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SILICA MODIFIED NATURAL DYE OF *Caesalpinnia sappan* L. ON COTTON FABRICS

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Abstract

Sappana (*Caesalpinnia sappan* L.) has been known as a natural dye in textiles and food. This research aimed to develop a sappan-based natural dye for fabrics dyeing by SiO_2 modification as the UV protection agent. The sappan dye and its color were measured by colorimetric methods on UV-Vis spectrophotometry. The testing of the material includes a standard color detection test on the solution and washing resistance on cotton fabrics. The product is the prototype of a stable natural dye product of SiO_2 modified - sappan (Si-Cs) which will be performed consistently on cotton fabrics. The result showed that SiO_2-modified sappan dye had a higher absorbance in UV-Vis Spectrometer. The performance of the coloring product was also better than the standard sappan dye, indicated by the higher Ultraviolet Protection Factor and the fastness value. Variations of coloring products affected by the mordant agents varied from orange-red-purple caused by non-mordant–alum acetate and iron mordant respectively.

INTRODUCTION

The utilization of natural dyes in textile production indicates increasing awareness among people regarding eco-friendly products. Natural dyes are derived from natural resources such as plants and minerals. These dyes are obtained from natural materials, such as plant parts or specific minerals [1]. Traditional fabrics like batik utilize natural dyes sourced from local plant resources [2]. In certain regions of Indonesia, natural dyes have been incorporated into batik and other traditional textiles.

One of the multifunctional natural ingriedient found in Indonesian is sappanwood (*Caesalpinnia sappan* L.). Extensive research has been conducted on this plant for over 15 years, revealing numerous benefits [3] [4]. *Caesalpinnia sappan* L. is renowned as a natural source of dye, commonly used in both food and textile industries [5]. The sappan dye produces a vibrant red color. Sappan wood extract serves as a renewable natural resource for obtaining natural dyes [6]. Among the bioactive compounds present in sappan wood are brazilin, brazilein, 3'-O-methyl brazilin, sappanaone, chalcone, sappanacalchone, as well as other common components like amino acids, carbohydrates, and palmitic acid, which are relatively present in small quantities [7]. The presence of brazilin components imparts a distinct red color when oxidized or exposed to an alkaline atmosphere [8].

However, natural dyeing using wood has encountered certain challenges. The resulting dyed products often exhibit weak color intensity and poor stability. The instability of color formation depends on the composition and condition of the ingredients, which, in turn, are influenced by the source of the wood.

Several studies have been conducted to address the aforementioned issues in the development of natural dyes from *Caesalpinnia sappan* L. One of the previous studies focused on the color standardization of *C. sappan* natural dye using the UV-Vis spectrophotometric method. As reported in Arum *et al*., (2017), the color intensity of the sappan wood extract consistently peaked at 545 to 560 nm [9]. Other studies have explored ed the modification of sappan dye to improve the quality of coloring products. Chemical modification involving acids, bases, and cations from salt have yielded higher-quality dyeing products [10]. Additionally, the modification with kaolinite has shown increased transport properties [11]. In a recent study, the use of natural dye derived from the heartwood of *Caesalpinnia* *sappan* L. for paper-based packing materials, along with its toxicity analysis, was reported [12].

Studying the modification of C. sappan dye products is essential to achieve consistent and stable colors. One potential supporting material in the dyeing and coating process is silica (SiO_2) nanoparticles. SiO_2 nanoparticles are commonly used as pigments in applications such as wall paint, sunscreen, toothpaste, solar cells, sensors, memory devices, and photocatalysts [13]. The application of nanoparticles has been developed to support the formation of dyestuff particles with specific qualities. SiO_2 particles can be doped into dyestuff components to enhance photosensitivity.

Silica particles serve as effective ultraviolet-blocking agents, protecting against UV light exposure. They possess characteristics such as high surface area, mechanical strength, inertness, and good UV resistance. Coating fabrics with SiO_2 particles can offer protection against ultraviolet light [14]. Dyeing cotton fabrics using reactive dyes impregnated with SiO_2 nanoparticles through the nano-sol method has been investigated. The addition of SiO_2 nanoparticles does not affect the dye chromophore group but exhibits good UV protection properties, with a value above 50 [15]. Silica nanoparticles showed a high performance in ultraviolet protection and have demonstrated excellent Ultraviolet Protection capability, as indicated by their high Ultraviolet Protection Factor Value [16]. Furthermore, cloth coated with SiO_2 nanoparticles has shown both ultraviolet protection and antibacterial capabilities [17].

Silica nanoparticles are nano-sized silica materials that have the potential to serve as supporting material in the production of dyestuff particles. The silica-doped natural dye can be produced through the sol-gel coating or micro-emulsion method. Previous studies have reported the use of this method on cotton fabrics and cotton-polyester blends [18] [19]. The products obtained through this method have met the desired criteria in terms of particle type, size, homogeneity, and compatibility as supporting materials for the production of high-quality natural dyes. In this research, the modification of SiO_2 particles on *C. sappan* dye aims to enhance the stability and consistency of the resulting colors on cotton fabric

EXPERIMENT

The novel method of dyeing in this study is the modification of silica in sappan natural dye.

