukey-Kramer multiple comparison test

pH value: The pH of carbon black constitutes a useful indicator of the nature of the functionalities present on the carbon surface. According to Table 1, carbon blacks produced from PKS were slightly alkaline while carbon blacks from CS were slightly acidic with pH values ranged from 7.2-8.4 and 6.2-7.0, respectively. The alkaline nature of

Table 2: Analysis variance (ANOVA) for the ash content, volatile content, fixed carbon content and iodine number of CS and PKS carbon black

Carbonization temperature (°C)	Reaction time (min)	Ash content (%)	Volatile content (%)	Carbon content (%)	No. of Iodine (mg g ⁻¹)
Coconut shell					
Untreated		0.2015	9.235	88.853	1.710
400	30	30.491 ^a	27.368 ^l	41.813 ^l	161.624 ^k
400	45	31.645 ^b	26.138 ^h	41.949 ^{hi}	165.348 ^k
400	60	32.246 ^d	25.571 ^h	42.032 ^{hi}	178.165 ^j
400	75	32.511 ^e	25.201 ^{gh}	42.218 ^g	178.643 ^j
400	90	32.836 ^f	24.591 ^{gh}	42.212 ^g	187.687 ⁱ
500	30	30.711 ^a	26.268 ^h	42.807 ^f	204.782 ^h
500	45	31.916 ^c	25.063 ^{gh}	42.840 ^f	212.492 ^g
500	60	32.289 ^{de}	24.684 ^f	42.890 ^f	217.247 ^g
500	75	32.520 ^e	23.215 ^e	44.242 ^g	251.725 ^f
500	90	34.109 ^g	23.209 ^e	42.659 ^f	202.845 ^h
600	30	32.816 ^f	22.284 ^e	44.745 ^e	275.260 ^e
600	45	32.794 ^f	22.273 ^e	44.784 ^d	279.971 ^e
600	60	32.425 ^{de}	20.639 ^d	46.906 ^c	304.140 ^d
600	75	33.525 ^e	19.480 ^c	46.977 ^c	316.543 ^c
600	90	34.596 ^h	19.346 ^c	46.042 ^{de}	299.386 ^d
700	30	34.070 ^g	19.696 ^{cd}	46.098 ^{de}	301.494 ^d
700	45	34.505 ^h	17.830 ^b	47.610 ^b	329.342 ^b
700	60	34.943 ⁱ	16.758 ^a	48.292 ^a	330.820 ^b
700	75	35.444 ⁱ	16.106 ^a	48.443 ^a	348.744 ^a
700	90	36.437 ^k	16.098 ^a	47.464 ^b	328.512 ^b
Palm kernel shell					
Untreated		0.1741	16.581	81.969	1.277
400	30	30.116 ^a	28.652 ^l	40.902 ^g	75.989 ^t
400	45	30.142 ^a	28.502 ^l	41.033 ^g	139.285 ^r
400	60	30.508 ^b	27.601 ^k	41.785 ^{ef}	187.687 ⁿ
400	75	31.238 ^c	27.514 ^k	41.162 ^g	206.304 ^k
400	90	31.942 ^{ef}	25.830 ^j	42.149 ^{de}	148.593 ^p
500	30	31.803 ^d	26.862 ^j	41.012 ^g	107.637 ^s
500	45	31.917 ^e	26.724 ^j	41.199 ^g	191.410 ^m
500	60	31.977 ^f	25.519 ^{hi}	42.412 ^d	211.889 ^j
500	75	32.089 ^g	25.248 ^{hi}	42.581 ^d	249.121 ^d
500	90	32.417 ^h	25.197 ^h	42.367 ^{de}	200.719 ^j
600	30	33.971 ⁱ	23.795 ^g	42.146 ^{de}	143.008 ^q
600	45	34.675 ^k	22.882 ^f	42.382 ^{de}	213.750 ⁱ
600	60	34.640 ^j	22.631 ^f	42.688 ^{cd}	230.505 ^g
600	75	35.093 ^l	20.909 ^{de}	43.981 ^a	282.631 ^b
600	90	36.875 ^o	20.427 ^{cd}	42.687 ^{cd}	221.197 ^h
700	30	36.274 ^m	21.455 ^e	42.204 ^{de}	169.071 ^o
700	45	36.617 ⁿ	20.067 ^c	43.256 ^{bc}	239.813 ^e
700	60	37.337 ^p	19.282 ^b	43.356 ^b	269.599 ^c
700	75	38.536 ^q	17.307 ^a	44.150 ^a	304.971 ^a
700	90	38.942 ^r	17.294 ^a	43.861 ^{ab}	234.228 ^f

