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ORIGINAL ARTICLE

Formulation and Characteristics of Sunscreen Cream based on Isolated Lignin from Oil Palm Empty Fruit Bunch (OPEFB)

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ABSTRACT – Lignin was recovered from black liquor during the biorefinery process and has prospective applications in pharmaceutical, cosmetic, and health care. Lignin, which has substantially smaller particles, was used as the active ingredient in the sunscreen cream formulation. The isolated lignin was examined for physicochemical parameters such as yield, purity, particle size, total phenol, and morphology. The obtained lignin was used in the preparation of sunscreen cream. The isolated lignin concentration in the cream varied between 0.1, 1, and 2 wt%. The sun protection factor (SPF) of the designed sunscreen creams was assessed, and antioxidant activity and stability were studied, which included pH, particle size, and appearance during the observation period. The formulated cream has an SPF of approximately 15, which is sufficient to protect human skin from the sun's ultraviolet (UV) radiation. Furthermore, the most significant antioxidant activity was found to be 68.94%. As a result, the developed sunscreen cream has the potential for further research because it is composed of natural active ingredients that are safe for humans and the environment.

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INTRODUCTION

Human skin health is at risk from ultraviolet (UV) rays emitted by sunshine. Long-term exposure to UV-B radiation (280–320 nm) typically results in skin erythema, and UV-A radiation (320–400 nm) gradually ages the skin and eventually causes skin cancer [1]. Excessive exposure to UVB rays on the skin will cause problems such as sunburn. Exposure to UV-A rays penetrates the skin, causes skin discoloration, and accelerates aging. The UV-A and UV-B rays induce photoaging and can cause skin cancer [2]. Currently, many clinical studies support the application of sunscreen to minimize damage due to excessive sun exposure. People prefer to use chemical sunscreens since they are less uncomfortable than physical sunscreens [3]. Chemical active compounds are considered concerning from an environmental and health standpoint when used in skin and sun care products [4]. For sun lotions or creams, to meet the basic requirements for a sun protection factor (SPF) of 15, a minimum of 20% of the total weight of the sunscreen must consist of chemical sunscreen actives [5].

Interest in lignin polymers, a bio-sourced material with various functional and bioactive qualities, has grown in light of recent research into skin care products, including sunscreens [6]. The second most common component of plants is lignin, a special aromatic polymer [7],[8]. Cellulose and hemicellulose found in plants are extracted in the pulping and bioethanol production processes to create paper or bioethanol, whereas lignin is released as a by-product [9]. Over 50 million tons of industrial lignin are produced annually, and increasing attention is paid to using lignin to create value [10]. Numerous functional groups in the lignin structure can absorb UV light. There are generally five types of lignin chromophores that are capable of absorbing UV light: (1) quinone methide and quinones; (2) double bonds (CH=CH) coupled with the aromatic ring; (3) chalcone structures; (4) free radicals; and (5) metal complexes with catechol structures. The primary component influencing lignin's ability to ward against ultraviolet light is the number of methoxy groups; the more methoxy groups there are, the more effective these groups are at protecting against UV light because they contain free electron pairs from oxygen atoms [11].

Unlike most chemical UV filters, lignin functions as a broad-spectrum sunscreen, shielding against UV-A and UV-B rays [3]. Additionally, it is a non-toxic substance with antibacterial and antioxidant qualities pertinent to skincare goods [12]. Thus, lignin has a promising future as a natural active component. Lignin is widely known

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for its complex chemical compositions with a wide range of properties, including its characteristics as a sunscreen agent [13],[14]. Using lignin as a sunscreen agent was conducted by another research group that added lignin to commercial sunscreen cream and lotion and then observed its efficacy [15], [16]. In order to protect against UV rays, this study tries to expand the efforts to formulate the sunscreen cream with isolated lignin as the active ingredient. Therefore, this work aims to find the optimal formulation of sunscreen cream that utilizes isolated lignin as the primary active material. The formulated sunscreen creams were determined for their sun SPF, antioxidant activity, and stability analysis, and they were composed of pH, particle size, and appearance during the observation time.

