



Synthesis and Characterization of Activated Carbon from Lignocellulosic Biomass: Oil Palm Empty Fruit Bunches and Mahogany Sawdust

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Abstract

Lignocellulosic biomass is a biological residue from the agricultural or forestry industry which is composed of polymeric cellulose, hemicellulose, lignin, and other extractive components. One of the products in the utilization of lignocellulosic biomass waste is activated carbon products. In this study, two types of lignocellulosic biomass waste were used, namely Empty Palm Oil Bunches (OPEFB) and Mahogany Sawdust (MS) to be converted into activated carbon using the hydrothermal-pyrolysis method. Potassium hydroxide (KOH) was used as an activating agent at high concentrations (50% w/w) to improve the adsorption mechanism in activated carbon material. Proximate analysis was carried out to obtain information related to yield, moisture content, and ash content. In addition, activated carbon samples were characterized using FTIR, XRD, and FESEM to observe the chemical bonds, structure, and morphology of activated carbon, respectively. The proximate analysis showed that the activated carbon sample had met the SNI 63-3730-1995 standard for technical activated carbon on the parameters of water content and ash content, while the FTIR spectrum showed the mechanism of biomass conversion from raw materials to activated carbon on a chemical bond approach. Furthermore, the XRD graph shows a reduction in the crystal size of the material from raw material to activated carbon material. Finally, the FESEM image shows a significant increase in the quality and quantity of pores on the carbon material before and after activation.

INTRODUCTION

Lignocellulosic biomass refers to dry matter plants which especially composed of cellulose, hemicellulose, and lignin. The lignocellulosic biomass feedstocks are mainly from the agriculture residue (i.e., palm trunk and empty fruit bunch, corncobs, wheat straw, wheat rice sugarcane bagasse, corn stover, coconut husks and coir), forest residue (i.e., hardwood and softwood), and industry sectors (i.e., food waste, wastepaper,

and demolition wood) (Haghighi Mood et al., 2013; Limayem & Ricke, 2012). Indonesia as an agricultural country has many resources in the agriculture and forest sectors. Agricultural wastes and forest residues are the most promising biomass feedstocks due to their abundance and competitively low price among other lignocellulose materials (Jiang et al., 2018). Examples of residues in the agricultural and forestry industries in Indonesia are palm oil industrial waste and industrial forest products, such as oil palm empty

fruit bunches and mahogany sawdust, respectively. Nowadays, many studies have been conducted to utilize lignocellulosic biomass in high economic value products. One example of the utilization of lignocellulosic biomass waste is activated carbon (AC).

Many researchers have been studied AC from wood sawdust such as Rubber wood (Srinivasakannan & Abu Bakar, 2004), Meranti wood (Borhan et al., 2013), Chengal wood (Foo & Hameed, 2012) and so on, but not specifically for Mahogany Sawdust type *Swietenia mahagoni* (MS) which will be presented in this paper. Mahogany Sawdust is most common waste in Indonesian local furniture industry. Moreover, the chemical components in MS are promising to be made into activated carbon which contains cellulose (47.26%), hemicellulose (27.37%), and lignin (25.82%) (Karlinsari et al., 2010). In the other side, the characteristic of AC from Oil Palm Empty Fruit Bunches (OPEFB) had been widely studied by many researchers especially from Malaysia (Osman et al., 2016; Bakhtiar et al., 2019) and Indonesia (Haryanti et al., 2014) as the oil palm commodity countries. According to Gaol et al., (2013), OPEFB components are consisting of cellulose (28%), hemicellulose (25.9%), holocellulose (20.27%), and lignin (25.83%). The carbon yield from the conversion process is highly dependent on their mass fractions of lignin, cellulose and hemicellulose (Cai et al., 2017). Therefore, this plant-based biomass has been promising material for biomass-derived carbon, especially for AC products.

Activated carbon (AC) is a porous solid material that contains 85-95% carbon which is produced from biomass as raw material through a process of carbonization and activation. There are two general methods of carbonization which are hydrothermal (wet method) and pyrolysis (dry method). The hydrothermal process has been a potential method to be applied for AC synthesis. Generally, this method has several superiorities such as low cost (by using low temperatures and water as the carbonization medium), rich oxygen functional group, and the product can be a good precursor which has a large surface area and mesoporous structure (Sevilla & Titirici, 2012). On the other hand, pyrolysis process is a decomposition process by heating the sample in the thermodynamic condition to produce chars in the absence of air/oxygen or in an inert gas condition, such as N₂ and Ar (Indayaningsih et al., 2017).