Means followed by the same letter in the same column are not significantly different at $p \leq 0.05$ according to Tukey-Kramer multiple comparison test

the carbon black resulted from the presence of larger amounts of inorganic material in the form of mineral ash. It is well known that solution pH is a critical factor in adsorption, not only carbon surface properties change with variations of the pH but this parameter can also affect the state of the ionic species in solution²⁵. Carbonization

temperature and carbonization reaction time have no significant effects on the pH value of CS and PKS.

Effect of carbonization temperature and reaction time on the chemical characteristics of produced carbon black:

Carbon black derived from CS and PKS and its chemical properties are summarized in Table 2. The ANOVA analysis was showed $p < 0.01$ for the carbonization parameter (carbonization temperature and carbonization reaction time), which showed that the chemical characteristics were strongly significant at the 99% confidence level. Significant interaction ($p < 0.01$) between the independent variable (carbonization temperature and carbonization reaction time) on ash content, volatile content, carbon content and iodine adsorption were observed from carbonization of CS and PKS. The Tukey-Kramer multiple comparison test was employed to determine the interaction among the independent variables.

Ash content: The ash content of carbon is the residue that remains when the carbonaceous portion is burnt off²⁴. Table 2 shows the ash content of the lignocellulosic biomass derived carbon blacks increased paralleled with the increasing of carbonization temperature and carbonization reaction time. When temperature increased from 400-700 °C, the ash content increased from 32.5-35.4 and 31.2-38.5% for CS and PKS, respectively. The increase in ash content is the result of a progressive concentration of minerals and destructive volatilization of lignocellulosic matters as temperature increased²⁶⁻²⁸. Additionally, ash content of the carbon black samples shows an important increase with increasing reaction time (Table 2) which is expected as ash remains in the solid fraction, whereas the organic matter undergoes thermal decomposition, resulting in weight loss in the C-containing fraction²⁹. It is known that materials with the lowest ash content are most active³⁰. Ash may interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions¹³. Thus, the low iodine adsorption of carbon black derived from the lignocellulosic biomass with high ash content may be due to the plugging of pores during carbonization by inorganic compounds present in the lignocellulosic biomass.

Volatile content: The volatile content to some extent may be informative to understand the stability of the material³¹. As the severity of carbonization condition increases, the volatile

content in the produced carbon black similarly increases, with carbonization temperature having a more notable impact than the reaction time in these experiments yet. Lowest volatile matter content was recorded from carbon black produced at 700°C, 16.09% for CS and 17.29% for PKS. Carbon black produced at lower carbonization temperature contained higher volatile compounds. These volatile compounds can "block" pore spaces resulting in lower surface area and this can be diminished when carbon black production temperature is high enough (>650°C) as the volatile matter is burnt off at higher temperatures³². With increasing carbonization temperatures, more volatiles were released and more micropores were formed³³. On the other hand, lower volatile matter content was recorded when longer reaction time was used in the carbonization process for CS and PKS carbon black produced indicated that carbon black produced at longer carbonization reaction time obtained higher stable carbon among the experimental carbon black. The highest removal rate of volatile content for CS and PKS were achieved using 700°C for 60 min and 700°C for 75 min, respectively.

Fixed carbon content: The yield of fixed carbon in lignocellulosic biomass was practically sensitive to the carbonization temperature and carbonization reaction time. With the increasing of carbonization temperature and reaction time, the volatile matter content of the produced carbon black declined, whereas fixed carbon contents increased as shown in Table 2. Carbon black with the highest fixed carbon content (47.464% for CS and 43.861% for PKS) indicated that both of the lignocellulosic biomass carbonized at 700°C achieved the highest stable carbon. It is expected at high temperature, more volatiles and impurities would be consumed as non-flaking ash, thereby leaving the relatively pure carbon. Table 2 also showed that reaction time was also playing an important role on fixed carbon content property apart from carbonization temperature. Fixed carbon is determined by removing the mass of volatiles¹³. As mentioned before, more volatile matters have been forcibly expelled out when longer reaction time has been applied. Hence, the highest fixed carbon content was obtained using carbonization temperature 700°C and with carboniferous period of 60 or 75 min for CS carbon black and 75 min for PKS.

