COMPARISON OF VARIOUS SOURCES OF HIGH SURFACE AREA CARBON PREPARED BY DIFFERENT TYPES OF ACTIVATION

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Abstract

Activated carbon has been known as an excellent adsorbent and is widely used due to its large adsorption capacity. Activation condition and types of activation influence the surface area and porosity of the activated carbon produced. In this study, palm kernel shells and commercially activated carbon were used. To convert palm kernel shells into coal, two methods were employed, namely chemical activation and physical activation. For chemical activation, two activating agents, zinc chloride and potassium carbonate, were used. The activated carbons were analyzed using Fourier Transform Infrared (FTIR) spectroscopy, single point BET and free emission scanning electron microscopy (FESEM). The commercial activated carbon was also characterized. FTIR results indicate that all the palm kernel shells were successfully converted to carbon. Single point BET surface area of all the carbons prepared were obtained. From FESEM micrograph, the chemically activated palm kernel shells shows well highly defined cavities and pores. This study also shows that palm kernel shells can be used to be a better source of high surface area carbon.

Karbon teraktif dikenali sebagai bahan penjerap yang baik dan digunakan secara meluas kerana kapasiti penjerapannya yang tinggi. Kaedah dan jenis pengaktifan yang digunakan mempengaruhi luas permukaan dan sifat keliangan karbon teraktif yang dihasilkan. Dalam kajian ini, tempurung kelapa sawit dan karbon teraktif komersial digunakan. Bagi menukarkan tempurung kelapa sawit kepada arang, dua kaedah digunakan iaitu, pengaktifan secara kimia dan fizikal. Bagi pengaktifan secara kmia, dua jenis agen pengaktifan digunakan, zink klorida dan kalium karbonat. Karbon yang telah diaktifkan seterusnya dianalisis menggunakan spektroskopi Inframerah Transformasi Fourier (FTIR), penjerapan titik tunggal BET dan mikroskopi imbasan electron pancaran bebas (FESEM). Karbon teraktif komersial juga turut dianalisis. Keputusan FTIR menunjukkan bahawa kesemua tempurung kelapa sawit berjaya ditukarkan kepada karbon. Luas permukaan penjerapan titik tunggal BET bagi kesemua sampel telah diperolehi. Daripada mikrograf FESEM, tempurung kelapa sawit yang diaktifkan secara kimia menunjukkan liang dan rongga yang jelas. Kajian ini juga menunjukkan bahawa tempurung kelapa sawit boleh menjadi sumber karbon berluas permukaan tinggi yang lebih baik.

Introduction

Activated carbons are disordered, microporous forms of carbon, with very high porosity and surface area. They can be prepared from a large number of raw materials, especially agro-industrial by-products such as olive stones [1], coconut shells [2], walnut shells [3] and macadamia nutshells [4]. These by-products are often considered as wastes and have caused significant disposal problems in some countries. Their utilization in the activated carbon industries is a feasible solution to this environmental issue.

In Malaysia, palm kernel shell is one of the main agriculture wastes from the palm oil industries. It is estimated that for every one million tonnes of palm oil produced, 0.8 million tonnes of palm shells is created [5]. Based on a total oil production of 7.4 million tonnes in 1993, the amount of palm shell generated in that year alone was about 6 million tonnes. Palm kernel shell is proposed to be used as a prospective starting material for activated carbon because of its relatively high fixed carbon content (about 18 %w/w), low ash content (less than 0.1 % w/w) and the presence of inherent porous structures [6].

Activated carbon is widely used for a number of applications, such as separation of gases, recovery of solvent, removal of organic pollutants from drinking water and as a catalyst support, among many other operations. It is most widely used because of its large adsorption capacity and low cost. Activated carbons are important adsorbents in various industrial sectors such as the food, pharmaceutical and chemical industries [7]. For an

example, Ghana imports large quantities of activated carbon annually especially for gold mining industries to recover gold from cyanide solution using the carbon-in-pulp or carbon-in-leach processes [8]. Furthermore, as environmental pollution is increasingly becoming a serious problem, the demand for activated carbon is growing.