Moreover, in order to activate the carbon products into the activated carbon, there are two types of activation processes which are chemical activation and physical activation. Chemical activation is a process that mixes the carbon precursor with activating agents (i.e., KOH, NaOH, H₃PO₄) (Wei & Yushin, 2012) while the physical activation is a process to convert the carbon precursor at high temperature in inert conditions (Guclu et al., 2021).

Activated carbon is widely used for decolorizing, deodorizing, and purifying agents in the industry (Viena et al., 2018). Activated carbon with a high surface area and good pore structure has been widely used in wastewater treatment, gas purification, supercapacitors, and as a catalyst/electrocatalyst (Lin et al., 2021). The adsorption ability on activated carbon is influenced by surface area, porosity, and surface functional groups. As the environmental problems acquire increasingly attention, activated carbon could be promising and eco-friendly materials for future applications. The objectivity of this research is the utilization of Indonesian local commodity biomass waste (OPEFB and MS) into activated carbon material with excellent pore structures as a functional adsorbent material in the environmental field. Therefore, in this study, we conducted a synthesis and characterization of ACs using the hydrothermal-pyrolysis method to improve the pore structure by optimizing the hydrothermal temperature and high concentration activator agent.

MATERIALS AND METHODS

Materials

The feedstocks used in this study were obtained from the local market in Indonesia. The Oil Palm Empty Fruit Bunch (OPEFB) material was collected from the local market based on Palm Oil plantation Riau, Sumatera while the Mahogany Sawdust (MS) material was from the local furniture industry in Ciawi, West Java. Potassium Hydroxide (KOH) analytical grade (Merck, CAS Number: 1310-58-3) was used as an activator agent and Hydrochloric Acid Fuming 37% analytical grade (Merck, CAS Number: 7647-01-0) was used for the neutralization process. In addition, deionized water (DI) was used in the hydrothermal and neutralization process.

The equipment used in this study including the hydrothermal and activation process was

autoclave KPI Thermo-Mighty Stirrer (model HHE-19G-U, Japan) and muffle furnace through local assembly quality. The XRD analysis was performed by using Shimadzu MAXima_X XRD-7000 for structural and crystallographic analysis while the FTIR spectra to determine the functional groups in the sample were carried out by Perkin Elmer FTIR Spectrum Two Frontier. Then, the morphology of the samples was observed by using FE-SEM Thermo Scientific Quattro-S.

Methods

The activated carbon was prepared through the two-stage process that involved carbonization and activation process. The original OPEFB and MS materials were named as RAW materials. The RAW materials were carbonized through hydrothermal carbonization to produce the hydro-char as a precursor for our activated carbon samples. Hydrothermal carbonization was carried using a hydrothermal reactor (Liquid Hot Water). In the hydrothermal process, OPEFB and MS were put in a hydrothermal reactor where the samples were immersed in deionized water (DI water). The hydrothermal process was carried out at 180°C and 220°C for 3 hours. The output of the hydrothermal process is called hydro-char (HTC) samples. The HTC samples were dried in the oven at 105°C for 24 hours.

The activation process was performed through two process activation which are chemical activation and physic activation. Chemical activation was conducted by soaking hydro-char in 50% (w/w) KOH solutions for 24 hours. Then, the sample was neutralized using 1 M HCL and washed with DI water until the pH is close to neutral. The sample was dried in the oven at 100°C for 24 hours before the pyrolysis process in the furnace at 700°C for 2 hours. Thus, the output of samples is called activated carbon (AC). Furthermore, several characterizations were carried out for AC samples including proximate analysis (yield, moisture content, and ash content), FTIR, XRD, and FESEM. The flowchart of activated carbon synthesis can be seen in Figure 1.

