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Pore Diameter and Carbon Composition of Walnut Shells of Tidore Islands, North Maluku, Indonesia

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ABSTRACT

Walnut shell carbon was produced using the pyrolysis method at 350 °C. The pyrolyzed carbon was activated using 3M of KOH activator. The pyrolyzed and KOH-activated carbon were analyzed with FTIR, SEM-EDX, and XRD. The functional group identified from the KOH-activated carbon of the walnut shell is the aromatic C-H group, C-H aliphatics, C-O alcohol, C-O acetic acid, and C-O ester. The diameter of the pyrolyzed carbon pores is 333.9-2839 nm, while the KOH-activated one is 1217-2137 nm. The composition of the carbon elements increased from 70.6% (pyrolised carbon) to 79.40% (KOH-activated). Based on the results of the XRD analysis, both carbons show widening and amorphous peaks.

Keywords: Walnut Shell, Carbon, Pyrolysis, Carbon activation, FTIR, SEM, EDX, XRD.

INTRODUCTION

Walnut (*Canarium vulgare leenh*) is a native Indonesian plant that grows mostly in Eastern regions, such as Maluku and Tidore. Walnuts are very popular with consumers in Maluku because of their good taste. Maluku and Tidorean people like to consume walnuts that have not been dried. Walnuts are rich in saturated and unsaturated fatty acids.[1] A walnut shell is a part of the walnut fruit not utilized by the community, is discarded as waste, and is considered to have no economic value. Walnut shells have a strong physical structure sufficient to be utilized as charcoal. In Indonesia, about 86 tons per year of walnut shells are not optimally utilized, some of which are only used as firewood, and the rest are thrown away.[2] Walnut skin and shells are a major source of lignocellulose.[3] However, walnut shell waste can be converted into activated carbon, a processed product of walnut shell pyrolysis.[4] The chemical composition of the walnut shell consists of 39.24% cellulose, 38.00% lignin, 11.72% water, 9.25% hemicellulose, and 1.79% ash.[5] The main products resulting from the pyrolysis of walnut shells are charcoal 36.80%, liquid smoke 42.58%, tar 4.48%, and 15.79% volatile noncondensable gas components.[5] Their functional groups vary, namely hydroxy 3 groups (R-OH), carbonyl (R-C=O), esters (R-CO-O-R'), alkanes (R-CH_2), carboxyl (R-COOH) and aromatic groups (R-CH).[6,7]

Charcoal is a porous material; tar, hydrocarbons, and other organic compounds cover most portions. Besides generating charcoal, this heating or decomposition process produces other products, such as liquids and gases. [8,9] Pyrolysis is the process of heating at a high or a predetermined temperature without oxygen, and activation uses

chemicals.[10,11,12] Activated carbon with high porosity and surface area can be obtained through hydroxy alkalis chemical processes.[13,14] Among the existing hydroxy alkalis (NaOH, LiOH, and KOH), KOH is the most effective activator that has been widely studied.[15,16] The activated carbon widely used as an absorbent material in industry.[15,17.]

In this study, walnut shells were taken from the mountains in Tidore Islands Regency. Walnut trees that grow in the mountains affect the composition of the elements that make up the walnut shell. The choice of KOH as an activator for the chemical activation process on carbon materials is considered very appropriate due to its strong base and hygroscopic properties.[18, 19] The chemical activation process is to activate walnut shell carbon by adding certain chemicals to the sample and increase the pore diameter so that the carbon pores are open.[20,21] After the carbonization process, the carbon is chemically activated with the help of chemical solutions such as acidic.[22] or basic compounds.[23] Furthermore, walnut shell charcoal was characterized using instruments Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), and X-ray Diffraction (XRD). XRD is used to obtain structural information and the character of walnut shell charcoal. XRD analysis can reveal significant changes in crystal size for samples carbonized at a wide temperature range (900-1500°C).[24]

EXPERIMENTAL

Tools and materials

The tools used were glassware, oven, furnace, porcelain cup, 100 mesh filter, FTIR, SEM-EDX, XRD. The materials used were walnut shells from the Tidore Islands district, North Maluku, Indonesia, 3M KOH, distilled water, filter paper and universal indicator.

