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ORIGINAL STUDY

Isolation and Characterization of Lignin from Oil Palm Shells using a Precipitation Method with Sulfuric Acid and Polyaluminum Chloride as Coagulant

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ABSTRACT

Lignin has useful and significant properties such as stiffness, resistance to UV radiation, antioxidant, antimicrobial, high thermal stability, and high carbon content. Due to these properties, lignin can be used for several applications including wood adhesive and carbon-based material, and can be developed as a functional material composite. Isolation and utilization of lignin from lignocellulosic biomass offers significant opportunities in various now and future industrial applications mainly for development of advanced materials. In this study, isolation and characterization of lignin from oil palm shells (OPS) was conducted. Lignin was isolated from OPS using the precipitation method with sulfuric acid and coagulation using polyaluminum chloride (PAC). The isolated lignin was identified using Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Based on the FTIR analysis, lignin was successfully separated from cellulose. The crystallite size of isolated lignin is the smallest (25.37 nm) as compared to commercial alkaline lignin (28.49 nm) and OPS (25.99 nm). The isolated lignin is amorphous with crystallinity of 6.43% and its morphology is a spherical. Overall, this study shows that the isolation method using sulfuric acid (H_2SO_4) and PAC is not only effective in separating lignin from OPS, but also minimizes the environmental impacts, thus certainly making it a promising choice for more environmentally friendly industrial applications.

Keywords: Hydrothermal, Lignin, Oil palm shell, Precipitation method, Sulfuric acid and Polyaluminum chloride

1. Introduction

Biomass is non-fossil organic matter derived from plants and animals, including microorganisms. Potential biomass includes wood, animal, and plant wastes [1]. Usually biomass is grouped into six main groups, namely (i) wood and woody, (ii) herbaceous and agricultural plants, (iii) aquatic organisms, (iv) animals,

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(v) industrial semi-biomass, and (vi) mixed biomass [2]. Numerous studies have explored biomass for many applications including adsorbent to eliminate emerging contaminants from water sources [3, 4]. Biomass is not expensive material, thus has attracted for many researchers. The sol-gel process produced xerogel from palm kernel shell biochar (PKSB) to be used as an adsorbent has been investigated by Mahdi et al. [3].

On the other hand, Reghioua et al. [4] reported kaolin clay functionalized with cellulose extract obtained from peanut shells as adsorbents for the removal of organic dyes, such as cationic (methylene blue, MB) and anionic (Congo red, CR) from an aqueous environment. It is noted that biomass from plants has high contents of cellulose, hemicellulose, and lignin, but has relatively low contents of pectin, protein, extractives, and ash. Therefore, this biomass is often referred to lignocellulosic biomass [5]. Lignocellulosic biomass includes various agricultural residues, such as wood from deciduous and coniferous trees, municipal solid waste (MSW), and waste from the pulp and paper industry. The main components of lignocellulosic biomass are cellulose (35%–50%), hemicellulose (20%–35%), and lignin (10%–25%) [6]. Lignin can be found in the plant cell wall, usually about 10 – 40% weight of biomass [7]. In plants, lignin is used for strength and stability of cell walls, and forms essential hydrophobic surface and enhances the structurcal integrity [8]. The functional groups and molecular weight of lignin can be different depending on the source of lignin and type of plant or wood.

The utilization of biomass of date palm (*Phoenix dactylifera*) and pineapple (*ananas comosus*) as adsorbents has been reported to produce a sulphonated date palm [9] and activated carbon [10]. Isolation and utilization of lignin from lignocellulosic biomass offers significant opportunities in various industrial applications. Lignin is a friendly biopolymer and has various antimicrobial, antifungal, antioxidant, and functional physical properties, such as stiffness, resistance to UV radiation, high thermal stability, and high carbon content [11, 12]. Due to these properties, lignin can be applied as wood adhesive, carbon-based material, and can be developed as a functional composite material [13]. On the other hand, nano lignin can be used in various fields such as food packaging, emulsion, drug delivery, and biomedical applications [7].