RESULTS AND DISCUSSION

Proximate Analysis

Proximate analysis of activated carbon was performed to define the yield, moisture content, and ash content as shown in Table 1. Based on the data

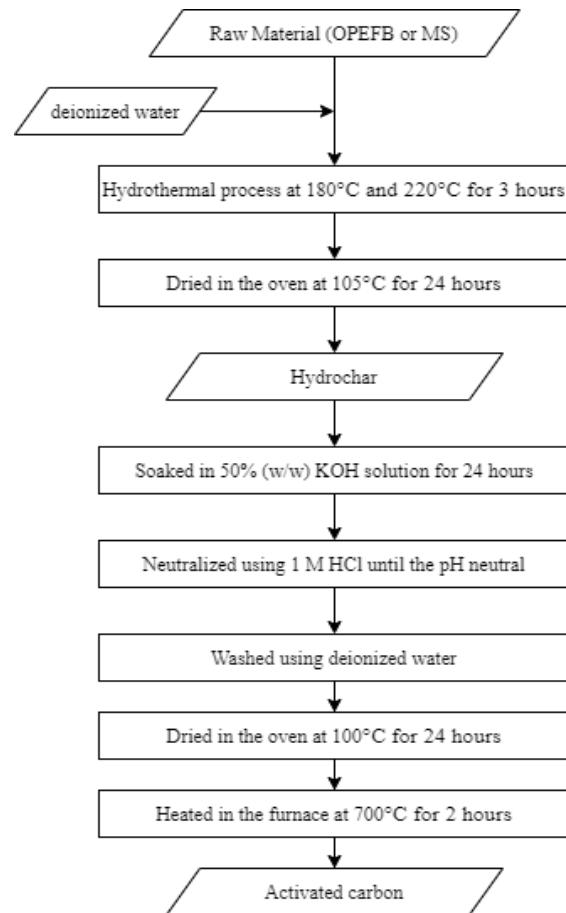


Figure 1. Flow Chart of Activated Carbon Synthesis

shown in the table, the yield from higher hydrothermal temperatures (220°C) is higher than the yield from lower hydrothermal temperatures (180°C). This can happen because at 220°C the conversion of biomass into hydro-char becomes more effective than at low temperatures. It also refers to the decomposition process of lignocellulosic material which begins to occur at a temperature of 220-315°C for cellulose and hemicellulose materials (Waters et al., 2017). Moreover, the yield from OPEFB material gives us a higher number compared to the yield from MS material. The presence of low yield might be caused by the large number of volatile matter compounds that are released in MS materials. This characteristic is highly influenced by the chemical composition of raw materials. In lignocellulose materials, which contain cellulose, hemicellulose and lignin, the carbon yield is very dependent on the lignin component. Lignin is the component that plays an important role in the carbonization process with the higher decomposition temperature. On the other side, cellulose has a lower decomposition temperature, so that, the material with a high

Table 1. Proximate Analyses of OPEFB and MS

Materials	Temp.	Yield (%)	Moisture (%)	Ash Content (%)
OPEFB	180°C	15.2	7.25	2.45
	220°C	17.0	4.92	8.95
MS	180°C	13.7	6.59	1.07
	220°C	15.9	5.13	4.87

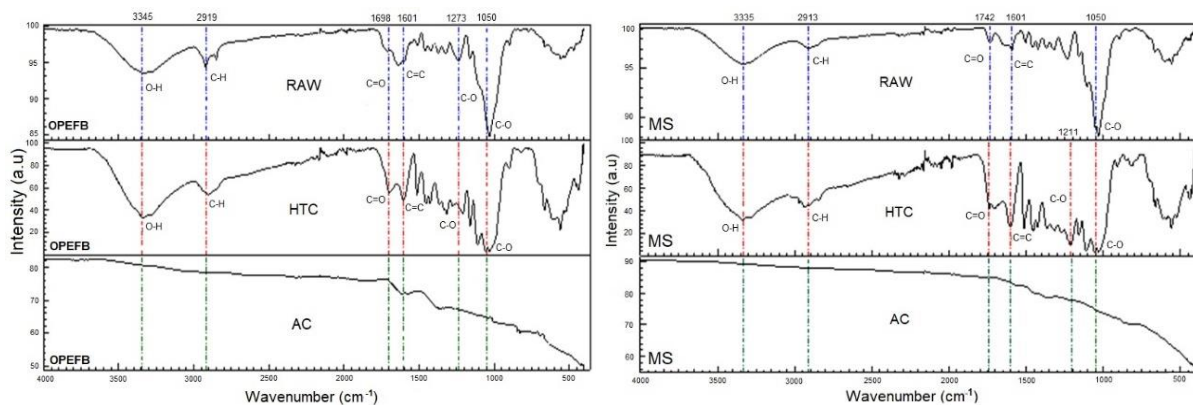


Figure 2. FTIR spectra of OPEFB (left) and MS (right)

cellulose component will produce more volatile matter and reduce the amount of sample yield.