Research procedure

The walnut shell samples were cleaned from the shells attached to the outside and dried in the sun to reduce the water content. The walnut shell samples were pyrolyzed in a pyrolysis reactor and heated to 350°C for 6 hours. The resulting charcoal or carbon was allowed to cool, and then it was ground using a mortar and sieved and filtered through a 100 mesh sieve. A fine filtered 20 g of walnut shell carbon was immersed in 100 mL of 3M KOH solution for 24 hours. The mixture was filtered using filter paper, then washed with distilled water until the washing solution became neutral at pH ±7. The residue was dried in an oven at 110-120 ^{o}C for 4 hours. After that, it was stored in a desiccator until the carbon stabilized.[17, 20, 25] FTIR measurements using a Shimadzu type IRprestige-21 FTIR Spectrophotometer working at a scan range of 4000-340 cm-1, resolution of 4 cm-1, and scan of 2-3 seconds. Paired with an EDX device, SEM was used to examine the morphology and determine the relative carbon content or composition [26]. X-ray diffraction (XRD) analysis is the basic method to evaluate the structure of carbon arrays or determine the crystal structure.[17, 27]

RESULTS AND DISCUSSION

FTIR Analysis

FTIR analysis determines the functional groups present and lost after carbon activation based on the absorption band pattern at the wavenumber. The FTIR characterization results of pyrolyzed (control) and KOH-activated walnut shell carbon are shown in Figure-1. The FTIR spectra of pyrolyzed and KOH-activated walnut shell carbon have almost the same absorption band pattern. A comparison of the two spectra showed that after KOH activated the carbon, there was a shift in the wavenumber from 3028.24 cm^{-1} to 3068.75 cm^{-1}. Absorption intensity decreased at wavenumbers 1259.52 cm^{-1} and 879.5 cm^{-1}, down to 1234.44 cm^{-1} and 875.68 cm^{-1}. There is also new absorption of KOH-activated carbon wave numbers 2422.59 cm^{-1}, 1317.38 cm^{-1}, 1234.44 cm^{-1}, and 590.22 cm^{-1}. The loss of several absorption peaks and the decrease in absorption intensity indicate the reduction of impurities in carbon. It indicates the formation of aromatic compounds, constituents of the carbon structure.[28]

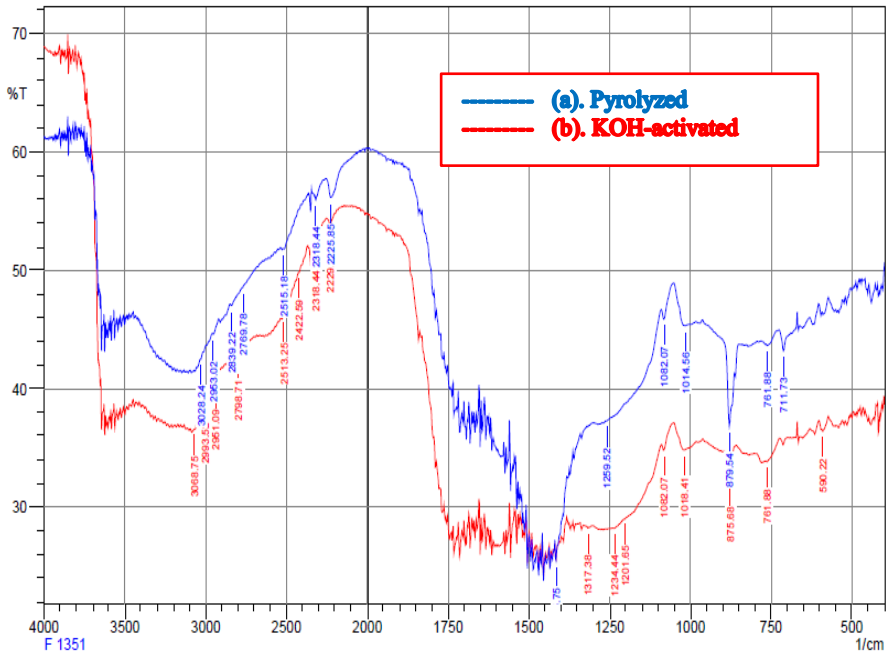


Fig.-1: FTIR Spectra of Pyrolyzed (a) and KOH-Activated Walnut Shell Carbon (b).

