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Sunscreen from Coconut Coir Based Lignin Nanoparticles with Extraction Method and pH Shifting as an Anti-UV Material

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ABSTRACT

Indonesia is a tropical country located on the equator with high sun exposure, so sunscreen is needed to reduce the risk of exposure to ultraviolet (UV) light. In this research, a sunscreen was developed that uses natural active ingredients in the form of lignin made from coconut coir. The aim of this research is to determine the comparison between the mass of coconut coir and the volume of ethanol solution that produces the highest lignin content, as well as the concentration comparison between lignin nanoparticles and commercial sunscreen that produces the highest SPF value. The synthesis of lignin from coconut coir was carried out using an extraction method using ethanol solvent, followed by a hydrolysis process with NaOH and acidification with H_2SO_4, while lignin nanoparticles were made using a pH shifting method using ammonia and HCl. The lignin nanoparticles formed are then added to the sunscreen's active ingredient. The variables used were the ratio of the mass of coconut coir to the volume of 80% ethanol solvent (1:5, 1:10, 1:15, and 1:20 (w/v)) and the concentration of lignin in commercial sunscreen cream (2%, 4%, 6%, 8%, and 10% (w/w)). The results of the research show that the higher the solvent ratio, the more lignin is produced, but will decrease after reaching the optimum point. The optimal solvent volume occurs at a ratio of 1:15 (w/v) with a yield of 12.94% (w/w). In addition, the higher the lignin concentration, the resulting SPF value will also increase. The best concentration is 10% (w/w) at a solvent ratio of 1:15 (w/v) with an SPF value of 22.23.

Keywords: *Lignin; nanoparticles; sunscreen; coconut coir*

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ABSTRACT

Indonesia merupakan negara tropis yang terletak di garis khatulistiwa dengan paparan sinar matahari yang tinggi, sehingga diperlukan tabir surya untuk mengurangi risiko paparan sinar ultraviolet (UV). Pada penelitian ini dikembangkan tabir surya yang menggunakan bahan aktif alami berupa lignin berbahan dasar sabut kelapa. Tujuan dari penelitian ini adalah untuk mengetahui perbandingan antara massa sabut kelapa dan volume larutan etanol yang menghasilkan kadar lignin tertinggi, serta untuk mengetahui perbandingan konsentrasi antara nanopartikel lignin dan tabir surya komersial yang menghasilkan nilai SPF tertinggi. Sintesis lignin dari sabut kelapa dilakukan dengan metode ekstraksi menggunakan pelarut etanol, dilanjutkan dengan proses hidrolisis dengan NaOH dan pengasaman dengan H_2SO_4, sedangkan nanopartikel lignin dibuat menggunakan metode perubahan pH menggunakan amonia dan HCl. Nanopartikel lignin yang terbentuk kemudian ditambahkan pada bahan aktif tabir surya. Variabel yang digunakan adalah perbandingan massa sabut kelapa dengan volume pelarut etanol 80% (1:5, 1:10, 1:15, dan 1:20 (b/v)) dan konsentrasi lignin dengan krim tabir surya komersial (2%, 4%, 6%, 8%, dan 10% (b/b)). Hasil penelitian menunjukkan bahwa semakin tinggi rasio pelarut maka semakin banyak lignin yang dihasilkan, namun akan menurun setelah mencapai titik optimum. Volume pelarut optimal terjadi pada perbandingan 1:15 (b/v) dengan yield sebesar 12,94% (b/b). Selain itu, semakin tinggi konsentrasi lignin maka nilai SPF yang dihasilkan juga semakin meningkat. Konsentrasi terbaik adalah 10% (b/b) pada perbandingan pelarut 1:15 (b/v) dengan nilai SPF 22,23.