The moisture content has shown that the OPEFB material has higher moisture content compared to MS materials either at 180°C or 220°C hydrothermal temperature. This could have happened because of the morphology of OPEFB material which has more natural pores that can contain more water than MS material. Moreover, both material gives us low moisture content in high hydrothermal temperature due to higher hydrothermal temperatures (220°C) being able to evaporate more water content compared to lower hydrothermal temperatures (180°C). However, the moisture content shows good results and met the SNI standard with the maximum water content of activated carbon being 15% for both OPEFB and MS materials.

For the ash content, both OPEFB and MS have good results and met the SNI standard based on maximum of 10% ash content in activated carbon. Furthermore, the OPEFB material has double value for ash content compared to MS material. This result is influenced by the chemical component that composes the material and the residue of the activator agent that may remain in the activated carbon sample.

Chemical Bond Analysis

FTIR spectrum analysis was used to investigate the chemical bonding of the materials including raw, hydro-char, and activated carbon samples. The FTIR spectra show how the experimental treatment can affect the chemical bonding of the material through the biomass conversion process. As a lignocellulosic material category, OPEFB and MS materials tend to have almost the same spectra. In Figure 2, raw material (RAW) and hydro-char samples (HTC) show the medium-broad peaks at 3000-3600 cm^{-1} wavenumber that indicates the presence of OH bonds from the hydroxyl groups of cellulose while the wider peaks indicate the more hydroxyl groups formed (Ali et al., 2020). Moreover, the wavenumber at 2900-2700 cm^{-1} shows a small peak for raw and hydro-char samples which represent the presence of C-H bonds from the methylene group of the hydrocarbon component with low intensity (Cuhadaroglu & Uygun, 2008).

Furthermore, the effect of the hydrothermal process can be seen at the peak of 1700-1000 cm^{-1} wavenumber for each sample. For both MS and OPEFB materials, the FTIR spectra showed the presence of C=O and C=C bonds from the aromatic structure of the raw material which

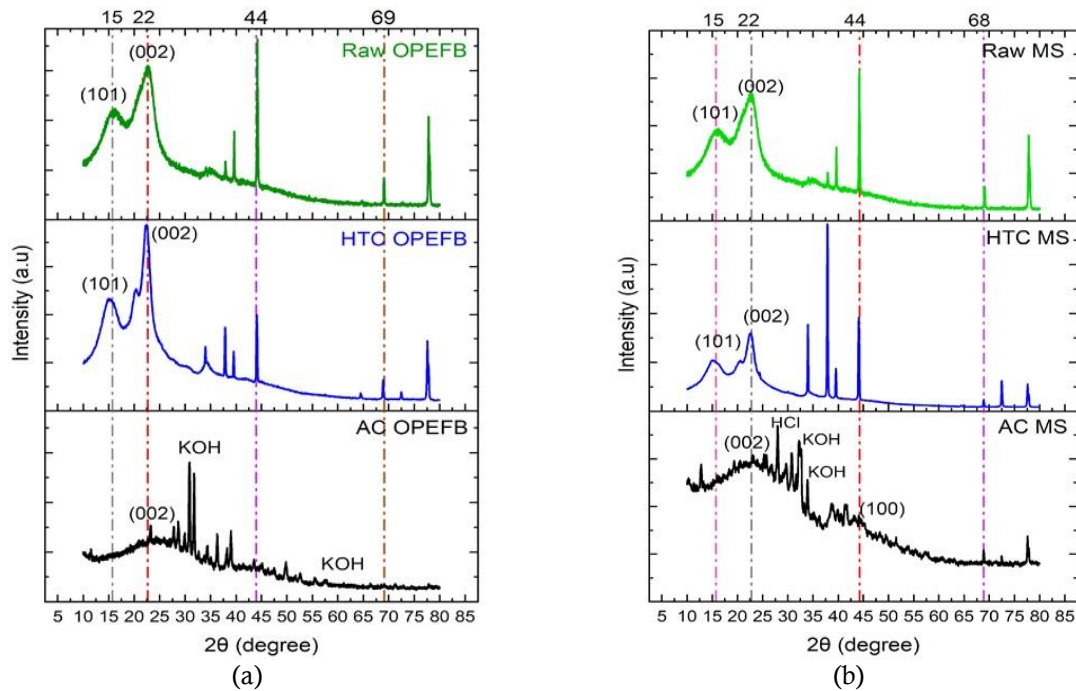


Figure 3. XRD patterns of OPEFB (a) and MS (b).