EXPERIMENTAL METHOD

Materials and Instruments

The black liquor obtained from the Research Center for Chemistry, The National Research and Innovation Agency (Badan Riset dan Inovasi Nasional, BRIN) in Serpong, Indonesia, was used to separate lignin. Black liquor (BL) was obtained from the pretreatment process of empty oil palm bunches using an alkali solution of 10% sodium hydroxide (NaOH) with a solid/liquid (S/L) ratio of 1:5. BL was obtained after a filtration process that aims to separate cellulose solids from empty fruit bunch (EFB) with BL. Lignin standard or commercial lignin was purchased from Sigma-Aldrich. Hydrochloric acid, sodium hydroxide, Tween 80, Span 80, 1,4-dioxane, tetrahydrofuran, methanol, and ethanol were obtained from Merck KGaA. Meanwhile, glycerine and ethyl alcohol were obtained from a local company in Indonesia (CV. Brataco). Euxyl was purchased from Schülke & Mayr GmbH (Norderstedt, Deutschland). Other chemicals were technical grade. Water came from a water purification system (Thermo Fisher Scientific). Each chemical was utilized without any additional purification.

The purity of lignin was evaluated using the ultraviolet-visible (UV-vis) spectrophotometric method (Agilent Carry 60) performed three times at a specified wavelength of 280 nm. Lignin is commonly measured at a wavelength of 280 nm due to its specific absorbance characteristics, which facilitate accurate quantification in various contexts. This wavelength is particularly advantageous for assessing lignin content in different samples, as it minimizes interference from other compounds [17]. A lignin standard was utilized in different concentrations (5, 10, 15, 20, 30, and 50 ppm), while a blank sample or reference was prepared by combining dioxane and water in a 1:1 ratio. Before characterization, the isolated lignin samples were diluted multiple times because of their darker coloration than the standard. The lignin yield was ascertained utilizing the equation provided in Equation (1). The yield was achieved by comparing the obtained mass with the initial black liquor.

$$Yield\ of\ lignin\ [\%] = \frac{weeight\ of\ isolated\ lignin}{weight\ of\ lignin\ in\ black\ liquor} \times 100 \quad (1)$$

The phenolic compounds in lignin were quantified by utilizing a UV-Vis spectrophotometer device (Agilent Carry 60) and employing the Folin-Cioucalteu method with gallic acid as a reference standard. Analysis for determining total phenol is carried out by making reagents first. The content of phenolic compounds in the extract is expressed in equivalent gallic acid units (mGEA/g extract) through the regression equation from the calibration curve [18]. Precisely 500 µL of the sample solution and different reference solutions of gallic acid with 25, 50, 100, 150, and 200 µl were put into a reaction tube using a pipette. Next, distilled water (4 ml) and Follin-Ciocalteu (250 µl) were introduced. Subsequently, the solution was thoroughly mixed using a vortex and remained at ambient temperature for 2 hours. The absorbance was measured at a precise wavelength of 765 nm. The phenol content was determined as the amount of gallic acid equivalent (µg/mL sample). The material was diluted ten times, resulting in a final 100 µg/ml concentration. The total phenolic content can be quantified by employing the formula in Equation (2). The total phenol content analysis produced a color change after being dripped with Follin-Ciocalteu solution and left for 2 hours. This color change indicates that lignin contains phenol due to the hydroxyl ions in the phenol compound reacting with Fe^{3+} in $FeCl_3$.

$$Total\ phenolic\ content = \frac{abs - intercept}{slope} \times df \quad (2)$$

where, Abs = sample absorption; df = dilution factor

The functional group in lignin was analyzed by Fourier-transform infrared (FTIR) spectroscopy using FTIR–an attenuated total reflectance spectrometer (Tensor II, Bruker, USA). The resolution was 4 cm^{-1} with 40 scans at a wavenumber of 4000–400 cm^{-1}. The extracted lignin was examined for particle size using a Horiba Nano Partica SZ-100 particle size analyzer. The laser used in the present study was a solid-state laser with an ad diode pump, operating at 532 nm and 90° and 173° laser angles. A scanning electron microscope (JEOL JSMIT300) was used to examine the surface of lignin. Following the photography, the surfaces were subjected to a gold sputtering treatment lasting roughly 2 minutes. The isolated lignin was bonded to carbon sample containers using adhesive tape. Micrographs were obtained at a magnification of 500 times. Antioxidant activity against 2,2- diphenyl-1-

picrylhydrazyl (DPPH) free radicals was measured using the approach described in reference [19]. Quercetin served as the reference solution for assessing antioxidant activity. The extract solution was mixed with methanol to create a stock solution sample at a concentration of 1000 ppm. The sample was tested by altering the concentrations to 10, 50, 100, and 200 ppm. 0.5 ml of DPPH solution (1 ml in methanol) was added to this solution. The solution was subsequently homogenized with a vortex, incubated at room temperature for 30 minutes to prevent light exposure, and stored at that temperature. The absorption was computed at a wavelength of 517 nm utilizing a UV-visible spectrophotometer after obtaining the incubation results. The sample's inhibition percentage was determined by comparing its absorption to that of the blank. The percent inhibition measurement is represented by Equation (3).