The kraft, soda, and organosolv are involved in pulping processes for isolating lignin from lignocellulosic biomass [14]. These pulping processes can produce high yields of lignin; especially the Kraft pulping process produces around 100 million tons of lignin annually in the form of black liquor. One of the common methods for isolation of lignin is the precipitation method using acid, such as sulfuric acid (H_2SO_4). However, the use of sulfuric acid can disrupt the balance of chemical cycles in solution. Therefore, some modifications are implemented in the precipitation method to minimize the use of acid. For instance, lignin was extracted from oil palm empty fruit bunch and purified from black liquor, or wastewater from bioethanol production, by acid precipitation using hydrochloride acid (HCl) and sulfuric acid (H_2SO_4) combined with coagulation using polyaluminum chloride (PAC) [15]. By extraction and purification using PAC 10% and H_2SO_4 5%, the lignin can be obtained about 98.6% and used as flame retardant additives [15].

PAC is used as a coagulant to reduce the use of strong acid such as sulfuric acid. In this study, PAC can be used to reduce the pH and help to precipitate lignin. The use of PAC as a coagulant in the lignin isolation process shows progress in reducing the environmental impacts caused by the use of sulfuric acid. In addition, the use of lignin as a raw material in various functional products shows high potential to support sustainability and efficiency in industry. With its high content of cellulose, hemicellulose, and lignin, lignocellulosic biomass is not only a renewable energy source, but also a valuable raw material for various technological applications. This potential needs to be continuously explored and developed to support the development of a greener and more sustainable industry.

In this study, the isolation of lignin from oil palm shell (OPS) using the precipitation method with sulfuric acid and PAC as a coagulant is investigated. Palm kernel shell (PKS) is well-known as OPS and has a lignin content of about 50% [16, 17]. As Southeast Asia is a largest producer of palm oil in the world, huge quantities of biomass wastes including empty fruit bunches, oil palm shells, oil palm trunks, and palm fibers are produced in this area. By production of lignin using OPS as a precursor, the problem of biomass waste in the oil palm industry can be reduced. On the hand, this research can support the circular economy by using biomass, and produce useful valuable products. This process is in parallel producing lignin useful for many applications such as wood adhesive, carbon nanofiber, functional composite material, food packaging, emulsions, drug delivery, and biomedical applications. This product is also a major source for production of renewable aromatic chemicals [18].

2. Materials and methods

2.1. Material

OPS as the main source in lignin isolation was obtained from local market of Riau Plantation (Sumatera, Indonesia). Technical sodium hydroxide is used in lignin delignification process that forms black liquor, while sulfuric acid was purchased from Merck Sigma-Aldrich EMSURE CAS: 7664-93-9. PAC was purchased from TUV CERT CPR-30. Commercial lignin in the from of alkaline lignin (CAS: 8068-05-1) was purchased from Merck Sigma Aldrich.

2.2. Method

Preparation of lignin from OPS was according to method reported by Burhani & Nugroho [15]. The collected OPS (250 g) was put into the digester containing 2 L NaOH with a concentration of 20% w/v to produce a black liquor. This black liquor was prepared by using the hydrothermal method at a temperature of 170°C for 6 h. 800 mL of the black liquor product was taken and put into a 2L beaker glass. The black liquor is very alkaline with the pH of 14, then sulfuric acid (H_2SO_4) 5% v/v was added until the pH reached 4, followed 10% w/v of PAC. The black liquor was mixed and homogenized using a hot plate stirrer for 1 h. The mixed solution was precipitated overnight until the filtrate and supernatant are formed. The filtrate and supernatant were separated and the filtrate was then soaked using distilled water, the process of precipitation, separation, and addition of distilled water was repeated until a neutral pH was achieved. After reaching a neutral pH of ≈6–7, the filtrate was dried at a temperature of 80 °C for 12 hours using an oven. The output from the oven was lignin in solid form. The solid lignin was ground using a mortar and sieved until it passed a size of 400 mesh. Scheme for isolation of lignin from OPS as a raw material using the hydrothermal method at 170°C for 6 h, which precipitated with 10% PAC and 5% sulfuric acid, is presented in Fig. 1.