Absorption functional groups (seen Tabel 1), at wave numbers 3028.24 - 3068.75 cm^{-1} indicates the presence of C-H functional groups in aromatic groups, followed by absorption at wave numbers 879.54-590.22 cm^{-1}, the vibration of secondary aromatic C-H groups.[29] The absorption at wave number 1317.38 cm^{-1} shows the vibration of the C-O group of alcohol and carboxylic acid. Absorption at wave numbers 1259.52-1234.44 cm^{-1} and 1082.07 cm^{-1} show the presence of C-O ester functional groups. The absorption at wave numbers 879.54-875.68 cm^{-1} and 761.88 cm^{-1} show aromatic C-H vibrations.[30]

Table-1: FTIR Spectra Absorption Bands of Pyrolyzed and KOH-Activated Walnut Shell Carbon.

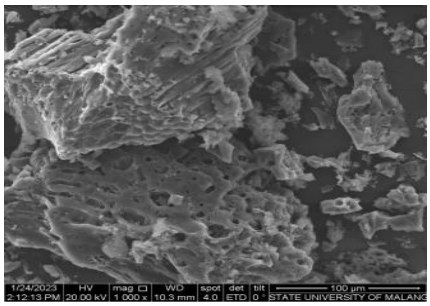
Wave number (cm^{-1})		Functional Group
3028.24	3068.75	C-H aromatic
2422.59	2422.59	C-H aliphatic
1317.38	1317.38	C-O alcohol/carboxylic acid
1259.52	1234.44	C-O ester
1082.07	1082.07	C-O ester
879.54	875.68	C-H aromatic
761.88	761.88	C-H aromatic
	590.22	C-H aromatic

SURFACE MORPHOLOGY ANALYSIS OF WALNUT SHELL CARBON

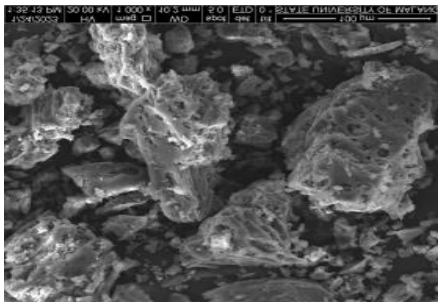
The pyrolysis process of walnut shells is an important step in obtaining carbon as the final product. Pyrolysis is a heating process without oxygen that aims to carbonize and increase carbon content. The surface morphological structure of carbon from pyrolyzed walnut shell and carbon after KOH activation was analyzed by Scanning Electron Microscopy (SEM). The results of SEM analysis on pyrolyzed walnut shell carbon and carbon after KOH activation are shown in Figure-2. Figure-2 (a, b, c) shows the surface morphology of walnut shell carbon from pyrolysis and after KOH activation (d, e, f) with magnifications of 1000, 3000, and 5000, both of which have different pore surfaces that are non-uniform and irregular. The pyrolysis process and the addition of the KOH activator produce outer pores with non-uniform surfaces scattered throughout the carbon surface.[31] Adding

a KOH solution activator to walnut shell carbon aims to dissolve metal elements contained in carbon and increase carbon content. The activation process causes many volatile compounds to be released or vaporized, thus opening carbon pores and reducing hydrocarbon closure which is in accordance with what has been previously stated.[9,32] that the formation and enlargement of pores caused by the evaporation of degraded cellulose components. There needs to be more uniformity in the pore structure on the carbon surface, indicating the presence of organic impurities or tar that has not evaporated and covered some pores.[21,33]