$$(\%\ \text{Inhibition}) = \left[1 - \left(\frac{\text{As}}{\text{Ao}}\right) \times 100\right] \quad (3)$$

where, Ao = Absorbance of blank; As = Absorbance of sample

The sample concentration was graphed against the percentage of DPPH-reducing activity. The IC50, or attenuation value of 50%, is determined by graphing the percentage attenuation of the sample concentration. The experiments were conducted in duplicate or two repetitions, employing quercetin as a standard for comparison.

Sun protection factor (SPF) value analysis is carried out by calculating the absorption at UV-B wavelengths using the Mansur equation [20]. In calculating the SPF value, the visible wavelength only hits UV-B. Therefore, the additional sample absorption information must be added to obtain the UV-A wavelength value. The spectrum produced by this sample was obtained from the UV-visible instrumentation at a wavelength of 230–400 nm. The absorption value was produced at a 5 nm interval in wavelength of 230–320 nm and a 10 nm interval in wavelength of 320–400 nm. The obtained absorbance value is multiplied by the EE × 1 determination factor at each interval absorption, as seen in Table 1. The amount of EE × 1 was multiplied by the final correction factor and the SPF value from the analyzed sample preparations [21],[22]. The SPF value was calculated using Equation (4).

$$\text{SPF} = \text{CF} \sum_{320}^{290} \text{Abs} \times \text{EE} \times 1 \quad (4)$$

where, CF = Correction factor (10); EE = Spectrum of Erythemal Effects; 1 = Intensity spectrum from the sun; Abs = Sample absorbance.S

Table 1. Erythemal effect spectrum (EE) x intensity spectrum from the sun (1) values

Wavelength (nm)	EE × 1
290	0.0150
295	0.0917
300	0.2874
305	0.4378
310	0.1864
315	0.0839
320	0.0180
Total	1

The stability of the prepared samples was analyzed by visually observing color, shape, odor, and phase transfer. Particle size and pH were also observed. Each sample was placed into a vial, stored at room temperature, and analyzed for stability parameters. This observation was carried out over several weeks, and weekly checks were conducted.

Method and Procedure

Lignin Isolation from black liquor [23]–[25]

Extracting lignin from the black liquor of oil palm empty fruit bunch (OPEFB) involved acidification to a pH of 2 employing hydrochloric acid with 1 M concentration. Approximately 200 gr of the black liquor underwent treatment with hydrochloric acid diluted to achieve the desired pH level. The mixture was continuously agitated at room temperature for eight hours and left undisturbed overnight. Subsequently, the solution underwent filtration using a technical-grade filter paper designed for vacuum filtration. Then, the separated lignin was rinsed multiple times with warm water to eliminate contaminants until the pH of distilled water reached around 5–6. The extracted lignin was dried in an oven at 50°C for approximately 24 hours and then stored in a desiccator until further use.

Preparation of lignin-based sunscreen

The formulation of sunscreen cream from isolated lignin was made with various concentrations of extracted lignin from black liquor. The materials used in this formulation are grouped by phase, as seen in Table 2. The formulation was carried out using the mixing methods. Initially, the ingredients of A was mixed. When the mixture of A reached a temperature of 75 °C, lignin solid (E) was added while stirring at 200 rpm until it dissolved completely. Separately, the Sepigel (C) was stirred and heated at 50 °C. After that, to the beaker containing mixture A and E, the ingredients of B were added one by one at 300 rpm and C at 500 rpm. When the temperature decreased to 50°C, Euxyl (D) was put into the mixture. Next, the mixture of the cream formulation was mixed for 30 minutes or until room temperature was reached after all the ingredients had been added.

Table 2. Formulation of isolated lignin-based sunscreen creams.