The process for manufacturing activated carbons involves two steps; the carbonization of raw carbonaceous materials and the activation of the carbonized product. Two methods are used to prepare activated carbons, namely physical activation and chemical activation. In the physical activation, the raw material is carbonized and consequently the prepared char is reacted with steam or CO_2. In chemical activation, the raw material is mixed with an activation reagent and the mixture is heated in an inert atmosphere.

The carbonization leaves an imprint effect on the final product [5]. The purpose of carbonization process is to enrich the carbon content and to create an initial porosity in the char. The activation process further develops the porosity and creates some ordering of the structure to generate a highly porous solid as the final product.

In this study, three types of activated carbon were prepared using palm kernel shell as the starting materials. Both chemical and physical activation were employed. For chemical activation, two activating agents were used; zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3). As a comparison, commercial activated carbon was used. $ZnCl_2$ was chosen because it is the most widely used chemical in the production of activated carbons. On the other hand, K_2CO_3 was used because it is non deleterious such as KOH or NaOH since it is also used as food additive [9]. As for physical activation, direct heating under vacuum atmosphere was carried out where the carbonization and activation steps proceed simultaneously.

EXPERIMENTAL

Reagents
Commercial activated carbon (99.9%) with molecular weight of 12.01 gmol^{-1} was purchased from Scharlau Chemise S.A. Zinc chloride ($ZnCl_2$) and sodium carbonate (Na_2CO_3) from Goodrich Chemical Enterprise were used along with concentrated hydrochloric acid (HCl), 37% w/w purchased from J.T. Baker. Potassium carbonate (K_2CO_3) was obtained from Fluka Chemie AG. The palm kernel shell was obtained from Kulai palm oil mill.

Chemical Activation
100 g of $ZnCl_2$ was added to 100 g of palm kernel shell in a beaker of 1 L. $ZnCl_2$ acts as the chemical activating agent. 100 mL of concentrated HCl (37% w/w) and 10 mL deionized water were added to the beaker. The mixture was stirred and heated at 100 - 110°C until it was fully dried. The treated char was kept in oven overnight for dehydration purpose. About 0.5 g of the dehydrated char was placed in a quartz tube and then connected to a vacuum line system. The sample was then heated at 800°C for two and four hours respectively under 1×10^{-3} mbar pressure. The activated samples were neutralized with diluted Na_2CO_3 solution and deionized water. The washing process was repeated until the pH is approximately 7. Sample was then dehydrated in oven at 100°C. The sample obtained was labeled as CZ-AC 2h and CZ-AC 4h.

As for the second activating agent, 100 g of K_2CO_3 was added to 100 g of palm kernel shell in 1 L beaker. 100 mL of distilled water was added to the beaker. The mixture was then treated with the same heating and activation processes as above. The activated samples were then neutralized using hot distilled water. The washing process was also repeated until the pH is approximately 7. The sample was then dehydrated in oven at 100°C. The sample obtained was labeled as CK-AC 2h and CK-AC 4h.

Physical Activation
About 0.5 g of crushed palm kernel shells was placed in a quartz tube. The sample was subjected to the same activation under vacuum atmosphere for two and four hours as described above. The samples were heated at 800°C. The samples obtained were labeled as P-AC 2h and P-AC 4h.

Characterization of Samples
Fourier Transform Infrared (FTIR) analysis was carried out using Shimadzu 8300 spectrometer with wave number ranging from 400 to 4000 cm^{-1}. Single point BET surface area was measured at temperature of   77 K

using Micromeritics Pulse Chemisorb 2705. Free emission scanning electron microscopy (FESEM) and energy disperse analysis through X-ray (EDAX) were performed using SUPRA 35VP.