2.3. Characterizations

The functional groups of the samples in this study were analyzed using Fourier transform infrared (FTIR) spectroscopy on Perkin-Elmer Spectrum Two with Universal ATR FT-IR Spectrometer over the range of 400–4000 cm^{-1} scanning number of 12, resolution of 4 cm^{-1} and temperature of 25° Celsius. The surface morphology of the samples was characterized using a Scanning electron microscopic (SEM) imaging on FEI Inspect F50 series. The crystallinity of the samples were analyzed by X-ray diffraction on MAXima_X

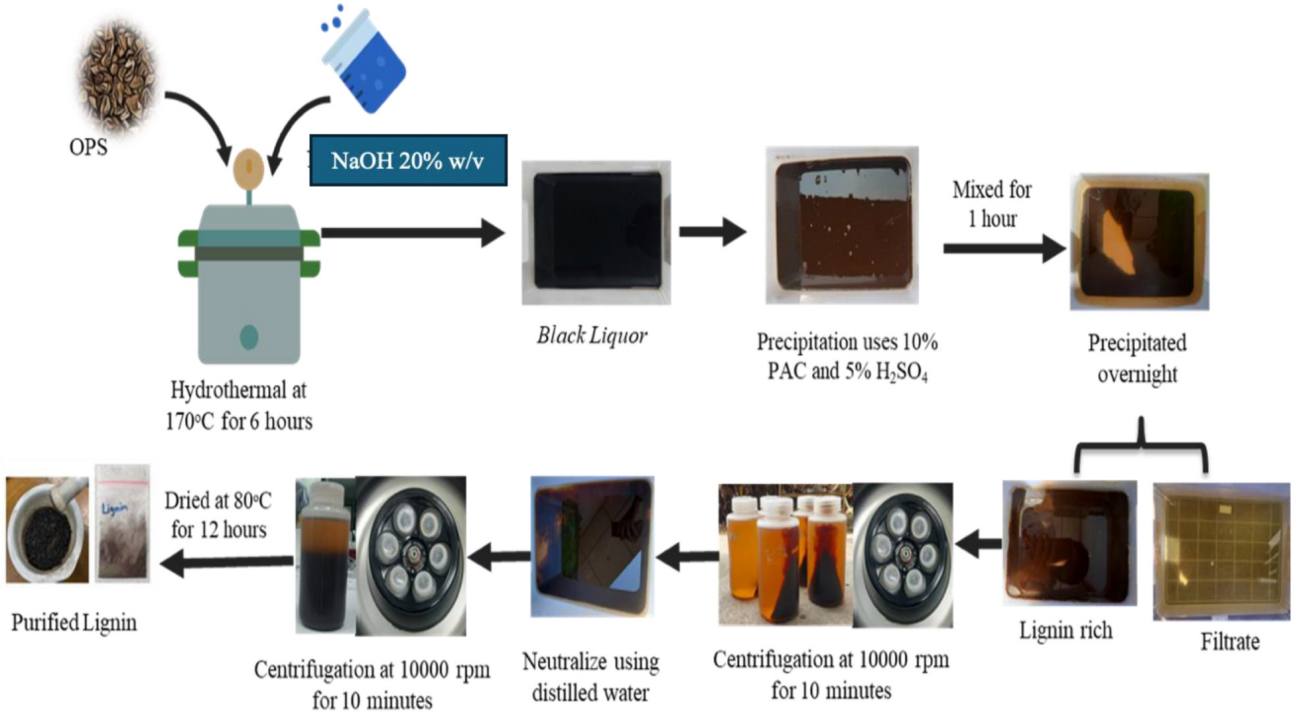

Fig. 1. Schematic for isolation of lignin from OPS as raw material with hydrothermal at 170°C for 6 hours, precipitated with 10% PAC and 5% sulfuric acid.

Table 1. Characteristics absorption bands of OPS, isolated lignin from OPS, and commercial lignin.