Iodine adsorption: The iodine number of the carbons were sensitive to temperature³⁴. Table 2 shows that high

carbonization temperature would result in a great amount of volatiles being released from the raw material and eventually influences the iodine adsorption. The highest iodine adsorption was obtained using carbonization temperature 700°C for 75 min with iodine value of 348.744 and 304.971 mg g⁻¹ for CS and PKS, respectively. This is clearly shown in Table 2 as the volatile content decreased, the iodine adsorption of both lignocellulosic biomasses derived carbon blacks increased. Iodine number indicates the development of pore¹³. Lower carbonization temperature caused lesser volatile substances and tar to be released and produced underdeveloped carbon structures³⁵. Apart from that, the reaction time of the carbonization has a significant effect on the development of the carbon's porous networks. The reaction time should just be enough to eliminate all the moisture and most of the volatile components in the precursor to cause pores to develop. The highest point of iodine adsorption for both of the lignocellulosic biomass derived carbon black occurred when the carbonization reaction time prolonged to 75 min. The iodine adsorption decreases when the carbon black was carbonized for 90 min. Since the end of the volatile evolution marks the formation of the basic pore structure, carbonization treatment should be halted up to that point. Prolong carbonization duration may cause enlargement of pores at an expense of the surface area which eventually reduce the iodine adsorption of the material³⁶. It was also reported by Olawale and Ajayi³⁷ that prolong the reaction time resulting in structural deformation, hence less surface area for adsorption.

Physical characteristics of the produced carbon black

Specific surface area: Figure 1a and b shows that the surface of untreated PKS was smooth without any ridges or pores whereas untreated CS showed holes that were spaced out on the surface with smooth edges. After the carbonization process, the surface morphology showed cracks but no visible pore development occurred on both of the lignocellulosic biomass derived carbon black. The formation of some cavities and rudimentary pores as a result of the space created by the volatilization of organic compounds and moisture content which showed in CS carbon black (Fig. 1c). The surface structures of the carbonized PKS (Fig. 1d) have burnt out the pores with tunnel or honeycomb-like structures. This is as a result of lack impurities such as tar that could clog up the pores and inhibit good pore structure