Keywords: *Lignin; nanopartikel; sunscreen; sabut kelapa*

INTRODUCTION

Indonesia is a tropical country located on the equator with high exposure to sunlight. Ultraviolet (UV) light based on its wavelength is divided into three parts: UV-A, UV-B, and UV-C. UV-C has the shortest wavelength, ranging from 200 nm to 290 nm. UV-C is unable to reach the earth's ozone layer. UV-B has a wavelength ranging from 290 nm to 320 nm. UV-B can reach the ozone layer and penetrate the epidermis layer of the skin. UV-A has a wavelength ranging from 320 nm to 400 nm, so it can penetrate the epidermis, dermis, and subcutaneous tissue. When UV light penetrates the skin, its main targets are oxygen molecules under the epidermis. This causes the formation of various free radical compounds, including reactive oxygen species (ROS), hydroxyl radicals, alkyl lipid radicals, and others. These free radicals on the skin can cause skin damage, such as skin aging, the darkening of pigment, and even skin cancer [1], [2], [3], [4]. The human body has a natural protective layer on the skin through skin thickening and pigmentation. However, this ability also has limitations, therefore, excessive exposure to ultraviolet light will have an impact on health. The body needs antioxidant nutrition from the outside if there are excess free radicals in the body. Antioxidants are substances that neutralize, paralyze, and inhibit the growth of free radicals, which are reactive and dangerous. The use of sunscreen products is chosen as an antioxidant solution for skin exposed to sunlight. Many sunscreen products contain synthetic chemicals. So continuous use also poses health hazards. To avoid this, use sunscreen made from natural lignin-based ingredients.

Lignin is the main component of plant cell walls. In addition, lignin plays an important role in maintaining the stiffness and strength of stems, making cell walls watertight, and protecting plants from pathogens. Lignin is very abundant in nature, lignin is the second most abundant organic polymer component on earth after cellulose [5]. Lignin production in nature ranges from 5-36 x 10^8 tons per year, while in the pulp and paper industry, more than 50 million tons of lignin are produced as a by-product every year [6], [7]. Lignin has been widely studied in the field of materials science due to its abundance in nature, high UV absorption ability, and good antioxidant properties. The complex chemical structure of lignin, which contains aromatic rings of methoxy and hydroxyl groups, allows lignin to be combined into different materials to produce antioxidant products that can be used in several applications. This functional group causes the cessation of oxidative propagation reactions through the donation of hydrogen. Apart from that, lignin also contains UV-absorbing functional groups such as phenolics, ketones, and other chromophores. Based on lignin's ability to absorb UV light and its good antioxidant properties, lignin can be applied in the cosmetic field as a sunscreen. Lu et al. reported the synthesis of lignin nanoparticles with an average size of 144 nm using a supercritical anti-solvent precipitation method. This research used lignin with a concentration 12.4 times higher than bulk lignin so that the resulting product had higher antioxidant and free radical scavenging activity. The resulting lignin nanoparticles are used in the food processing and pharmaceutical industries [8]. Yearla and Padmasree reported the synthesis of lignin dioxane nanoparticles with an average size of 104 nm using an anti-solvent precipitation method where lignin was dissolved in a mixture of acetone and water (9:1 v/v). The resulting lignin nanoparticles show greater antioxidant and UV protection properties than bulk lignin and are used in the food processing and pharmaceutical industries [9]. Based on lignin's ability to absorb UV light and its good antioxidant properties, it can be applied in the cosmetic field as a sunscreen.

In this research, coconut coir was used as a raw material for lignin because it is abundant in nature. Coconut coir is a solid waste from the coconut oil industry, as well as food waste sourced from coconuts, which are widely consumed by people in Indonesia. Indonesia itself is capable of producing 18.3 million tons of coconut a year, this number continues to increase from year to year, so Indonesia becomes the largest coconut producer in the world [10]. Apart from that, the reason for using coconut coir was that coconut coir has a fairly high lignin content of 33.15%, while the cellulose content is 30.47% and the hemicellulose content is 25.42% [11]. Research on lignin as a promising solution for application as sunscreen has been carried out for the last few years. Li et al. reported the synthesis of lignin from the extraction of organic acids submicrometer-sized (400 nm–5 µm) for sunscreen applications, where the lignin particles showed a high capacity to increase the sun protection factor value of 2.80–3.53 at a dose of 5% [12]. Qian et al. synthesized lignin with different sizes from enzymatic hydrolysis lignin (EHL) and organosolv lignin (OL) purified by alkaline solution, acidification, filtration, and washing. The lignin was then mixed with pure skin cream to develop a lignin-based sunscreen. The results obtained show that the sun protection factor (SPF) value of sunscreen decreases with increasing lignin particle size [13]. Ago et al. reported the synthesis of lignin nanoparticles using an aerosol reactor. There were 3 lignins used, namely kraft lignin, alkali lignin, and organosolv lignin, with concentrations of 0.5%, 1%, and 2%, where pure water was used as a solvent for alkali lignin and dimethylformamide (DMF) was used for kraft lignin and organosolv lignin. The atomizer is operated with nitrogen gas at a flow rate of 3 L/minute, then the aerosol is taken to the reactor, which is heated to 153ºC, and the particles are dried into solid particles to obtain solid spherical lignin nanoparticles with a size of 30 nm to 2 µm [14].