Results and Discussion

Fourier Transform Infrared Spectroscopy

Figure 1 shows the FTIR spectra of raw palm kernel shell (PKS), commercial activated carbon, X-AC and samples activated for two hours, CZ-AC 2h, CK-AC 2h, and P-AC 2h. The X-AC FTIR spectrum was used as a reference for comparison with other synthesized activated carbon. Figure 2 also shows the raw PKS and X-AC spectra along with samples activates for four hours, CZ-AC 4h, CK-AC-4h and P-AC 4h. By interpreting the infrared transmittance spectrums, the functional group in the sample can be determined.
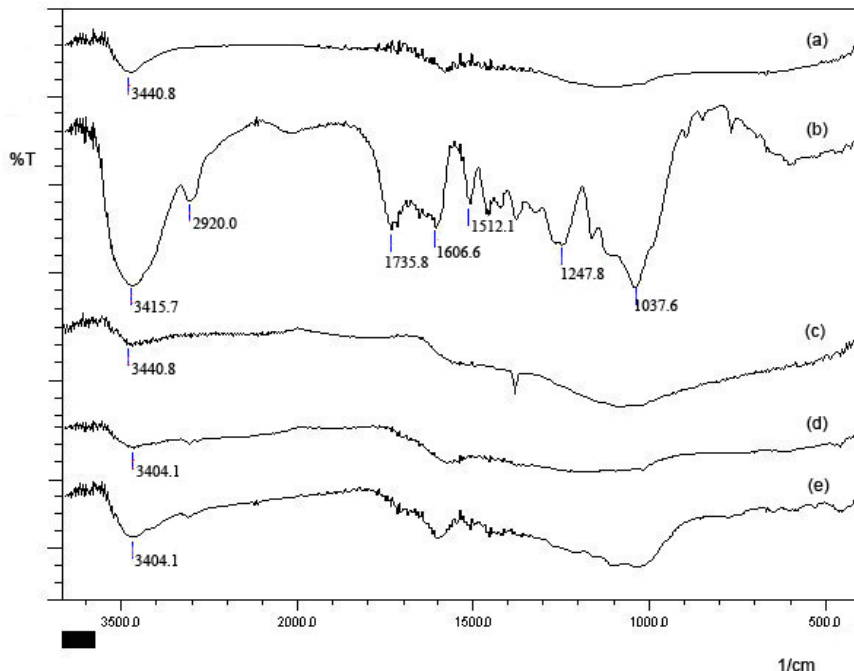

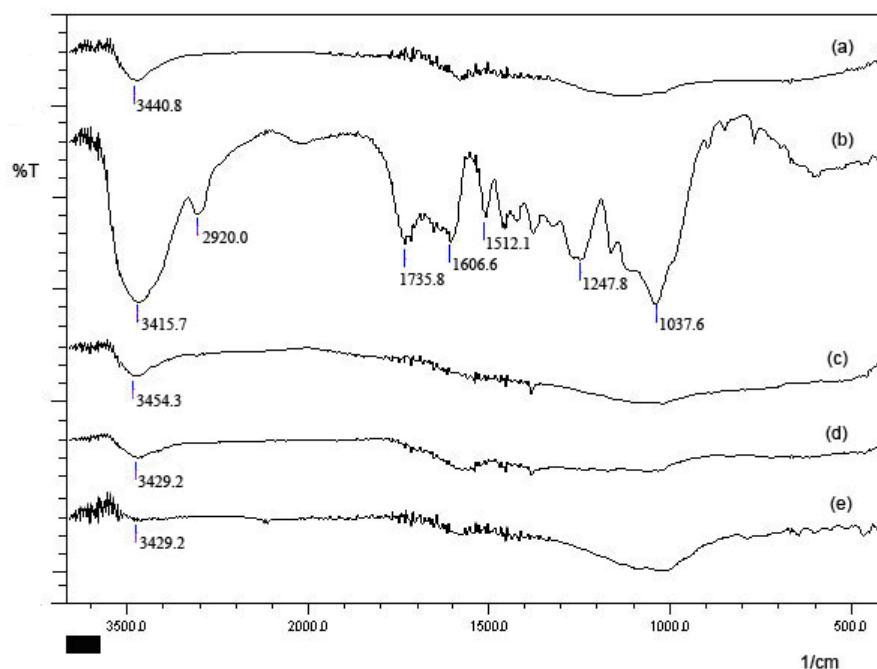Figure 1**.** FTIR spectra for (a) X-AC, (b) raw PKS, (c) CZ-AC 2h, (d) CK-AC 2h and (e) P-AC 2h