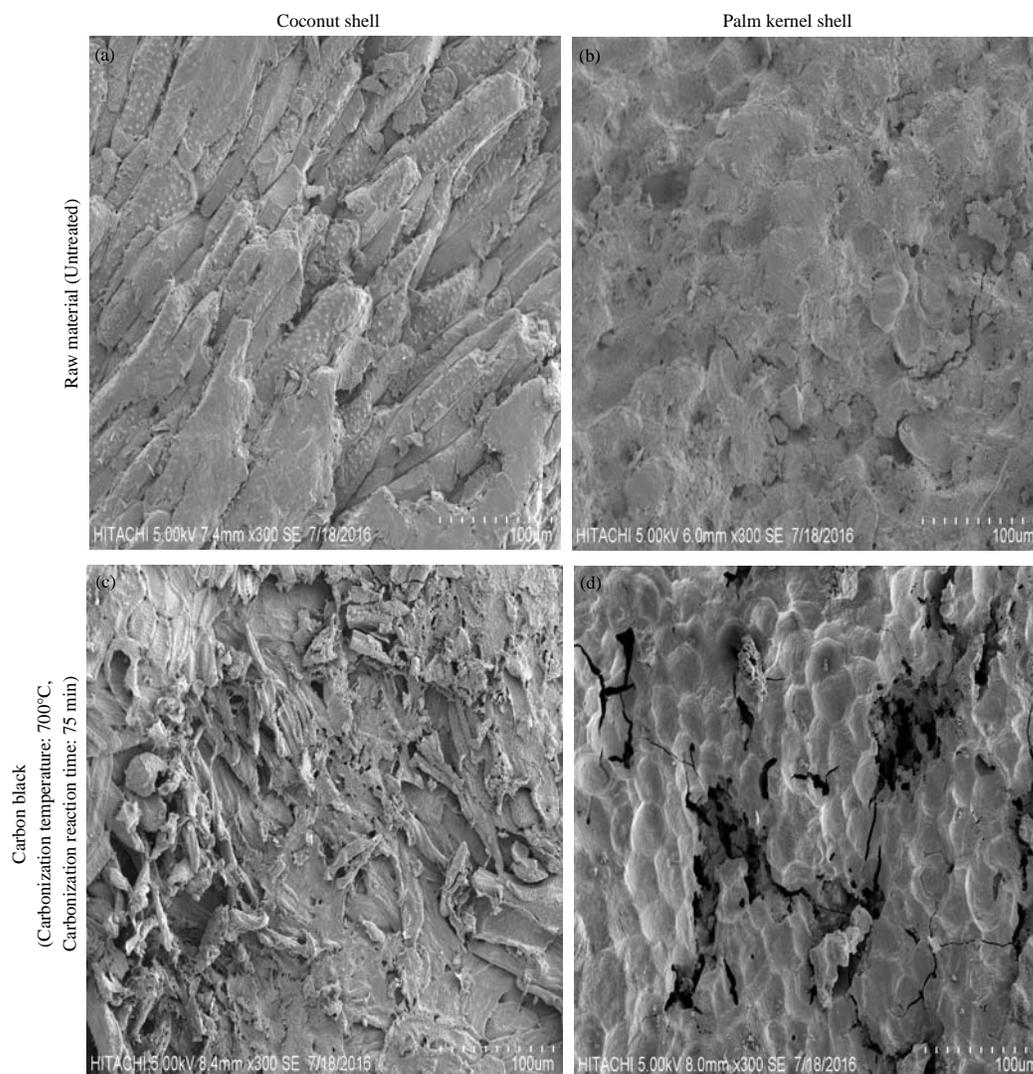


Fig. 1(a-d): Scanning electron micrograph of (a, b) Raw material CS and PKS and (c, d) Carbon black CS and PKS under combustion temperature at 700°C for 75 min

development³⁸. Nevertheless, an effort is being made to abate this phenomenon in our future study.

Pore structure characterization

BET surface area: Table 3 shows the BET surface area and total volume of untreated and carbon black produced from PKS and CS. Untreated sample for both of the lignocellulosic biomass had non-micropore which resulted in low BET value. The presence of micropore increased the surface area. The highest BET specific surface area of 132.7578 m² g⁻¹ was achieved by CS carbon black carbonized at the temperature of 700°C for 75 min. The BET specific surface area of PKS carbon black treated at temperature 700°C for 75 min was 101.9169 m² g⁻¹. The BET surface area of both of the lignocellulosic biomass

derived carbon black increased by 100% compared to the untreated sample. These high BET values are suggestive of highly developed pore network within the carbon³⁴. Besides, the increment of surface area may be achieved via the creation of new micropores as indicated by the rise in micropore surface area and pore volume after carbonization.

N₂-adsorption: Nitrogen adsorption is a standard procedure for determination of the porosity of carbonaceous adsorbents. The adsorption isotherm is the information source for the porous structure of the adsorbent, heat of adsorption, physical and chemical characteristics and so on. The N₂-adsorption isotherm of the PKS and CS carbon black is shown in Fig. 2a and b.