Wavenumber (cm^{-1})			
OPS	OPS lignin	Commercial lignin	Functional group
3288	3334	3318	-OH stretching vibration of aromatic and aliphatic (lignin)
2922	2875	2931	C-H_2 stretching vibration (guaiacyl-syringyl)
1622	—	—	C=O stretching vibration of carbonyl bond
1512	1511	1582	C=C stretching vibration of the aromatic ring (guaiacyl-syringyl)
—	1595	—	R-C=O
1455	1452	1452	C-H deformation in lignin
—	—	1335	C-H vibration
—	—	1259	C-O stretching in lignin
1235	1210	1213	C-O stretching in lignin and syringyl ring
—	—	1126	C-O stretching
—	1111	—	C-O-C stretching
1032	1029	1028	C-H in-plane deformation in guaiacyl
534	555	513	C-H bending

XRD-700 (Shimadzu) with $\lambda = 1.54184$ nm under ambient conditions. The isolated lignin from OPS was characterized using XRD to determine its structure and crystallite size. The average crystallite size of samples were determined using the Debye Scherrer Eq. (1);

$$D = K\lambda/\beta \cos\theta \quad (1)$$

where D is the nanoparticles crystallite size, K represents the Scherrer constant (0.98), λ denotes the wavelength (0.154 nm), β denotes the full width at half maximum (FWHM)

3. Results and discussion

3.1. FTIR analysis

The surface functional groups of isolated lignin from OPS as a raw material were identified through FTIR analysis. Two distinct regions of fingerprints and functional groups infrared region in the ranges from 400 to 4000 cm^{-1} were analysed. The FTIR spectra of OPS, lignin from OPS, and commercial lignin were described in Fig. 2 and Table 1. The raw OPS, isolated lignin from OPS, and commercial lignin have strong absorption at 3288, 3334 and 3318 cm^{-1},

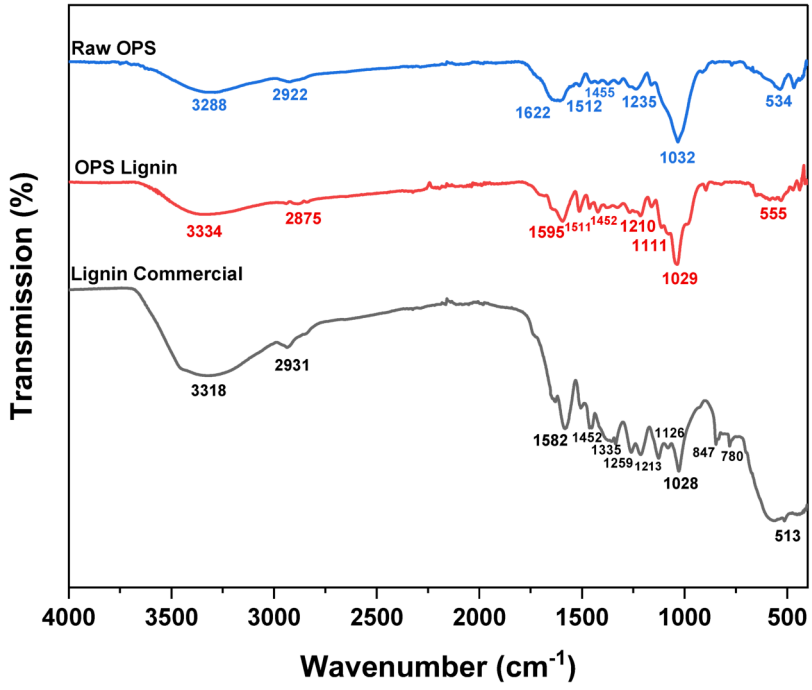

Fig. 2. Comparison FTIR spectra of OPS, isolated lignin from OPS and commercial lignin.

respectively, that represents the stretching vibrations of aromatic and alcoholic hydroxyl groups of lignin. These bands appear at frequencies lower than those found in the hardwood kraft lignin (HKL) at 3396 cm^{-1} [19].

The band at 2900 cm^{-1} was assigned as the C-H vibration of the $-CH_2$ asymmetric vibration of guaiacyl-syringyl in the structure of lignin. This peak is comparable with HKL at 2917 cm^{-1} [19]. The band of 1622 cm^{-1} was attributed to the C=O stretching vibration of carbonyl bond that commonly found in lignin and cellulose derivatives. However, this peak was not found in both the isolated lignin and commercial lignin, indicating that lignin was separated from cellulose during the lignin isolation process. The bands at 1511, 1512, and 1585 cm^{-1} were attributed to the C=C stretching vibration of the aromatic ring (guaiacyl-syringyl) found in the structure of lignin. This is similarly observed for industrial hardwood kraft lignin with the peak intensity of 1512 cm^{-1} that assigned for the aromatic ring vibrations of the phenyl-propane skeleton unit in lignin [19].