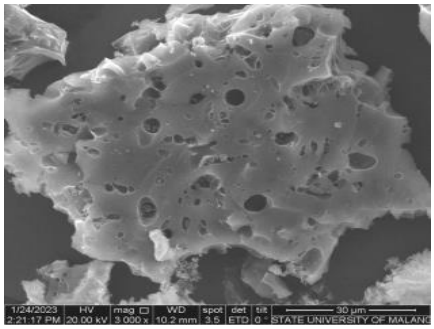
Control Charcoal | KOH-Activated Charcoal



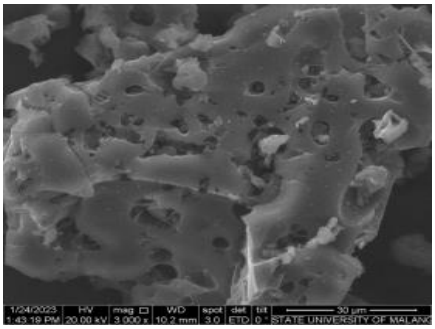
(a) 1000x



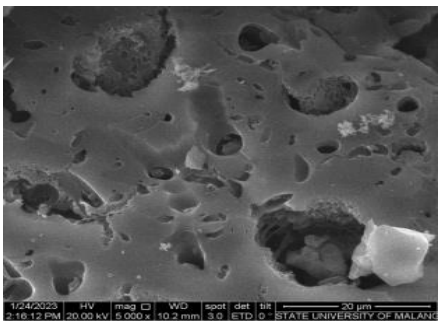
(d) 1000x



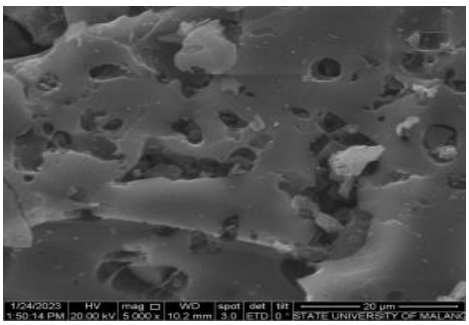
(b) 3000x



(e) 3000x



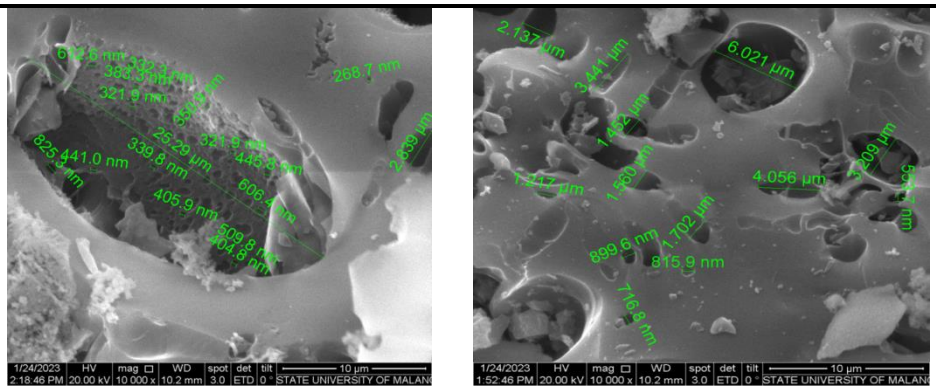
(c) 5000x



(f) 5000x

Fig.-2: SEM Surface Morphology of Pyrolyzed (a-c) and KOH-Activated (d-f) Walnut Shell Carbon With Magnification 1000, 3000, and 5000x.