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Figure 2. FTIR spectra for (a) X-AC, (b) raw PKS, (c) CZ-AC 4h, (d) CK-AC-4h and (e) P-AC 4h

Based on both Figure 1 and Figure 2, only raw PKS shows the most complicated and apparent spectrum. A strong and broad adsorption peak appeared at 3415.7 cm^{-1}, corresponding to the stretching of O–H functional group and this indicates the presence of bonded hydroxide in the raw sample. There was another peak observed at 2920.0 cm^{-1} corresponding to the C–H sp^3 stretching. A strong C=O peak could be observed at 1735 cm^{-1}. This sample also shows two important absorption peaks at 1247.8 and 1037.6 cm^{-1} which represents the stretching of C–O functional group.

Unlike the FTIR spectrum showed by raw PKS, spectra of CZ-AC 2h, CZ-AC 4h, CK-AC 2h, C-AC 4h, P-AC 2h and P-AC 4h illustrate less absorption peaks. Although the samples were prepared via various activation method, there was a similarity in the adsorption patterns. Basically all the samples showed a weak broad peak around 3350 – 3450 cm^{-1} which indicates the presence of hydroxide in the samples. It is suggested that the samples traps moisture on its surface during sample handling due to their adsorptive nature.

From the samples spectra obtained, clearly, most of the absorption peaks of functional groups were diminished. During the carbonization and activation processes, the functional groups as observed from the raw PKS spectrum were evaporated as volatile materials when heat was applied to the samples. This proved that the activation process have taken place successfully.

The trends of all the samples spectra were almost similar with the commercial activated carbon spectrum which was used as the reference sample. Consequently, this indicates that all the prepared samples were successfully converted into carbon. Table 1 summarized the FTIR absorption data incorporating functional groups from the FTIR spectra shown in both Figure 1 and Figure 2.

Furthermore, both figures shows apparent decrease in the broad C–O peak around 1250 – 1000 cm^{-1} and C=C absorption band around 1650 – 1500 cm^{-1} for the prepared samples spectra towards the raw PKS spectrum. Samples activated for four hours showed clearer peaks reduction than the two hours activation. This is best explained particularly by the P-AC 2h and P-AC 4h spectrums. The decreasing bands suggest that activation time influenced the prepared samples. This indicates that four hours activation time is favorable than two hours activation time.

Table 1. Absorption frequencies and functional groups of the samples

Sample	Absorption frequencies (cm^{-1})	Functional Group
raw PKS	3415.7	O – H stretching
	2920.0	C – H (sp^3) stretching
	1735.8	C = O stretching
	1606.6 , 1512.1	C = C (aromatic) stretching
	1247.8 , 1037.6	C – O stretching
X-AC	3440.8	O – H stretching
CZ-AC 2h	3440.8	O – H stretching
CZ-AC 4h	3454.3	O – H stretching
CK-AC 2h	3404.1	O – H stretching
CK-AC 4h	3429.2	O – H stretching
P-AC 2h	3404.1	O – H stretching
P-AC 4h	3429.2	O – H stretching