was increasingly evident in the hydro-char sample (Mistar et al., 2020). In addition, a very dominant peak is seen at $1300\text{-}1000\text{ cm}^{-1}$ wavenumber which indicates the presence of C-O bonds originating from alcohol, acid, and phenol. This peak is more clearly seen in the hydro-char sample where this occurs because of the cleavage of the double chain at C=O to C-O because of the hydrothermal process (Ali et al., 2020). The significant difference in FTIR spectra was seen in the activated carbon sample (AC) where the resulting spectra do not show many absorption peaks for both OPEFB and MS materials. This shows that the chemical groups in the lignocellulosic material in the activated carbon sample are degraded during the pyrolysis process and have been completely converted into carbon material (Cuhadaroglu & Uygun, 2008). This is due to the covalent bonding of the C atom in the carbon material not detected in the IR mode but in the Raman mode where further characterization of the carbon sample is carried out using Raman spectroscopy.

Structural Analysis

Structural analysis of the sample material was carried out using x-ray diffraction (XRD). XRD analysis was conducted for raw materials, hydro-char and activated carbon samples from OPEFB and MS materials. XRD measurements were observed in the range of $2\theta\ 10^{\circ}\text{-}80^{\circ}$ to obtain

the overall diffraction pattern of the samples. XRD results show that the diffraction pattern in the raw material has diffraction peaks at $2\theta\ 15^{\circ}$ and 22° for 101 and 002 lattice planes which represent the diffraction peaks of polymorphs type I of cellulose (Azubuike & Okhamafe, 2012). In general, this polymorph type I consists of I_{α} and I_{β} (often called α -cellulose and β -cellulose) which alpha-cellulose has a triclinic structure and beta-cellulose has a monoclinic structure (Klemm et al., 2005). Basically, the proportion of these two allomorphs varies depending on the source of the lignocellulosic material.

The hydro-char sample shows a shoulder peak at $2\theta\ 20$ with 110 lattice planes due to the hydrothermal process (Ahmad Kuthi et al., 2015). In this process, alpha-cellulose extraction has occurred which resulted in the structural change of the material into polymorph type II (Godbout, 2013). The hydrothermal process has hydrolyzed the chemical compounds of the material and changed the structure of the material into polymorph type II where the transformation of polymorph type I to polymorph type II is irreversible (Wertz et al., 2010).

Moreover, the deformation of crystalline carbon into an amorphous structure as part of the biomass decomposition process has dominated the diffraction pattern in the activated carbon material. In the activated carbon material, the amorphous

structure dominates the sample with diffraction peaks 2θ 23° and 44° in the crystal planes 002 and 100 with characteristically wide peaks. In the activated carbon sample material, it was found that many impurity crystal peaks came from the KOH and HCl where the KOH crystal peaks were found at 2θ 30° - 33° and 52° and the HCl peak was at 2θ 27° , respectively. This is due to the incomplete washing process that remains activator agent and a small number of acidic compounds from the activation and neutralization process.

In general, the diffraction patterns on the raw material and hydro-char are quite similar. This is because the structural decomposition due to the hydrolysis process in the hydrothermal method was conducted at a relatively low temperature (180-220°C). In this temperature, there are several mechanisms such as breaking chemical bonds, releasing free radicals, and forming carbonyl groups (Wertz et al., 2010), but this is not sufficient to decompose all components of lignocellulosic constituents such as lignin which decompose at high temperatures ($>500^\circ\text{C}$) (Waters et al., 2017). In the activated carbon sample, all the constituent components in lignocellulosic material have been successfully decomposed due to the breaking of C-H and C-O bonds to create an amorphous carbon structure as a fingerprint of the activated carbon material.

XRD analysis was carried out using the Scherer equation to determine the crystallite size of the material based on the peak data of the diffraction pattern. Crystallite size is one of the parameters related to the crystal structure of cellulose, referring to the smallest single crystals in powder form (Wang et al., 2017). The results of the crystallite size measurement are shown in Table 2. Based on the data from the measurement results, the value of crystallite size (L_c) was decreased through the conversion process from raw materials to activated carbon.

Table 2. Structural Parameters of OPEFB and MS

Sample	Crystallite size (L_c) (nm)
Raw OPEFB	54.692
HTC OPEFB	46.428
AC OPEFB	30.645
Raw MS	61.383
HTC MS	47.177
AC MS	32.428

Naturally, lignocellulosic materials are arranged from the crystalline and amorphous structure of cellulose which has a certain crystallite size. The carbonization process, either hydrothermal or pyrolysis, causes the lignocellulose material to decompose and damage the crystal structure of the material and produces more amorphous structures. This decomposition process reduces the crystallite size of the lignocellulosic material from raw to activated carbon.