Figure-3 shows the SEM morphology of pyrolyzed (a) and KOH-activated (b) walnut shell carbon with a magnification of 10,000x, respectively. It can be seen that the pore diameter of pyrolyzed and KOH-activated walnut shell carbon varies greatly. The pore diameters are not uniform (Table-2). The pore diameter of pyrolyzed walnut shell carbon ranges from 339.8 nm to 2,839 µm. In contrast, the pore diameter of KOH-activated walnut shell carbon ranges from 1,217 µm to 2,137 µm. The pore diameter of KOH-activated walnut shell carbon is larger than the pyrolyzed one, but the difference in pore diameter between one and the other is not too large.[28]



(a) (b)

Fig.-3: SEM Morphology of Pyrolyzed (a) and KOH-Activated (b) Walnut Shell Carbon at 10,000x Magnification.

The results showed that these pores are macro pores.[34,35], with a pore diameter of over 50 nm. The non-uniformity of pore diameter is influenced by factors KOH activator[36] and contains other chemically bound elements such as oxygen and hydrogen.[37,38,39]

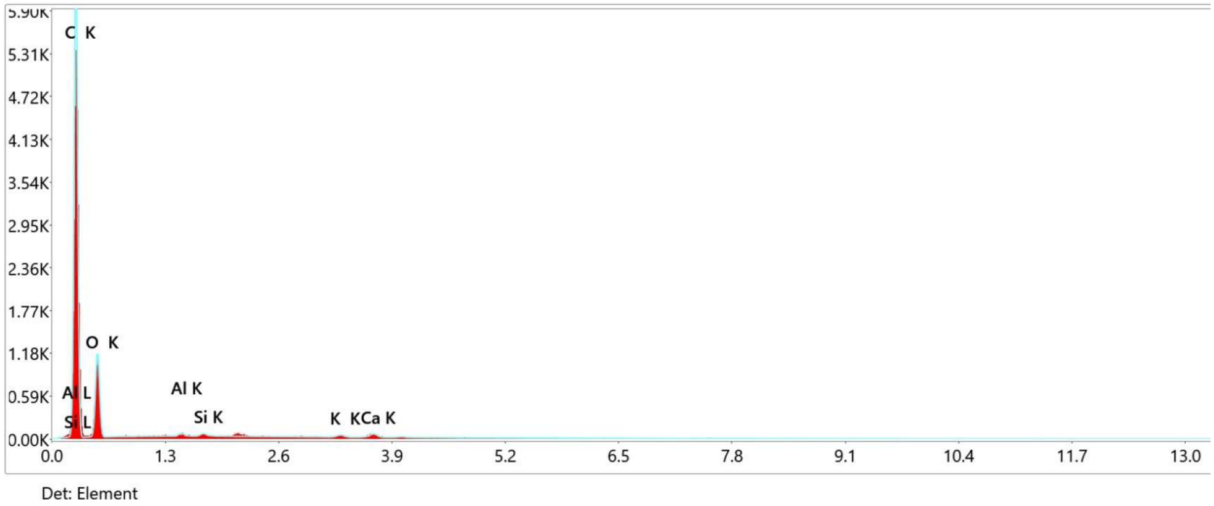
Table 2: Pore Diameter of Pyrolyzed and KOH-Activated Walnut Shell Carbon.

Pyrolysis		KOH-activated	
Pore diameter	Unit	Pore diameter	Unit
2.839	µm	2.137	µm
25.29	µm	1.217	µm
268.7	nm	1.452	µm
612.6	nm	1.560	µm
339.8	nm	1.702	µm
404.8	nm		
509.8	nm		
350.9	nm		
445.8	nm		
321.9	nm		

EDX ANALYSIS

SEM technique combined with EDX can identify the elements from the phase seen in the microstructure image.[40] Analysis of EDX spectra of pyrolyzed and KOH-activated walnut shell carbon (Figure-4). Table-3 shows that the amount of photoelectron kinetic energy of each element is different. The photoelectron kinetic energy graph of pyrolyzed walnut shell carbon can be seen in Figure-5 (a, b, c). At the same time, the photoelectron kinetic energy graph of KOH-activated walnut shell carbon can be seen in Figure-5 (d, e, f). The photoelectron kinetic energy of pyrolyzed and KOH-activated walnut shell carbon is the same. Element C has a small photoelectron kinetic energy of 0.277 keV, while element Ca has the highest photoelectron kinetic energy of 3.692 keV.