Group	Chemicals	Composition (wt.%)			
		F1	F2	F3	F4
A	Aquadest	84.9	81.9	81	80
	Glycerin	3	3	3	3
	Triethanolamine	-	2	2	2
B	Cetyl Alcohol	5	5	5	5
	Sunflower Oil	2	2	2	2
	Caprylic Acid	2	2	2	2
	Tween 80	-	0.25	0.25	0.25
	Span 80	-	0.75	0.75	0.75
C	Sepigel	2	2	2	2
D	Euxyl	1.1	1	1	1
E	Lignin	-	0.1	1	2

RESULTS AND DISCUSSION

Physicochemical Characteristics of Extracted Lignin from Black Liquor

Lignin was derived from the isolation process from black liquor as a by-product resulting from the pretreatment process of oil palm empty fruit bunches (OPEFB) in bioethanol production. This black liquor is an essential solution with a pH of 12 and has a characteristic dark black color and a strong odor. The color produced from black liquor comes from a mixture of organic and inorganic compounds, which were reduced by the waste during the EFB cooking process [26]. Isolation of lignin in this study used 1 M of hydrochloric acid solvent. The cooking process and type of solvent influenced the characteristics of isolated lignin. The obtained lignin yields 0.56% and a purity of 74.87%. Based on several previous studies, the yields produced are still lower than those of several previous studies, which is 0.93%. Despite the same method used by acid precipitation, the previous study used two stages of precipitation that might differ in the yield value [27], [28]. The total phenol content obtained from lignin isolated using 1 M hydrochloric acid solvent was 32.71 ± 4.60 mg gallic acid equivalent/g extract. Comparing this finding to earlier studies on modified lignin, which had a TPC of 1.08–1.52 mg gallic acid equivalent/g extract, this isolated lignin is more favorable [29]. Nevertheless, compared to black liquor as the raw material, its TPC varied between 91.6 and 1099.6 mg of gallic acid equivalent/g extract [30]. The isolated lignin from black liquor used in this research produced characteristics as shown in Table 3.

Table 3. Characteristics of isolated lignin.

Parameter	Value
Yield (%)	0.56 ± 0.16
Purity (%)	74.87 ± 1.02
Total phenol (mg GAE/g extract)	32.71 ± 4.60

Functional Group of Isolated Lignin

The functional group of isolated and conventional lignin was identified using Fourier-transform infrared (FTIR) analysis. Although the functional group spectra of isolated and conventional lignin differ in intensity, they are comparatively similar (Figure 1 and Table 4). Hydroxyl (OH), aromatic rings (C=C groups), C-C, C-O groups, phenolic OH, and ether in syringyl and guaiacyl are the functional groups present in both isolated and standard lignin. Table 4 lists each band's relative intensity and assignment. This result was in line with the previous studies [23], [24].