In commercial lignin, both bands at 1135 cm^{-1} and 1259 cm^{-1} were attributed to the stretching vibration of C-H and C-O of methoxy group. These peaks are related to the type of alkaline lignin and only found in alkaline lignin because the latter has more phenolic groups. These bands were comparable with methoxy group of lignin for stretching vibrations of C-O at 1270 and 1151 cm^{-1} [20, 21].

Different bands of lignin spectra at 1210, 1213, and 1235 cm^{-1} were observed and assigned as the C-O stretching of lignin and syringyl ring for the isolated lignin, commercial lignin and OPS, respectively. The C-O stretching was observed for commercial lignin, showing the presence of ether and alcohol groups in alkaline lignin at 1126 cm^{-1}. The C-O-C stretching was only observed for isolated lignin from OPS at 1111 cm^{-1} because it is an acid lignin that cannot break the ether bond significantly. In the commercial alkaline lignin, this peak was not observed because this bond is broken in the present of alkaline. The bands at 1028, 1029, and 1032 cm^{-1} were assigned for the C-H in-plane deformation peaks in guaiacyl, while the bands related to the C-H bending appear at 513, 534, and 555 cm^{-1} found for all samples [22–24].

The OPS, isolated lignin, and commercial lignin have aromatic groups, dominated by guaiacyl and syringyl which represent a hardwood lignin. In FTIR spectrum of OPS, the C=O group is still observed to represent lignin and cellulose. However, after the isolation process of lignin, this band does not contain cellulose. There are differences in the peaks of isolated lignin from OPS and commercial lignin that caused by differences in the isolation processes. The sulfuric acid is used to produce an acidic lignin, while for the commercial lignin, alkaline is used, thus both spectra of lignin are different, as it has also been confirmed by Zhou et al. [25]. The FTIR spectrum of isolated lignin from OPS showed a new peak at 1595 cm^{-1} that related to R-C=O group. This peak has been assigned to lignin glyoxalation by ether bond formation, and the similar pattern has also been observed by Ghahri & Park [19] and Ding et al. [26].

3.2. X-ray diffraction analysis

XRD was used as an analytical method to provide an information about the structure of substances at the atomic level such as the crystallinity degree of substances. Usually, the diffractogram is divided into two phases, namely (i) crystalline cellulose and (ii) amorphous. These two phases are estimated based on XRD peak areas, which are further considered proportional to the volume of each phases. The XRD patterns of isolated lignin from OPS, and raw material OPS were compared to observe the structural changes that occur during the lignin isolation process. In the diffraction pattern of materials that have a crystal structure will produce a sharp peak pattern while for materials that have an amorphous structure will produce a broad peak. The diffraction pattern of OPS, lignin from OPS and commercial lignin is presented in Fig. 3.

In the raw OPS, a broad peak at 2θ of 15° and a sharp peak of 22° were observed, which represent the peaks of the type I cellulose polymorph which are commonly found in nature. On the other hand, the broad peak at 15° represents lignin and hemicellulose which have an amorphous structure and at 22° represents cellulose crystals [27]. In the isolated lignin, the 2θ peaks were observed at 15, 20, and 22.5°, where the peak at 15° and 20° are the hemicellulose and lignin originated from type II cellulose polymorphs, while 2θ at 22.5° is the hardwood acid lignin peak [28]. In this study, lignin was isolated from OPS using the hydrothermal method in sulfuric acid. OPS is classified a biomass that has a hardwood category [28]. In the commercial alkaline lignin sample, a broad hump-shaped peak was observed at 2θ of 20° and 30.6° which represent hemicellulose and lignin [29].