(a)



(b)

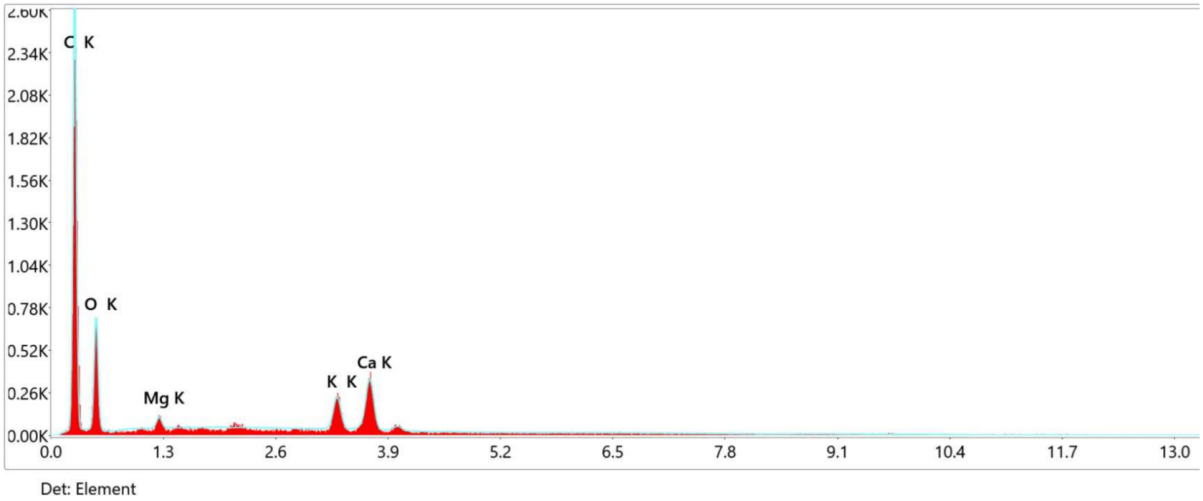


Fig.-4: EDX Spectra of Pyrolyzed (a) and KOH-Activated Walnut Shell Carbon.

Table-3: EDX Analysis Results of Pyrolyzed and KOH-Activated Walnut Shell Carbon.

No	Pyrolyzed				KOH-activated		
	Elements	Photoelectron KE (keV)	Mass (%)	Atoms (%)	Photoelektron KE (keV)	Mass (%)	Atoms (%)
1	C	0.277	70.60	78.20	0.277	79.40	83.80
2	O	0.525	24.10	20.00	0.525	20.10	16.00
3	Mg	1.254	0.30	0.20	1.254	0.00	0.00
4	Al	1.486	0.00	0.00	1.486	0.10	0.00
5	Si	1.740	0.00	0.00	1.740	0.10	0.00
6	K	3.314	1.60	0.60	3.314	0.10	0.00
7	Ca	3.692	3.30	1.10	3.692	0.20	0.10
Total		12.288	99.90	99.90	12.288	100.0	99.90

Karakteristik energi kinetik fotoelektron dari unsur karbon hasil pirolisis dan karbon hasil aktivasi KOH adalah sama, sedangkan persen (%) massa dan persen (%) atom masing-masing unsur berbeda[28].