Single Point BET Surface Area
The single point BET surface area analysis at temperature of 77 K was performed to determine the surface area obtained for the activated carbon prepared by different activation method. All the data collected, including the raw PKS and commercial activated carbon were presented in the form of a bar chart in Figure 3.
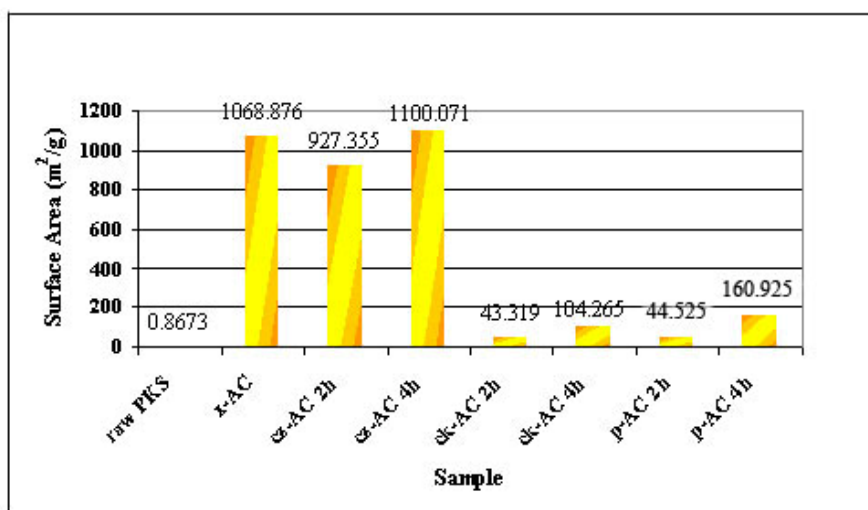

Figure 3. Single Point BET surface area of raw PKS, X-AC and synthesized carbons

Raw PKS gives only 0.8673 m^{2}g^{-1} of BET surface area. From the graph, all the synthesized carbon gave extensively higher BET surface area which drastically increased after the activation process. Based on the results obtained, CZ-AC 4h showed the highest BET surface area among the prepared carbons with 1100.071 m^{2}g^{-1}. Moreover, CZ-AC 4h also exhibits slightly higher surface area compared to the commercial activated carbon with only 1068.876 m^{2}g^{-1}.

It is also found that CK-AC 2h, CK-AC 4h, P-AC 2h and P-AC 4h gave relatively low BET surface area. When it was compared to CZ-AC 4h and CZ-AC 2h obviously there was a pronounced decrease in the BET surface area. This result suggests that the chemical activating agent used, ZnCl$_2$, has contributed to the higher surface area. The used of ZnCl$_2$ as the activating agent resulted in more new pores being created and the existing pores widened to give activated carbon with higher BET surface area [10].
From the results obtained, samples activates for four hours shows relatively higher BET surface area than

samples activates for only two hours. This findings support the previous results obtain from FTIR that suggested that the activation duration affects the final product in preparing high surface area activated carbon. However, the surface areas for CK-AC 2h, CK-AC 4h, P-AC 2h and P-AC 4h which are, 43.319, 104.265, 44.525 and 160.925 m^2g^{-1} respectively didn't achieve the range of activated carbon surface area. Typically, the surface area of activated carbon ranges from 500 to 1400 m^2g^{-1} [8].

Free Emission Scanning Electron Microscopy
The surface morphology of the samples was studied using FESEM. Figure 4 shows the micrograph of X-AC. The commercial activated carbon was in highly amorphous form. From the micrograph, no pores could be detected even though it has a high BET surface area results. It is suggested that the pores were diminished during the product manufacturing in order to get a powder form. Nevertheless, the micrograph also illustrate that the X-AC have fine particle size.
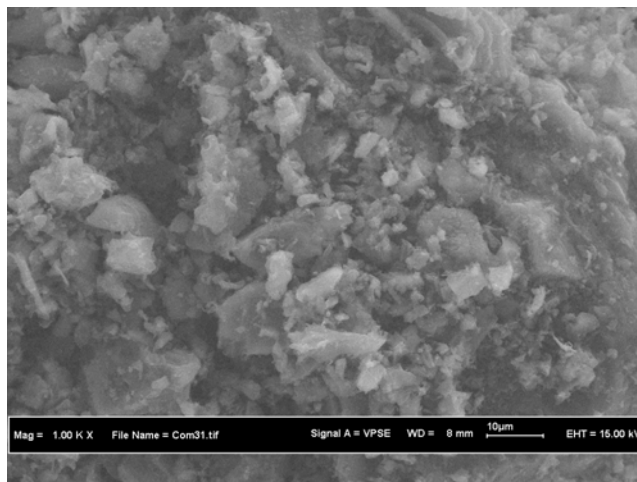