Based on the XRD diffraction pattern, lignin peaks were observed, but a hemicellulose was still observed in the lignin sample. This could be because some lignins may contain hemicellulose fractions that are left behind or physically bound to lignin during the extraction and isolation process. In addition, hemicellulose and lignin have some structural similarities

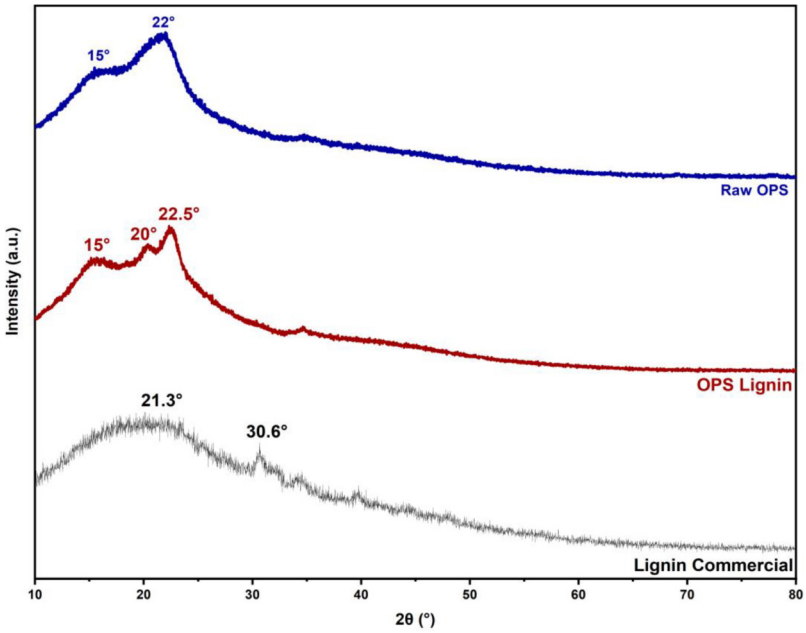

Fig. 3. Comparison XRD patterns of OPS as raw materials, isolated lignin from OPS and lignin commercial.

Table 2. Crystallite size and crystallinity index of samples.

Samples	2θ (°)	hkl	Crystallinity (%)	Crystal size (nm)
Raw OPS	15	(101)	8.45	25.99
	22	(002)		
Isolated lignin from OPS	15	(101)	6.43	25.37
	20	(200)		
	22.5	(002)		
Alkaline Lignin (commercial)	21.3	(200)	15.32	28.49
	30.6	(004)		

in terms of polymerization and structural arrangement, which may result in overlapping in the XRD pattern. However, based on the FTIR analysis, the functional groups of lignin is dominated by S and G which represent hardwood lignin, and also carbonyl bonds, indicating that lignin and cellulose were only observed in OPS, indicating that cellulose is only found in OPS.

The crystal size of each sample is listed and compared in Table 2. The isolated lignin from OPS has a smaller crystallite size (25.37 nm) as compared to commercial alkaline lignin (28.49 nm). These crystallite sizes of isolated lignin from from OPS and commercial lignin were smaller than those found in lignin nanoparticles (31 nm) that isolated from almond peel [7]. This lignin crystallite particles were isolated using almond peel extract through a straightforward hydrothermal method. The difference may be caused by the different raw materials and the isolation methods. Based on several studies, the crystallite size of lignin ranges from 2-200 nm. There are a decrease in crystallinity from raw OPS with lignin due to the absence of a peak in the crystalline cellulose structure after the lignin isolation process, thus reducing the crystallite sizes of lignin [30, 31]. Crystallinity of isolated lignin is the smallest (6.43%). Based on the XRD pattern, the isolated lignin is amorphous. In contrast, commercial lignin shows higher crystallinity at 15.32%, compared to 6.43% for the isolated lignin from OPS.

3.3. The surface morphology

The surface morphology of isolated lignin particles showed stacked layer, like a plate-compact, fragile, many void like a porous, and unregular size. Non-uniform particle distribution and morphology were observed in hardwood lignin, where hydrophobic lignin will melt upon re-polymerization during the isolation process and form a morphology like spherical and plane stacking (see Fig. 4). The formation of spherical droplets in lignin may be occured during the