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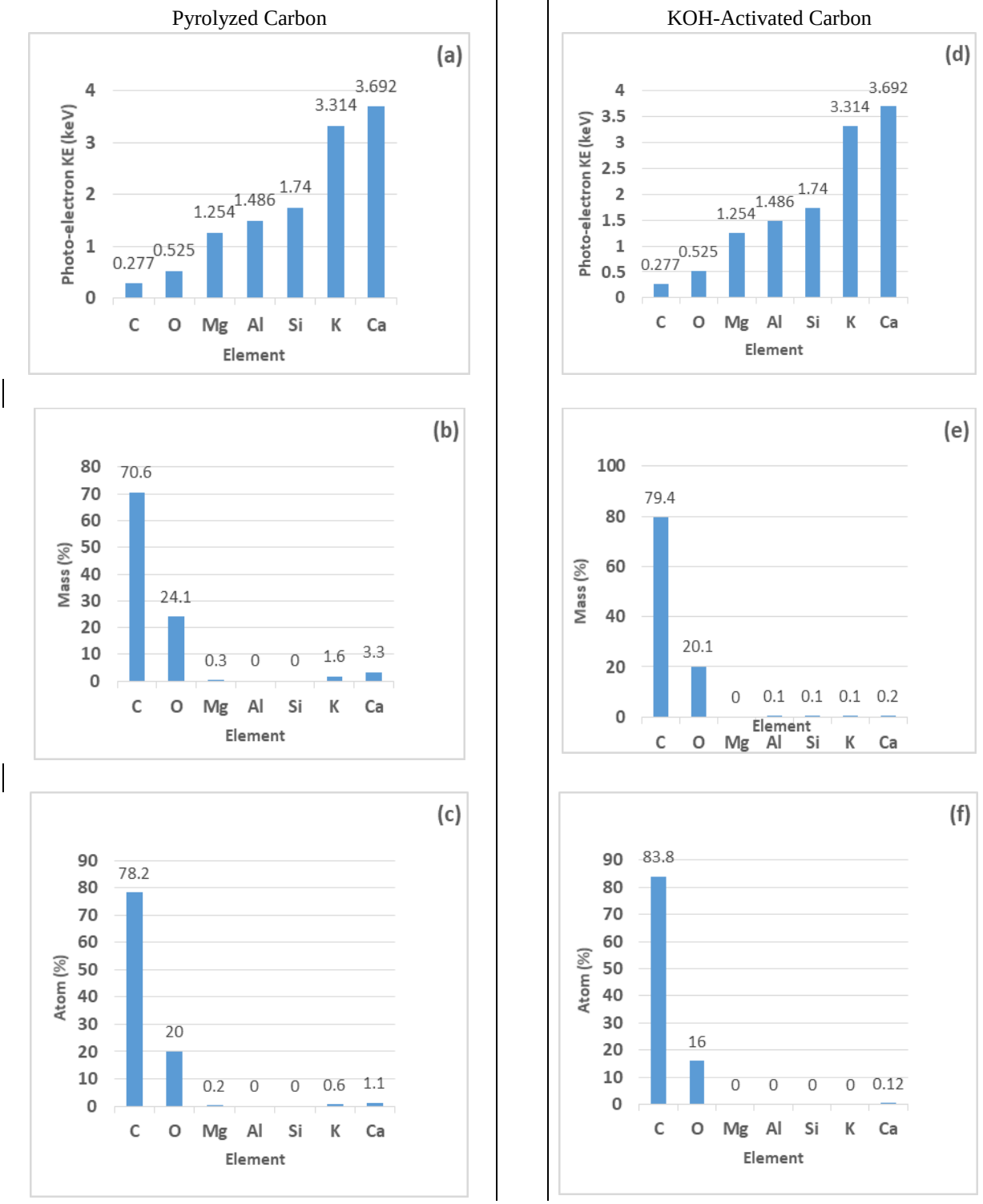

Fig.-5. Graphs of (a and d) KE Photo Electron, (b and e) Mass %, (c and f) Aomic % of Pyrolyzed and KOH-Activated Walnut Shell Carbon.

The percent mass and C atoms from the pyrolyzed were 70.60 and 78.20%, respectively. While, for the KOH-activated one is 79.40% and 83.80%. The presences of O, Mg, Al, Si, K, and Ca indicate an incomplete pyrolysis or carbonization process. The increase in carbon content in each carbons is associated with an increase in the number of pores.[41,42] While the increase in pore diameter is due to the loss of impurities, namely O, Mg,

Al, Si, K, and Ca, which are also in accordance with the decrease in impurity. The increase in pore diameter indicates that the walnut shell carbon is purer after activation with the KOH activator.