The synthesis of lignin as sunscreen has its own challenges, one of which lies in particle size. The large particle size is a causal factor that limits the performance of lignin in absorbing UV light, making it ineffective when used as a sunscreen. Therefore, this research develops the synthesis of nanoparticle-sized lignin because lignin nanoparticles provide the advantage of having higher antioxidant activity. In addition, lignin nanoparticles can increase lignin's ability to absorb UV light. There are various methods to synthesize lignin nanoparticles, including solvent exchange, pH shifting, interfacial bonding, mechanical treatment, and aerosol. Of the various lignin nanoparticle syntheses, the pH shifting method was chosen because it has several advantages, including high yields and simple and cheap equipment. Next, we observed the effect of lignin concentration on the SPF value.

METHOD

Materials

The materials used in this study were coconut coir from a local market in Nguling, Pasuruan, Indonesia. Ethanol and aquadest were purchased from UD. Sumber Ilmiah Persada, Indonesia. NaOH, NH_4OH, HCl, and H_2SO_4 were purchased from Merck. All chemicals were of analytical grade and used as received without further purification.

Experiment

Sample Preparation

The coconut coir was dried in the sun. Then the coconut coir was ground in a grinding machine. Then the coconut coir was sieved at a size of 100 mesh.

Extraction Process

Dried coconut coir was wrapped in filter paper, then tied and put into the extractor tube. The next step was to add an 80% ethanol solution as a solvent. The variables used are the ratio of the mass of coconut coir to the volume of an 80% ethanol solution of 1:5, 1:10, 1:15, and 1:20 (w/v). For example, in a ratio of 1:5, 20 grams of coconut coir requires 100 mL of an 80% ethanol solution. Then the mixture was extracted at 80ºC for 5 hours. The packed coconut coir extract solids were then weighed and hydrolyzed.

Hydrolysis Process

The extracted coconut coir was mixed with 250 mL of a 5% NaOH solution. Then this mixture was put into a two-neck flask. The next step is to assemble the extraction tool and drain the Leibig cooling water as shown in Figure 1. This hydrolysis stage was carried out at a temperature of 80°C for 5 hours. The cooking results were filtered with filter paper to remove the filtrate, which is a dark-colored liquid (black liquor). Acidification was carried out on black liquor to pH 4 using 15 mL of a 72% H_2SO_4 solution by adding it slowly. Then leave it until it precipitates. The precipitate was obtained by filtering the solution using filter paper and then washing it with distilled water until neutral. Lignin was placed in an oven at 60ºC to remove the water content.

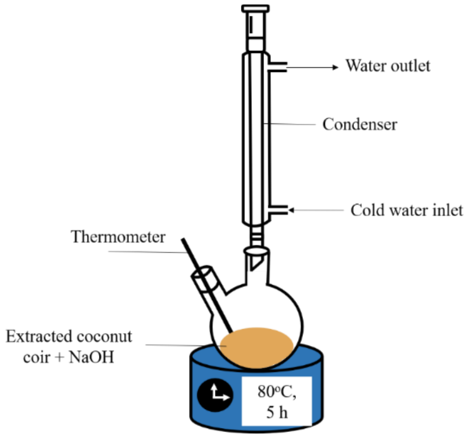


Figure 1. Schematic diagram of hydrolysis

Lignin Nanoparticle Synthesis

Lignin was added to a concentrated ammonia solution (37 wt%) until the lignin was completely dissolved. The pH value is around 11 at this time. Then the pH value of the lignin solution was adjusted to around 3 by adding HCl (1 M).

Analysis of Sun Protection Factor (SPF) Value

Lignin nanoparticles were mixed with commercial sunscreen cream SPF 15 with variables of 2%, 4%, 6%, 8%, and 10% (w/w) using a magnetic stirrer at a speed of 600 rpm for 5 hours. The mixing process was carried out at room temperature in a dark place to prevent light from entering. To check whether lignin was dissolved or mixed in the cream, the sample was centrifuged at 200 rpm for 1 hour. After centrifugation, no precipitate was visible, indicating that all the lignin used in this study was dissolved in the cream. This mixture was then measured for its absorption value using a UV-Vis spectrophotometer. A 400 mg sample was then put into a 100 mL measuring flask and diluted with 80% ethanol, and the absorbance was measured using a UV-Vis spectrophotometer. As a blank, an 80% ethanol solution was used. The absorption curve test used was with a wavelength of 290–320 nm, and then the average absorption was determined at 5 nm intervals three times.