Morphological Analysis

The morphological structure of all samples was observed using FESEM, as shown in Figure 4. Figure 4 (a) and (c) show the hydro-char of OPEFB and MS materials without chemical activation treatment while Figure 4 (c) and (d) show the activated carbon of OPEFB and MS materials, respectively. In general, the morphology of hydro-char samples shows the very coarse structure for both OPEFB and MS materials. In Figure 4 (a), the OPEFB fiber was observed in the partial degraded condition due to the hydrothermal process. Furthermore, the activation process with 50% KOH reveals the improvement of pore structure in OPEFB material. The small new pores were created in the middle of pore wall structure. It was also observed that the activator agent remains in OPEFB's pore. On the other hand, Figure 4 (c) shows the rough sponge-like structure of MS hydro-char without activation process. This structure looks completely different from the OPEFB material that seems more rigid. By performing the activation process, the pore formations in the MS sample are easier as shown in Figure 4 (d). It was clearly seen that the chemical activation treatment can improve the pore structure of the MS material.

CONCLUSION

Activated carbon has been successfully made from lignocellulosic OPEFB and MS waste using the hydrothermal-pyrolysis method. The proximate analysis showed that both OPEFB and MS samples had met the requirement of SNI 63-3730-1995 standard for technical activated carbon including moisture and ash content. Moreover, the highest yield of activated charcoal was produced by OPEFB material. The results of FTIR characterization show the mechanism of biomass conversion from raw materials to hydro-char then activated carbon based on the chemical bond

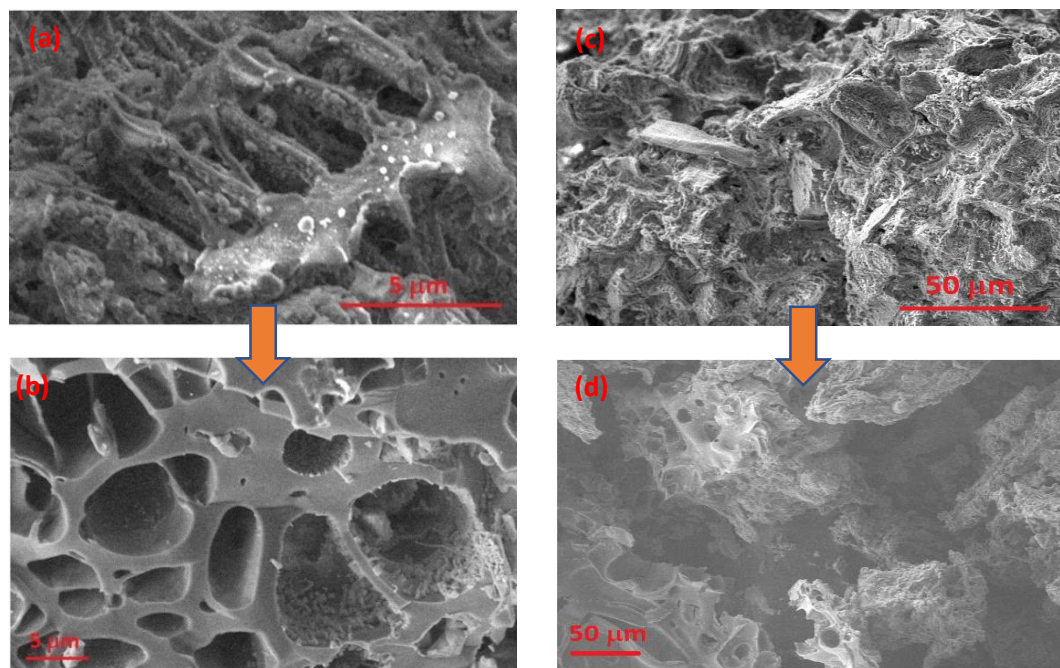


Figure 4. FESEM Images of (a) HTC OPEFB, (b) AC OPEFB, (c) HTC MS, and (d) AC MS.

analyses. Furthermore, the XRD structure showed the structural degradation of the lignocellulosic crystalline material to amorphous carbon which also indicated by decreasing crystallite size. Finally, the FESEM images show improvisation in the term of pore formation for both OPEFB and MS activated carbon materials which is MS material shows relatively excellent pore structure than OPEFB material.

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