Figure 4**.** Micrograph for X-AC with magnification of 1000×

Figure 5(a) shows the micrograph for raw PKS. The surface was rough and dented. Small pores are also evident on the surface. Figure 5 (b) shows the P-AC 4h micrograph. Generally, the morphology is similar with the raw PKS except, larger pores are observed, resulted in the formation of larger pores from activation. Figures 5(c) and (d) show the micrograph of CZ-AC 4h and CK-AC 4h respectively. The CZ-AC 4h micrograph shows highly defined pores and cavities. The surface differs from the raw PKS surface in that it is cleaner and smooth. However, small particles are randomly scattered among the pores.

As for the CK-AC 4h micrograph, major development of pores could be seen. However, the pores size distributions are non-uniform. Similar to CZ-AC 4h, the surface is clean and smooth. The pore development was so rapid, resulting in too much cavity and lead to cracks formation. The pores are large and are external pores. This explains why the BET surface area value for CK-AC 4h was lower than CZ-AC 4h.

It is also identified that the pores and cavities for CZ-AC 4h were internal pores because the pores could only be seen under the FESEM after being crushed into smaller fraction, though this damages some of the pores formed. This finding corroborates the BET surface area results gathered earlier.
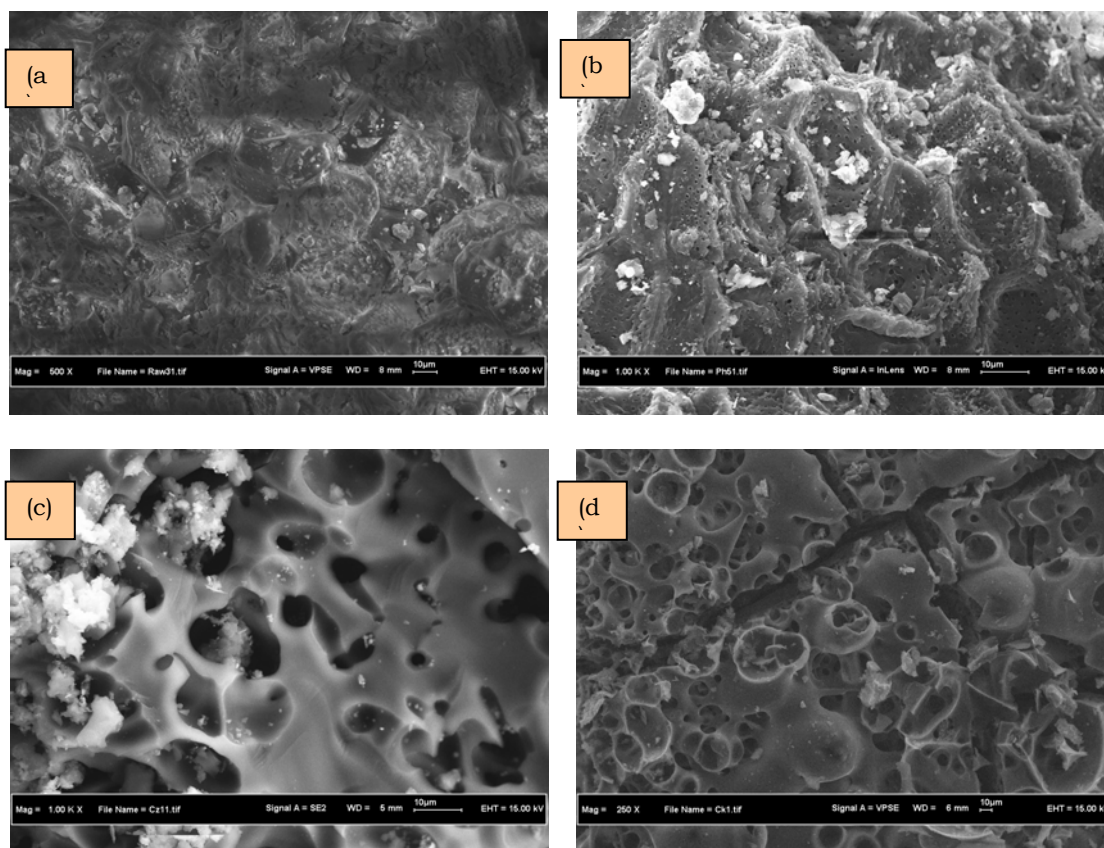
Figure 5. Micrograph for (a) raw PKS with magnification of 500×, (b) P-AC 4h with magnification of 1000×, (c) CZ-AC 4h with magnification of 1000× and (d) CK-AC 4h with magnification of 250×