RESULTS AND DISCUSSION

The specifications for coconut coir that will be used are that coconut coir has a texture that is not too hard, so grinding is easier. Before carrying out the delignification process on coconut coir, a sample preparation process was carried out in the form of drying, grinding, and sieving up to a size of 100-mesh, as shown in Figure 2. Then the 100-mesh coconut coir will enter the extraction process.

Figure 2. Coconut coir 100 mesh

The extraction process is a separation process that utilizes the solubility properties of a compound. Separation is carried out by mixing two immiscible solvents to isolate a particular compound in one solvent from the other solvent. This extraction process can be applied to the process of separating compounds contained in plant tissue into certain solvents [15]. The extraction process used is soxhletation extraction to separate impurities in coconut coir. The advantage of the soxhletation method is that extraction occurs continuously with a relatively constant amount of solvent and back cooling. Repeated filtration using the soxhletation method is considered more economical because relatively little solvent is used, but the yield obtained is greater than that obtained using the maceration extraction method [16].

The process of extracting coconut coir begins with making a simplicial by processing it into powder form. The use of simplicial powder makes it easier to extract active compounds due to the increased surface area needed to interact with the solvent. The smaller the powder particle size, the greater the surface area-to-volume ratio, thus speeding up the reaction rate and accelerating the dissolution of the active compounds contained in simplicial. Particle size is an important factor affecting the washing process during extraction. A smaller particle size results in a larger surface area, which further increases the rate of solvent diffusion into the particle. Increasing the diffusion rate causes the extraction of desired compounds from coconut coir simplicial to become more efficient [17].

In the extraction process, the variable used is the ratio between the mass of coconut coir and the volume of the solvent of 1:5, 1:10, 1:15, and 1:20 (w/v). The solvent used in this extraction process is an 80% ethanol solvent. The consideration for using ethanol solvent is that ethanol solvent is a solvent that meets the requirements for making extracts and is universal, so it can dissolve almost all substances, both polar and nonpolar [18]. Ethanol solvents can attract phenolic and flavonoid compounds, which have the potential to act as antioxidants [19]. The ethanol solvent has a low boiling point of 80^{o}C, so the evaporation process does not require high temperatures that can damage the active compounds in the sample [20]. In this research, ethanol solvent was used at a concentration of 80% because this concentration produces high antioxidant activity. This was shown in research on katuk leaves extracted using 80% ethanol and 96% ethanol, where the 80% ethanol extract of katuk leaves showed greater antioxidant activity than the 96% ethanol extract [21]. This antioxidant activity is related to the application of sunscreen, where antioxidants function to stabilize free radicals by completing the lack of free radical electrons, thereby inhibiting chain reactions. Antioxidants can act as hydrogen radical donors or as free radical acceptors, so they can delay the initiation stage of free radical formation. The extraction process using the soxhletation method is carried out by wrapping the coconut coir sample according to the variables in filter paper and then putting the sample in an extractor tube. After that, an 80% ethanol solution was added according to the variable as a solvent in the process. The extraction process in this research was carried out for 5 hours at 80^{o}C. The extraction results are liquid in a solvent container and a sample still wrapped in filter paper in a solid extractor tube. The resulting extract is a solid that has been extracted and then dried using an oven at 60^{o}C to remove the water content.

The data obtained during the extraction process using the soxhletation method is presented in Table 1. Table 1 shows the relationship between the mass ratio of coconut coir and the volume of 80% ethanol solvent on the yield of coconut coir produced during the extraction process. From Table 1, it can be seen that the greater the volume of solvent used, the greater the yield of extracted coconut coir. The greatest yield (97.69% w/w) was obtained at a solvent volume of 300 mL or a ratio of 1:15 (w/v). This is because the greater the ratio of solvent to sample, the higher the concentration difference between the solvent and the components contained in the sample. Thus, the extraction yield will increase. In addition, the increase in the yield value is thought to be caused by increasing the area of contact of the sample with the solvent. At a ratio of 1:20 (w/v), the resulting yield decreased to 96.82% w/w. This occurs because the ratio exceeds the optimum condition. Rifai et al. stated that the higher the amount of solvent used, the more optimal the release of the target compound into the solvent, and the solvent's saturation can also be avoided. However, after the amount of solvent is increased by a certain amount, the increase in extracted compounds is relatively small and tends to become constant. However, a further increase causes a decrease in extract yield [22]. This provides an indication of the optimum conditions for coconut coir extraction in terms of the solvent-to-material ratio aspect, which is found in the use of a solvent ratio of 1:15 (w/v). Teresa et al. added that the greater the amount of solvent used, the lower the yield because a state of equilibrium between solid and liquid has been achieved [23].