XRD ANALYSIS

XRD analysis was conducted to identify the sample's crystal phase, crystal structure, and crystallinity.[43] In the XRD characterization, observed diffractograms of pyrolyzed and KOH-activated walnut shell carbon samples are shown in Figure-6 and Figure-7, respectively. Figure 6 shows a broad diffraction background, irregular background intensity, and the absence of sharp peaks, revealing a highly amorphous structure.[30, 43] The KOH-activated walnut shell carbon peaks showed 2Θ peaks of 27.7509° and 29.3071°. The scattering of crystallinity in the KOH-activated shell carbon is higher than the pyrolyzed one. The profile of carbon after KOH activation looks simple and only shows two broad diffraction bands in the 2Θ angle range, namely 27.7509° and 29.3071°, almost the same as the results of research from Gisgis et al.[44], which peak 2Θ = 23-30° and 43-48°.

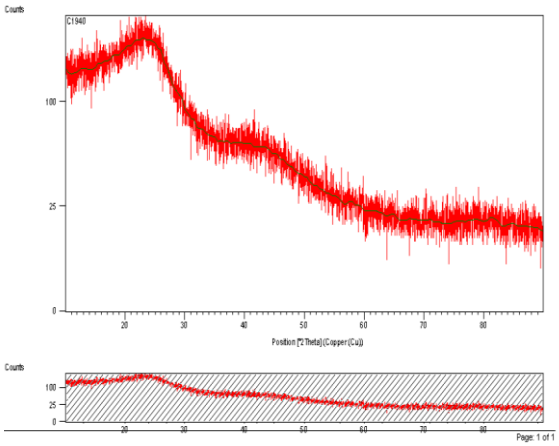

Fig.-6: Diffractogram of Pyrolyzed Walnut Shell Carbon.

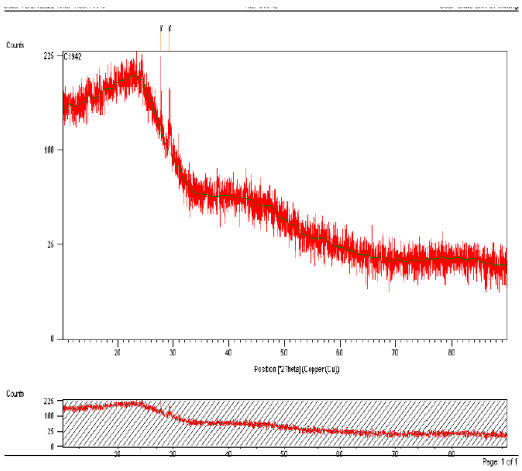

Fig.-7: Diffractogram of KOH-Activated Walnut Shell Carbon

CONCLUSION

The results of FTIR analysis showed that carbon has functional groups of C-H aromatic, C-H aliphatic, C-O alcohol, C-O carboxylic acid, and C-O esters. Pore diameter of walnut shell carbon from pyrolysis ranged from 339.8 nm to 2,839 µm and pore diameter of walnut shell carbon after KOH activation ranged from 1,217 µm to 2,137 µm. SEM morphology shows that the surface structure of carbon particles from pyrolysis and carbon after KOH activation are inhomogeneous. The mass percent and atomic percent of carbon from walnut shell carbon from pyrolysis are 70.60% and 78.20%, while walnut shell carbon after KOH activation is 79.40% and 83.80%. The chemical activation process with the KOH activator can enlarge the carbon pores, increase carbon composition, and reduce the composition of minor elements contained in the walnut shell carbon. The XRD diffractogram shows that the pyrolyzed walnut shell carbon has a dense peak and relatively low intensity compared to the walnut shell carbon after KOH activation, which shows a denser peak and relatively higher intensity. The appearance of diffractograms with broad diffraction, irregular diffraction intensity, and the absence of sharp peaks revealed the structure of both carbons to be highly amorphous.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing it, and approved the final draft for publication.

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