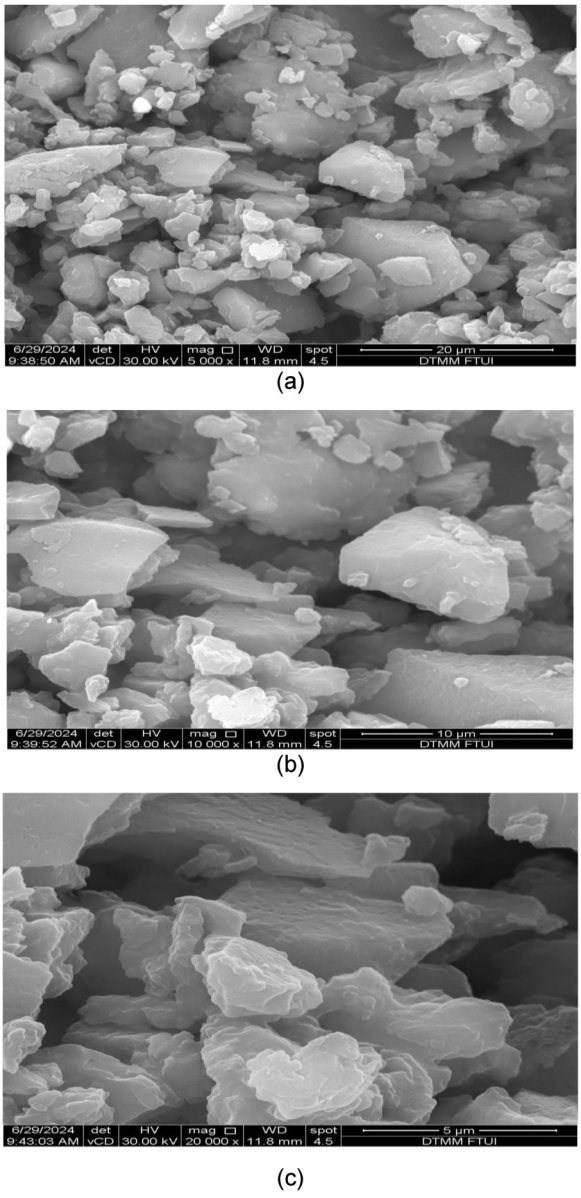

Fig. 4. SEM images of isolated lignin from Oil Palm Shells with different magnifications; a) 5,000×, b) 10,000× and 20,000×.

hydrothermal process at 170°C for 6 h. SEM results of the isolated lignin from OPS show likely a composite of lignin or lignin-like (pseudo lignin) materials [32]. This isolated lignin is a promising candidate for further applications, such as the production of carbon nanofibers for supercapacitor technologies. This is also in accordance with previously research that reported by Arundina et al. [33] that palm oil empty fruit bunches are as cellulosic sources for preparing the activated carbon-based electrodes for supercapacitors application with specific capacitance of 389.122 F/g at a current density of 1 A/g with energy and power densities of 13.511 Wh/kg and 125 W/kg, respectively.

4. Conclusions

Isolation of lignin, separated from cellulose of oil palm shells (OPS) has been investigated using the hydrothermal treatment. In this process the precipitation with sulfuric acid and coagulation using polyaluminum chloride (PAC) were employed. FTIR spectra confirmed that isolated lignin from OPS was obtained, and revealed differences in functional groups between isolated lignin and commercial alkaline lignin, which were related to the use of sulfuric acid isolation methods for isolated lignin from OPS and alkaline for commercial lignin. XRD analysis showed that isolated lignin had a smaller crystallite size than that of commercial lignin. These results provide important insights into the physical and chemical characteristics of lignin from OPS, which may affect lignin applications in various industries. The lignin isolated from OPS is a promising candidate due to its significant potential for further applications, such as the production of carbon nanofibers, composites, and its use in supercapacitor technologies.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethics approval

No ethic was conducted. this research is not involving animals.

Data availability

Data is available on request. The data underlying this article will be shared on reasonable request to the corresponding author.

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Author contributions

Eny Kusrini: Supervision, Conceptualization, Methodology, interpreted the data, Writing review, editing and fine tuning.

Ria Yolanda Arundina: Performed the experiments, Preparing the data, characterization, first Draft of paper in bahasa

Anwar Usman: Editing and Review of paper

Resti Marlina: Analyst and Characterization

Bambang Subiyanto: Supervision, review and editing

Volkan Degirmenci: Review and editing

Nofrijon Sofyan: Characterization of SEM

Yudan Whulanza: Interpreted the data

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