Table 1. The ratio between the mass of coconut coir and 80% ethanol solvent to the percentage yield of extracted coconut coir

Ratio (mass of coconut coir and 80% ethanol) (w/v)	**% Yield of extracted coconut coir (w/w)**
1:5	96.05
1:10	96.21
1:15	97.69
1:20	96.82

Delignification is the process of releasing lignin from complex compounds [24]. The delignification of coconut coir uses a 5% NaOH solution as a solvent. The hydrolysis process was carried out for 5 hours at 80°C. The addition of NaOH as a solvent is because lignin dissolves easily in alkaline conditions. NaOH aims to break down the complex compounds contained in coconut coir in the form of lignin, cellulose, and hemicellulose. In addition, NaOH also functions as a catalyst in the hydrolysis process. The hydrolysis process of coconut coir produces dissolved lignin, which is called black liquor.

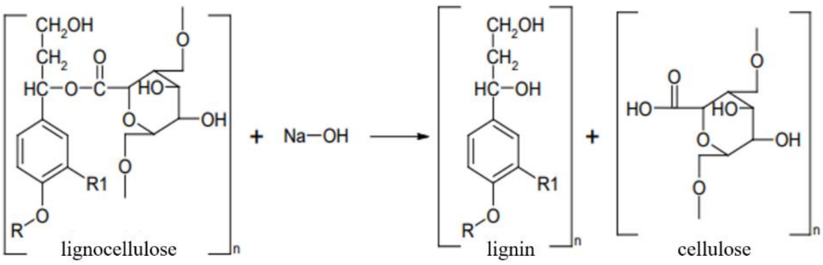
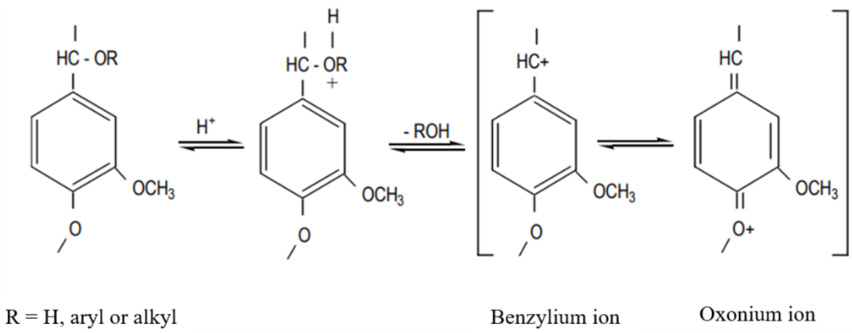


Figure 3. Mechanism of breaking the bonds between lignin and cellulose using NaOH [25]

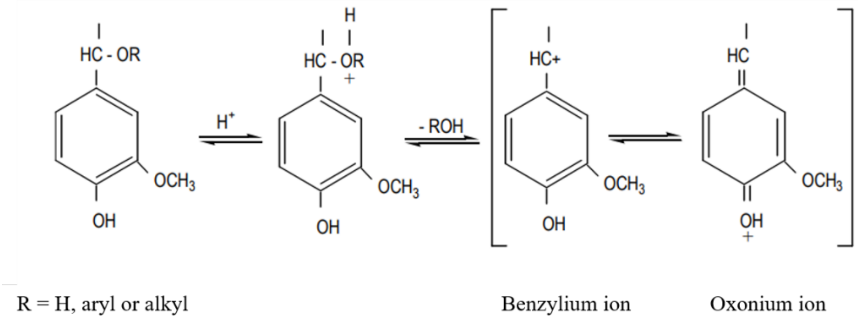
Figure 3 shows the reaction between coconut coir containing the complex carbohydrate compound lignin and a sodium hydroxide (NaOH) solution. During this reaction, hydroxide ions (OH^-) from NaOH break bonds in the basic structure of lignin, while sodium ions (Na^+) bind to lignin, resulting in the formation of sodium phenolate [25]. The phenolic compounds contained in lignin dissolve easily and give a black color to the solution called black liquor. In the hydrolysis process, other compounds in coconut coir, such as cellulose and hemicellulose, are released. This indicates that more lignin is obtained. To separate cellulose and hemicellulose from black liquor, filtration was carried out before the lignin was isolated.