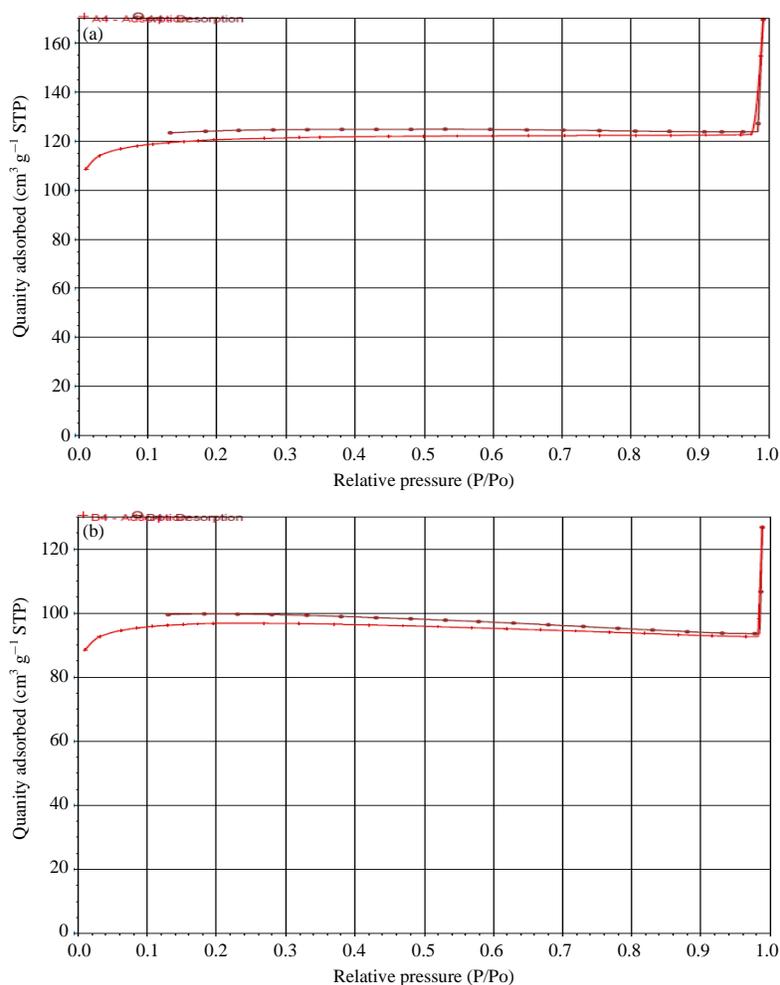


Fig. 2(a-b): N₂-adsorption isotherm for the sample at 77 K for (a) Treated CS and (b) Treated PKS

Table 3: Surface area and pore size characterization of the prepared carbon black

Parameters	Condition	BET result (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Micropore volume	Micropore surface area	Mesoporous surface area
Raw CS	-	0.8398	0.0013	6.2975	0	0	0.8398
Carbonized CS	700°C, 75 min	132.7578	0.2429	7.3175	0.1699	94.6960	38.0618
Raw PKS	-	0.7930	0.0014	7.2097	0	0	0.793
Carbonized PKS	700°C, 75 min	101.9169	0.1952	7.6620	0.1419	84.1988	17.7181

Most isotherms have been shown to conform to one of the five types of IUPAC classification. These samples were carbonized in a temperature of 700°C for 75 min, respectively. It was also observed that both of the lignocellulosic biomass derived carbon blacks conform to type IV isotherm. The isotherms belong to type IV, as defined by the International Union of Pure and Applied Chemistry (IUPAC) and provide an approximate assessment of the pore size distribution. In Fig. 2a and b, the initial part of the type IV isotherm for carbon represents micropore filling and the slope of the plateau at high relative pressure is due to multilayer adsorption on

non-microporous surfaces, i.e., in mesopores, in macropores and on the external surface^{39,40}. This indicated that the sample had a mesoporous structure that contained plenty of mesopores and micropores with fewer number of macropores³⁹.

CONCLUSION

This study was carried out to determine the effect of carbonization temperature and reaction time on the quality of the carbon black produced from coconut shell and palm

kernel shell. While the carbonization temperature has a relatively stronger impact on the quality of produced carbon black, the effect of reaction time was considerably lesser. As a whole, when the carbonization severity (temperature and reaction time) increase, the activation reaction within the sample will increase. Thus, the surface area and adsorption capability of the lignocellulosic biomass derived carbon black increase. However, when the reaction time exceeded 75 min, the activation reached its limit, the destruction of the pore formation becomes dominant and consequently decreases the surface area and adsorption capability. The findings of this study will serve as fundamental tool for treatments involving in the production of carbon black from CS and PKS.