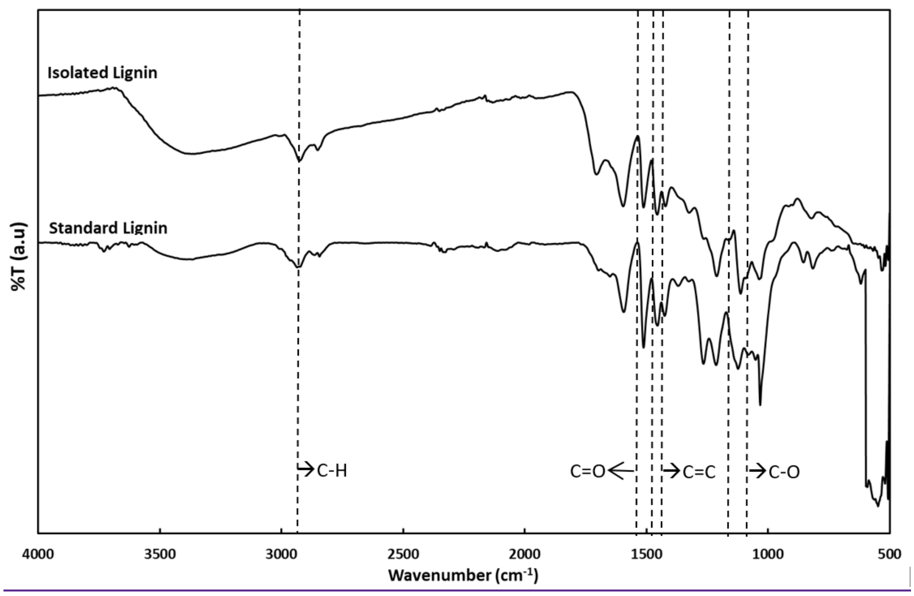

Figure 1. Spectra of isolated and standard lignin

Table 4. Wavenumber of spectra from isolated and standard lignin

No	Functional group	Wavenumber (cm^{-1})	
		Standard Lignin	Isolated lignin
1.	O-H stretching	3626.567	3390.854
2.	C-H methyl stretching	2935.798	2922.013
3.	Aromatic rings	1593.339	1595.977
		1511.846	1512.024
4.	C-H asymmetric	1454.622	1457.936
5.	C-O stretching (syringil ring)	1213.551	1212.289
6.	C-O(H) + C-O (Ar) (guaiacyl ring)	1123.466	1113.936

Particle Size and Morphological Analysis of Isolated Lignin

The isolated lignin has a particle size of approximately 32.90 ± 17.50 µm, while the particle size of standard lignin is about 34 µm. The morphology of isolated lignin was assessed using a scanning electron microscope (SEM) at a magnification of 500×. The acid solution's utilization influenced particle size and distribution [24]. From the resulting morphology, it can be seen that the isolated lignin has a reasonably even distribution and varies in size (Figure 2).

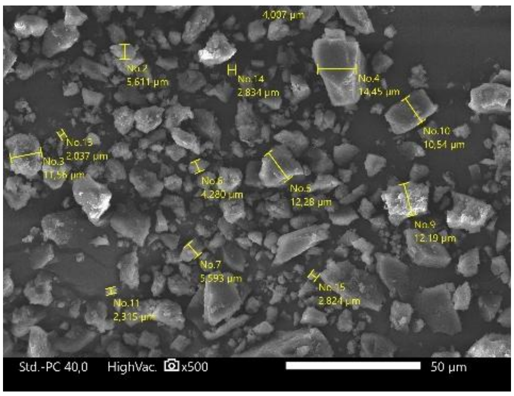

Figure 2. Morphological image of isolated lignin

Characteristic of Lignin-based Sunscreen Cream

Antioxidant activity

Ultraviolet-visible (UV-Vis) spectrophotometer equipment was used qualitatively to assess the cream's antioxidant activity. Following the acquisition of absorbance data, a standard curve was constructed, and antioxidant efficacy values for lignin sunscreen formulations were produced. These results are displayed in Figure 3. This high level of antioxidant activity in the isolated lignin may be attributed to polyphenolic chemicals [31]. Phenol lignin acts as an antioxidant primarily due to its rich source of phenolic hydroxyl groups, which are crucial for its antioxidant activity. The presence of these phenolic structures allows lignin to effectively scavenge free radicals, which are unstable molecules that can cause oxidative damage to cells and contribute to various diseases and aging processes [32]. The antioxidant activity of lignin is directly related to the stability of phenoxy radicals and the dissociation enthalpy of phenolic hydroxyls. Therefore, the antioxidant activity of lignin is directly related to its phenolic hydroxyl content. The level of antioxidant activity increases with lignin concentration. This is because lignin's phenolic compound increased, increasing the antioxidant activity. The previous study by Antunes et al. (2023) also reported good antioxidant activity for raw lignin and cream-formulated lignin with IC_{50} less than 50 mg/ml [33]. This finding demonstrates lignin's superior antioxidant properties [15].