To produce lignin isolates, a lignin isolation process, or a process of separating and extracting lignin from black liquor, is carried out. Lignin is a three-dimensional polymer consisting of phenylpropane units and has various other functional groups such as hydroxyl, carbonyl, and methoxy. The characteristics of black liquor after going through the hydrolysis extraction process are that it has a dark black color, a strong odor, and a pH > 12. The acid precipitation method is used to isolate or separate lignin from black liquor. This method is also considered simple, efficient, and economical because it does not require huge costs.

The process carried out at the acidification stage involves mixing black liquid with an acid solution. The acid solution used is 72% H_2SO_4, which aims to create acidic conditions during the isolation reaction. Lignin is insoluble in an acidic environment, so precipitation will occur during the acidification process. The addition of acid causes the ether group to undergo protonation, which results in the release of alcohol molecules and forms a benzylium and oxonium system, as shown in Figure 4. The condensation reaction between benzylium ions and nucleophiles can produce lignin precipitates. The characteristic that occurs in lignin isolation is the clumping of black liquor [26].



(a)



(b)

Figure 4. The addition of acid to lignin-containing phenolic ether groups causes the ether group (a), to undergo protonation, forming benzylium and oxonium ions (b) [26]

The acid was added until a pH of 4 was obtained, and the precipitation was carried out for 15 minutes. The precipitate produced in black liquor is centrifuged to obtain the maximum precipitate. The precipitate that has been centrifuged is washed using aquadest to neutralize the pH and accelerate the dissolution of hydrophilic polar residues so as to speed up the settling process. Centrifugation was carried out repeatedly until the pH was neutral. The resulting lignin was placed in the oven until it dried at a temperature of 60^{o}C to obtain a dry powder.

The data obtained during the hydrolysis process is presented in Table 2. Table 2 shows the relationship between the mass ratio of coconut coir to the volume of 80% ethanol solvent and the percentage of lignin yield produced. From Table 2, it can be seen that the largest yield (22.64% w/w) was obtained at a ratio of 1:15 (w/v).

Table 2. The ratio between the mass of coconut coir and 80% ethanol solvent (w/v) to the percentage yield of lignin (w/w)

Ratio (mass coconut coir and 80% ethanol) (w/v)	**% Yield of lignin (w/w)**
1:5	18.64
1:10	20.94
1:15	22.64
1:20	14.69

The lignin formed from the extraction and hydrolysis stages is then reduced in particle size to lignin nanoparticles. The large particle size is a causal factor that limits the performance of lignin in absorbing UV light, making it ineffective when used as a sunscreen. So in this research, lignin nanoparticles were made because lignin nanoparticles provide the main advantage of having higher antioxidant activity due to a higher surface area to volume ratio. In addition, lignin nanoparticles can increase lignin's ability to absorb UV light. The synthesis of lignin nanoparticles begins by dissolving the lignin in a concentrated ammonia solution with a pH of 11 and then precipitating by lowering the pH to 3 by adding HCl. In this study, researchers used in vitro testing with a UV-Vis spectrophotometer on samples of lignin. Tests were carried out to determine the SPF (Sun Protection Factor) value of lignin. In this study, lignin was mixed with commercial sunscreen cream SPF 15 to test the SPF value. To find out the SPF value, the following formula is used:

$$SPF = CF \times \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times abs(\lambda) \quad \ldots.(1)$$

Here, CF represents the correction factor, EE is the spectrum of erithermal effect, I is the intensity spectrum of the sun, Abs is the absorbance of the sample.

The test results on the UV-Vis spectrophotometer are used as a reference for the absorption values in the formula (1) so that the SPF characteristic values are obtained, which will be presented in Table 3. Based on Table 3, it can be seen that the higher the lignin concentration, the resulting SPF value will also increase. This happens because the higher the lignin concentration, the greater the ability of lignin to absorb UV light, so the SPF value is higher. The highest SPF value occurred at a concentration of 10% (w/w) at a ratio of mass coconut coir to 80% ethanol of 1:15 (w/v), which was 22.23. Meanwhile, the lowest SPF value occurred at a concentration of 2% (w/w) at a ratio of mass coconut coir to 80% ethanol of 1:5 (w/v), which was 16.82. All the lignin particles have a high SPF. This shows that lignin particles are effective at absorbing UV light.