SIGNIFICANCE STATEMENTS

- Utilization of renewable lignocellulosic biomass derived carbon black is an important approach
- Palm kernel shell and coconut shell have a high fixed carbon content
- Careful selection of carbonization parameters is important because this process leaves a significant effect on the final product
- Carbonization temperature had a strong impact on the iodine adsorption of lignocellulosic biomass derived carbon black

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REFERENCES

1. Guadagno, L., L. Vertuccio, A. Sorrentino, M. Raimondo and C. Naddeo *et al.*, 2009. Mechanical and barrier properties of epoxy resin filled with multi-walled carbon nanotubes. *Carbon*, 47: 2419-2430.
2. McIntyre, S., E. Hormann, F. Menges, S.P. Smidt and A. Pfaltz, 2005. Iridium-catalyzed enantioselective hydrogenation of terminal alkenes. *Adv. Synth. Catal.*, 347: 282-288.
3. Faria, P.C.C., J.J.M. Orfao and M.F.R. Pereira, 2004. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res.*, 38: 2043-2052.
4. Nakagawa, K., A. Namba, S.R. Mukai, H. Tamon, P. Ariyadejwanich and W. Tanthapanichakoon, 2004. Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes. *Water Res.*, 38: 1791-1798.
5. Chen, W., R. Parette, J. Zou, F.S. Cannon and B.A. Dempsey, 2007. Arsenic removal by iron-modified activated carbon. *Water Res.*, 41: 1851-1858.
6. Tan, X., Y. Liu, G. Zeng, X. Wang, X. Hu, Y. Gu and Z. Yang, 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*, 125: 70-85.
7. Gerçel, O., A. Özcan, A.S. Özcan and H.F. Gerçel, 2007. Preparation of activated carbon from a renewable bio-plant of *Euphorbia rigida* by H₂SO₄ activation and its adsorption behavior in aqueous solutions. *Applied Surf. Sci.*, 253: 4843-4852.
8. Abdulkarim, M.A., N.A. Darwish, Y.M. Magdy and A. Dwaidar, 2002. Adsorption of phenolic compounds and methylene blue onto activated carbon prepared from date fruit pits. *Eng. Life Sci.*, 2: 161-165.
9. Tseng, R.L., S.K. Tseng and F.C. Wu, 2006. Preparation of high surface area carbons from corncob with koh etching plus CO₂ gasification for the adsorption of dyes and phenols from water. *Coll. Surf. A: Physicochem. Eng. Aspects*, 279: 69-78.
10. De Letona Sanchez, M.L., A. Macias-Garcia, M.A. Diaz-Diez, E.M. Cuerda-Correa, J. Ganan-Gomez and A. Nadal-Gisbert, 2006. Preparation of activated carbons previously treated with hydrogen peroxide: Study of their porous texture. *Applied Surf. Sci.*, 252: 5984-5987.
11. Rugayah, A.F., A.A. Astimar and N. Norzita, 2014. Preparation and characterisation of activated carbon from palm kernel shell by physical activation with steam. *J. Oil Palm. Res.*, 26: 251-264.
12. Olafadehan, O.A., O.W. Jinadu, L. Salami and L.T. Popoola, 2012. Treatment of brewery wastewater effluent using activated carbon prepared from coconut shell. *Int. J. Applied Sci. Technol.*, 2: 165-178.
13. Mahanim, S.M.A., I.W. Asma, J. Rafidah, E. Puad and H. Shaharuddin, 2011. Production of activated carbon from industrial bamboo wastes. *J. Trop. For. Sci.*, 23: 417-424.
14. Chowdhury, Z.Z., S.B.A. Hamid, R. Das, M.R. Hasan, S.M. Zain, K. Khalid and M.N. Uddin, 2013. Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution. *BioResources*, 8: 6523-6555.
15. Sentorun-Shalaby, C., M.G. Ucak-Astarlioglu, L. Artok and C. Sarici, 2006. Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones. *Microporous Mesoporous Mater.*, 88: 126-134.