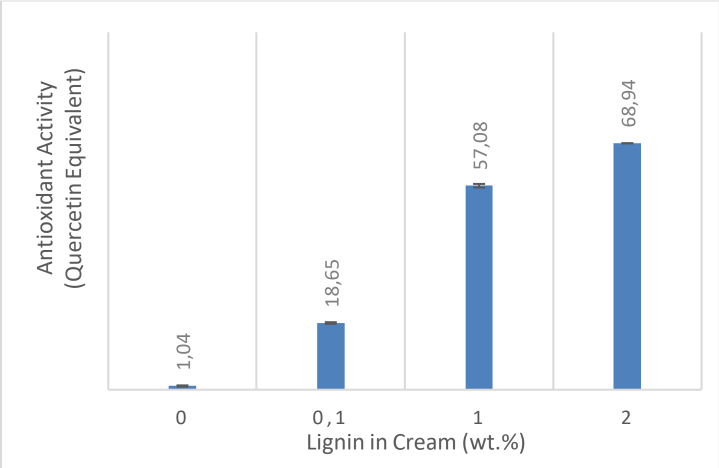

Figure 3. Antioxidant activity of lignin-based sunscreen creams

Sun Protection Factor (SPF) Value

The efficacy of sunscreen material was assessed using the in vitro technique employing a UV-visible spectrophotometer instrument. The absorbance data was then processed based on the SPF equation, and an SPF value was produced, as seen in Figure 4. It shows that adding lignin to the cream resulted in a higher SPF value. The addition of lignin enhanced the SPF of sunscreen creams. The presence of UV-absorbing groups, such as carbonyl, phenolic, and other chromophores, can explain this phenomenon. These groups influenced the SPF value because they absorb UV with a wavelength range of 250–400 nm due to the existence of the bonds from the aromatic ring and lone pair electrons from oxygen atoms. UV photon energy causes an electron to jump from a bonding or nonbonding orbital to an empty antibonding orbital. The energy fluctuates depending on the chemical structure and the state of electronics [11]. Therefore, lignin, as the sole aromatic biopolymer found in nature, is likely responsible for this phenomenon [16].

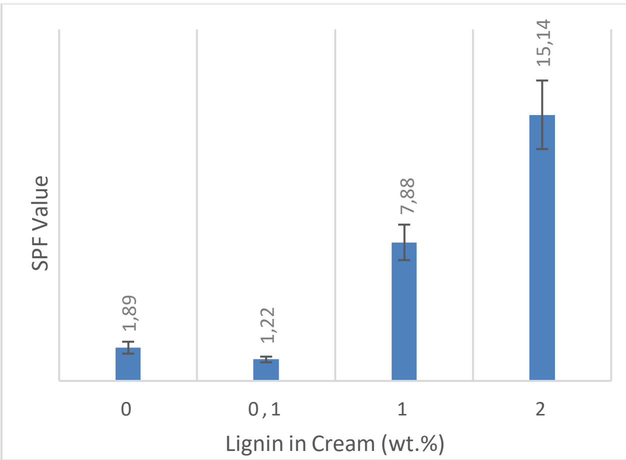

Figure 4. SPF Value of lignin-based sunscreen creams

Stability Analysis

Lignin cream was analyzed for physical stability by observation and particle size on days 0 and 28. According to the physical observation data shown in Table 5, the visual appearance of the lignin cream became more compact in texture and vivid in color. This shows that sunscreen cream is relatively stable in physical observations. In terms of particle size, the smaller the particle size, the more chromophores may interact with UV radiation, leading to a better absorption efficiency [11]. Therefore, the effectiveness of sunscreen is affected by lignin particle size. As a result, better UV protection could be achieved per weight of lignin, which is advantageous for developing sunscreen compositions that work well. Based on the result, there was a trend of decreasing in size along the time interval. This might be due to the homogeneity of the chemical ingredients in the creams and also the smooth texture of the creams [34]. The decrease in particle size over storage time was rather contradictory to the widely known stability trend. However, the study by De Cleyn et al. (2021) also showed a decreasing trend during the stability test. The process in which smaller particles form instead of the larger particles is called the process of digestive ripening or reversed Ostwald ripening. A current hypothesis is the presence of an area of the component concentration and interaction energies where smaller particles are more stable than the larger ones. The surfactant, such as tween, might make the energy of the small particle become negative. Mass would move from the larger particle to the smaller one, consequently narrowing the particle size distribution [35].

Table 5. Stability of lignin-based sunscreen creams.

Lignin content (wt.%)	Particle size (μm)		Physical appearance	
	D-0	D-28	D-0	D-28
0.1	26.39 ± 35.81	25.15 ± 12.42		
1	32.90 ± 17.50	22.27 ± 10.44		
2	57.83 ± 46.74	48.71 ± 29.04		

CONCLUSION

Research findings indicate that lignin, the sole aromatic biopolymer found in nature, can absorb ultraviolet (UV) rays and develop sunscreen protection. The activity of sunscreen on lignin creams can be seen from the sun protection factor (SPF) value at each lignin level. The highest SPF value was obtained on the 2% lignin with an SPF value of 15.14. This value has met the Indonesian National Standard (SNI) requirement that requires an SPF value of 15 for sunscreen formulations. This study highlighted the inherent capabilities of lignin in several high-value applications, including the field of cosmetics.

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DATA AVAILABILITY STATEMENT

The data supporting this investigation's findings can be obtained from the corresponding author upon reasonable request.

COMPETING INTEREST

The authors disclosed no competing interests.

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