Table 3. SPF values of lignin with commercial sunscreen

Ratio (mass coconut coir and 80% ethanol) (w/v)	**SPF Value**				
	2%	**4%**	**6%**	**8%**	**10%**
1:5	16,82	16,94	18,54	19,28	20,76
1:10	19,23	19,42	19,56	20,23	21,28
1:15	20,53	21,12	21,53	21,98	22,23
1:20	20,18	20,94	21,01	21,38	21,96

CONCLUSION

Based on the results of the research that has been done, it can be concluded that the volume of 80% ethanol solvent has an effect on lignin yield, where the greater the volume of 80% ethanol solvent, the greater the lignin produced, but will decrease after reaching the optimum point. A solvent ratio of 1:15 (w/v) is the best solvent ratio because it has the highest lignin yield (12.94% (w/w)). Apart from that, the lignin concentration also has an effect on the SPF value, where the higher the lignin concentration, the resulting SPF value will also increase. The best lignin concentration is 10% (w/w) at a solvent ratio of 1:15 (w/v) because it has the highest SPF value (22.23).

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REFERENCES

[1] E. A. Dutra, D. A. G. Da Costa E Oliveira, E. R. M. Kedor-Hackmann, and M. I. R. Miritello Santoro, "Determination of sun protection factor (SPF) of sunscreens by ultraviolet spectrophotometry," Rev. Bras. Ciencias Farm. J. Pharm. Sci., vol. 40, no. 3, pp. 381–385, 2004.

[2] D. Dondi, A. Albini, and N. Serpone, "Interactions between different solar UVB/UVA filters contained in commercial suncreams and consequent loss of UV protection," Photochem. Photobiol. Sci., vol. 5, no. 9, pp. 835–843, 2006.

[3] L. Borska et al., “Influence of dermal exposure to ultraviolet radiation and coal tar (polycyclic aromatic hydrocarbons) on the skin aging process,” J. Dermatol. Sci., vol. 81, no. 3, pp. 192–202, 2016.

[4] A. K. Srivastav et al., “Photosensitized rose Bengal-induced phototoxicity on human melanoma cell line under natural sunlight exposure,” J. Photochem. Photobiol. B Biol., vol. 156, pp. 87–99, 2016.

[5] W. Boerjan, J. Ralph, and M. Baucher, “Lignin Biosynthesis,” Annu. Rev. Plant Biol., vol. 54, pp. 519–546, 2003.

[6] G. L. F. Gellerstedt and E. G. Henriksson, “Lignins: Major sources, structure and properties,” Monomers, Polym. Compos. from Renew. Resour., pp. 201–224, 2008.

[7] T. Saito et al., “Turning renewable resources into value-added polymer: Development of lignin-based thermoplastic,” Green Chem., vol. 14, no. 12, pp. 3295–3303, 2012.

[8] Q. Lu et al., “Comparative antioxidant activity of nanoscale lignin prepared by a supercritical antisolvent (SAS) process with non-nanoscale lignin,” Food Chem., vol. 135, no. 1, pp. 63–67, 2012.

[9] S. R. Yearla and K. Padmasree, “Preparation and characterisation of lignin nanoparticles : evaluation of their potential as antioxidants and UV protectants,” J. Exp. Nanosci., vol. 11, pp. 289–302, 2015.

[10] Kambey E, Tooy D, Rumambi D, "Uji Kualitas Briket Sabut Kelapa Sebagai Sumber Energi Biomassa Alternatif," vol. 15, no. 1, pp. 1–8, 2023.

[11] F. A. Gonçalves, H. A. Ruiz, C. D. C. Nogueira, E. S. Dos Santos, J. A. Teixeira, and G. R. De Macedo, “Comparison of delignified coconuts waste and cactus for fuel-ethanol production by the simultaneous and semi simultaneous saccharification and fermentation strategies,” Fuel, vol. 131, pp. 66–76, 2014.

[12] S. X. Li, M. F. Li, J. Bian, X. F. Wu, F. Peng, and M. G. Ma, “Preparation of organic acid lignin submicrometer particle as a natural broad-spectrum photo-protection agent,” Int. J. Biol. Macromol., vol. 132, pp. 836–843, 2019.