Energy Disperse Analysis through X-ray Spectroscopy

Table 2 shows the element weight percent (wt %) obtained from EDAX analysis. The raw PKS showed the presence of carbon, oxygen, aluminum and silicon with 46.18, 45.08, 3.47 and 5.27 wt % respectively. While X-AC showed only two elements that are carbon and oxygen with 91.28 and 8.72 wt % respectively. The raw PKS exhibits lower carbon content and higher oxygen content compared to the X-AC. P-AC samples also have the same elements as the raw PKS. However, after the activation process, the carbon content was enriched to 75.77 wt % and the percentage of oxygen, aluminum and silicon are reduced. From the table, CZ-AC 4h showed the highest carbon content among the three prepared samples with 79.47 wt % and the lowest oxygen content, 13.67 wt %. However, CZ-AC 4h exhibits the highest aluminum content. No silicon was observed in this sample. Additional element, zinc, could be detected in this sample with 5.68 wt % suggesting that the chemical impregnation of $ZnCl_2$ took place during the sample preparation.

As for CK-AC 4h sample, it exhibits the lowest carbon content with 69.95 wt % and 19.22 wt % of oxygen. In contrary to CZ-AC 4h, CK-AC 4h shows the lowest aluminum content. No silicon was observed as in CZ-AC 4h. This suggests that the chemical activation removes silicon from the raw PKS. Potassium could be seen as expected for chemical impregnation with 10.22 wt %.

Table 2. Elemental analysis carried out by EDAX Spectroscopy

Sample	C	O	Al	Si	Zn	K	Total (wt %)
	Element (wt %)						
raw PKS	46.18	45.08	3.47	5.27	-	-	100
X-AC	91.28	8.72	-	-	-	-	100
CZ-AC 4h	79.47	13.67	1.18	-	5.68	-	100
CK-AC 4h	69.94	19.22	0.62	-	-	10.22	100
P-AC 4h	75.77	21.2	1.12	1.91	-	-	100

EDAX analysis strengthens the fact that CZ-AC 4h is the best activated carbon prepared with the highest carbon content and the lowest oxygen content. Still, the X-AC showed higher and finer form of activated carbon.

Conclusions

In this study, three different types of carbons were successfully prepared. The study showed that the type, condition and time of the activation process influenced the physical properties of an activated carbon. FTIR results indicate that all the palm kernel shell was successfully converted into carbon. Single point BET surface area of all the carbons prepared were obtained and CZ-AC 4h showed the highest surface area with 1100.071 m^2 g^{-1}, even higher surface area than the commercially activated carbon. From FESEM micrograph, the chemically activated palm kernel shells showed well developed pores and clean surface compared to the raw PKS. CZ-AC 4h exhibits internal and highly defined cavities and pores. EDAX analysis strengthens the fact that CZ-AC 4h is the best activated carbon prepared. This study also shows that palm kernel shells can be used to be a better source of high surface area carbon.

Acknowledgement

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