16. Sugumaran, P., V.P. Susan, P. Ravichandran and S. Seshadri, 2012. Production and characterization of activated carbon from banana empty fruit bunch and *Delonix regia* fruit pod. *J. Sustainable Energy Environ.*, 3: 125-132.
17. Cui, H., Y. Cao and W.P. Pan, 2007. Preparation of activated carbon for mercury capture from chicken waste and coal. *J. Anal. Applied Pyrolysis*, 80: 319-324.
18. Nunes, C.A. and M.C. Guerreiro, 2011. Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers. *Quimica Nova*, 34: 472-476.
19. Marsh, H. and F. Rodriguez-Reinoso, 2006. *Activated Carbon*. Elsevier, Amsterdam, The Netherlands, ISBN-13: 9780080455969, Pages: 554.
20. Adib, M.R.M., W.M.S.W. Suraya, H. Rafidah, A.R.M. Amirza, M.H.M.N. Attahirah, M.S.N.Q. Hani and M.S. Adnan, 2016. Effect of phosphoric acid concentration on the characteristics of sugarcane bagasse activated carbon. *IOP Conf. Ser.: Mater. Sci. Eng.*, Vol. 136. 10.1088/1757-899X/136/1/012061.
21. Ekpete, O.A. and M. Horsfall Jr., 2011. Preparation and characterization of activated carbon derived from fluted pumpkin stem waste (*Telfairia occidentalis* Hook F). *Res. J. Chem. Sci.*, 1: 10-17.
22. Samal, D.P., 2014. Characterization of activated carbon and study of adsorption of methylene blue dye using activated carbon. BTech Thesis, National Institute of Technology, Rourkela.
23. Laine, J., A. Calafat and M. Labady, 1989. Preparation and characterization of activated carbons from coconut shell impregnated with phosphoric acid. *Carbon*, 27: 191-195.
24. Gumus, R.H. and I. Okpeku, 2015. Production of activated carbon and characterization from snail shell waste (*Helix pomatia*). *Adv. Chem. Eng. Sci.*, 5: 51-61.
25. Budinova, T., D. Savova, B. Tsyntsarski, C.O. Ania, B. Cabal, J.B. Parra and N. Petrov, 2009. Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions. *Applied Surf. Sci.*, 255: 4650-4657.
26. Cao, X. and W. Harris, 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour. Technol.*, 101: 5222-5228.
27. Tsai, W.T., S.C. Liu, H.R. Chen, Y.M. Chang and Y.L. Tsai, 2012. Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. *Chemosphere*, 89: 198-203.
28. Rafiq, M.K., R.T. Bachmann, M.T. Rafiq, Z. Shang, S. Joseph and R. Long, 2016. Influence of pyrolysis temperature on physico-chemical properties of corn stover (*Zea mays* L.) biochar and feasibility for carbon capture and energy balance. *PLoS ONE*, Vol. 11. 10.1371/journal.pone.0156894.
29. Ronsse, F., S. van Hecke, D. Dickinson and W. Prins, 2013. Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *GCB Bioenergy*, 5: 104-115.
30. Khalili, N.R., M. Campbell, G. Sandi and J. Golas, 2000. Production of micro- and mesoporous activated carbon from paper mill sludge: I. Effect of zinc chloride activation. *Carbon*, 38: 1905-1915.
31. Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (Biochar). *Environ. Sci. Technol.*, 44: 1295-1301.
32. Mukherjee, A., A.R. Zimmerman and W. Harris, 2011. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, 163: 247-255.
33. Li, W., K. Yang, J. Peng, L. Zhang, S. Guo and H. Xia, 2008. Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars. *Ind. Crops Prod.*, 28: 190-198.
34. Arjmand, C., T. Kaghazchi, S.M. Latifi and M. Soleimani, 2006. Chemical production of activated carbon from nutshells and date stones. *Chem. Eng. Technol.*, 29: 986-991.
35. Park, S.J. and K.D. Kim, 2001. Influence of activation temperature on adsorption characteristics of activated carbon fiber composites. *Carbon*, 39: 1741-1746.
36. Gratuito, M.K.B., T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya and A. Dutta, 2008. Production of activated carbon from coconut shell: Optimization using response surface methodology. *Bioresour. Technol.*, 99: 4887-4895.
37. Olawale, A.S. and O.A. Ajayi, 2009. Thermal activation of *Canarium schweinfurthi* nutshell. *Aust. J Basic Applied Sci.*, 3: 3801-3807.
38. Abechi, S.E., C.E. Gimba, A. Uzairu and Y.A. Dallatu, 2013. Preparation and characterization of activated carbon from palm kernel shell by chemical activation. *Res. J. Chem. Sci.*, 3: 54-61.
39. Wang, X., D. Li, W. Li, J. Peng and H. Xia *et al.*, 2013. Optimization of mesoporous activated carbon from coconut shells by chemical activation with phosphoric acid. *BioResources*, 8: 6184-6195.
40. Rouquerol, F., J. Rouquerol and K. Sing, 1999. *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*. Academic Press, London, UK., ISBN-13: 9780080526010, Pages: 467.