[13] Y. Qian, X. Zhong, Y. Li, and X. Qiu, “Fabrication of uniform lignin colloidal spheres for developing natural broad-spectrum sunscreens with high sun protection factor,” Ind. Crops Prod., vol. 101, pp. 54–60, 2017.

[14] O. J. R. Mariko Ago, Siqi Huan, Maryam Borghei, Janne Raula, Esko I Kauppien, “High-throughput Synthesis of Lignin Particles (~ 30 nm to ~ 2 µm) via Aerosol Flow Reactor : Size Fractionation and Utilization in Pickering Emulsions,” ACS Appl. Mater. Interfaces, vol. 8, pp. 23302– 23310, 2016.

[15] Mukhriani, "Ekstraksi Pemisahan Senyawa, dan Identifikasi Senyawa Aktif," Kesehatan., vol. 7, no. 2, pp. 361-7, 2014.

[16] Dwi Puspitasari A, Proyogo LS, "Perbandingan Metode Ekstraksi Maserasi dan Sokletasi Terhadap Kadar Flavonoid Total Ekstrak Etanol Daun Kresen (Muntingia calabura)," Ilmu Farmasi dan Farmasi Klinik., vol. 12, no.2, pp. 1-8, 2016.

[17] Tambun R, Limbong HP, Pinem C, Manurung E, "Pengaruh Ukuran Partikel, Waktu dan Suhu Pada Ekstraksi Fenol Dari Lengkuas Merah," Teknik Kimia USU., vol. 5, pp. 1-5, 2016.

[18] Hasma, Wilda, "Identifikasi Senyawa Metabolit Sekunder Ekstrak Kulit Pisang Kepok (Musa paradisiaca L) dengan Metode KLT," Kesehatan Manarang., vol. 5, no. 2, pp. 125-31, 2019.

[19] Munte L, Max Runtuwene R, Citraningtyas G, "Aktivitas Antioksidan Dari Ekstrak Daun Prasman (Eupatorium triplinerve Vahl.)," Jurnal Ilmiah Farmasi-UNSRAT. 2015.

[20] Rahmawati IS, Widyanto RM, Maulidiana AR, Madani MS, Riski CN, "Aktivitas Antioksidan dan Antibakteri Ekstrak Etanol Buah Ihau (Dimocarpus longan var. malesianus Leenh) Terhadap Bakteri Gram Positif (Staphylococcus aureus)," Jurnal Al-Azhar Indonesia Seri Sains Dan Teknologi., vol. 7, no. 2, pp. 138, 2022.

[21] Arista M, "Aktivitas Antioksidan Ekstrak Etanol 80% dan 96% Daun Katuk (Sauropus androgynus (L.) Merr)," Ilmiah Mahasiswa Universitas Surabaya., vol. 2, no. 2, pp. 1-16, 2013.

[22] Rifai, G., Widarta, I. R., dan Nocianitri, K. A., "Pengaruh Jenis Pelarut dan Rasio Bahan dengan Pelarut Terhadap Kandungan Senyawa Fenolik dan Aktivitas Antioksidan Ekstrak Biji Alpukat (Persea americana Mill .), "Jurnal ITEPA, vol. 7, no. 2, pp. 22-32, 2018.

[23] Teresa, Y., Hidayati, N., dan Nugrahani, R. A., "Pengaruh Rasio Pelarut Kloroform (v/v) Pada Ekstraksi Trimiristin Biji Pala (Myristica fragrans HOUTT), "Teknik Kimia, vol. 2, pp 3-6, 2016.

[24] Baharuddin M, Fitriyani, "Produksi Bioetanol Dari Jerami Padi (Oryza sativa L.) dan Kulit Pohon Dao (Dracontamelon) Melalui Proses Sakarifikasi Dan Fermentasi Serentak (SFS)," Chimica et Natura Acta., vol. 4, no. 1, pp. 1-6, 2016.

[25] Permata D.A, Kasim A, Asben A, Yusniwati, "Delignification of Lignocellulosic Biomass," World Journal of Advanced Research and Reviews, vol. 12, no. 2, pp. 462–469, 2021.

[26] Arianie L, Idiawati N, "Analysis of Lignin and Glucose's Concentration in Organosolv and Acid Hydrolysis," Ilmiah berkala Sains dan Terapan Kimia., vol. 5, no. 2, pp. 140-51, 2011.