Material

Sappanwood (*Caesalpinnia sappan* L.) was obtained from Yogyakarta, Indonesia, in the form of dried, thin shaved wood as shown in **Figure 1**. Rice husk was acquired from a rice field near Sleman, Indonesia. All chemicals (SiO_2, ($Al_2(SO_4)_3$), ($FeSO_4$), $CaCO_3$, HCl, NaOH, ethanol, acetone) were obtained from Merck in technical grades.

Figure 1. Sappanwood (*Caesalpinnia sappan* L.) in dried thin shaved wood.

Instrumentation

UV-Visible spectrometer, SEM-EDX, X-Ray Diffraction, UPF and Fastness measurement tools, glassware.

Procedure

Preparation of Sappan (Caesalpinnia sappan L.*) Natural Dye*

The first step is the extraction of *C. sappan shaved wood* using water as the solvent. The sappan wood was soaked in hot water (250 mg/L) for 24 hours and then boiled for an hour. The resulting mixture was filtered using filter paper. The solution was subsequently characterized using a UV-Visible Spectrophotometer through colorimetric analysis. Analysis of the sappan extract included determining the maximum absorption wavelength, measuring the concentration of active compounds, and investigating the effect of pH on the solution. The absorption of dye was monitored over time to determine the stability of the solution.

Preparation and Modification of Silica on Sappan Dye

Silica (SiO_2) nanoparticles were prepared from rice husk ash using the calcination method. The rice husks were washed and dried in the sun for

6 hours, followed by roasting over low heat until they turned into charcoal. The charcoal was then crushed, sieved, and then calcined in a muffle furnace at 500˚C for 3 hours.

Twenty grams of rice husk ash was added to 160 mL of 3N NaOH and extracted for 3 hours at 60˚ C. The extraction mixture was then filtered, and then the filtrate was rinsed with 20 mL of boiling distilled water. To the filtered filtrate, 2M HCl was added drop by drop using a burette until pH reached 7 and a gel was formed. Once the gel formed, it was washed with 100 mL of deionized water, followed by 100 mL 98% ethanol, and finally 100 mL of acetone. The gel was then filtered and dried at 110˚C for 24 hours. The obtained results were characterized for crystallinity, particle size, morphology, and composition of silica nanoparticles. Subsequently, the silica nanoparticles were doped into the sappan extract obtained from the previous extraction step using the dispersion method. The sappan dye was modified with SiO_2 nanoparticles at three different concentrations: 0.1 g/L (1), 0.2 g/L (2), and 0.3 g/L (3). The mixture was stirred for 30 minutes at 1500 rpm. The resulting product was SiO_2-modified *C.sappan* (Si-Cs) dye.

Application of Silica-Modified Sappan Dye on Cotton Fabrics

The experimental design was arranged to investigate the effect of SiO_2 in various mordant agents on the dyeing product of (Cesappinnia sappan (Cs) and Silica modified sappan (Si-Cs) dye on cotton fabrics. The study also observed the effect of dipping frequencies. Several mordant agents were used in this experiment, and their respective concentrations are listed in **Table 1**.

Table 1. Mordant in cotton fabrics.

Code	Mordant agents	Concentration
M1	Alum ($Al_2(SO_4)_3$)	50g /L
M2	Ferrous sulfate ($FeSO_4$)	5 g/L
M3	Lime (Calcium Oxide, CaO)	30 g/L
M4	Alum acetate ($Al(Ac)_3$)	50 g/L
M5	Ferrous acetate ($Fe(Ac)_2$)	5 g/L
M6	Acetic acid (CH_3COOH)	25% (v/v)

The resulting coloring products on cotton were characterized by UV-Vis spectrometer on solid samples. The coloring quality was examined by evaluating washing resistance properties, indicated by the fastness and Ultraviolet Protection Factor (UPF) value.

RESULT AND DISCUSSION

Caesalpinnia Sappan (Cs) and Si-Cs dye

Caesalpinnia sappan L. (Cs) extract was prepared using water extraction. The Cs-dye was measured using a UV-Vis spectrometer to determine the relationship between absorption and concentration. Generally, according to the Lambert-Beer equation (A= a. b. C), the absorption measured by the spectrometer is proportional to the concentration of the analyte. This measurement was used to calculate the concentration of the absorbed sample.

The pH value also influenced the character of the active compound in the Cs dye solution. Changes in pH altered the absorption in the UV–Visible spectrophotometer. As depicted in **Figure 2**, the highest absorption was observed at pH 9, which is related to the balance of brazilin and brazilein content in Cs dye, affected by the concentration of H^+.

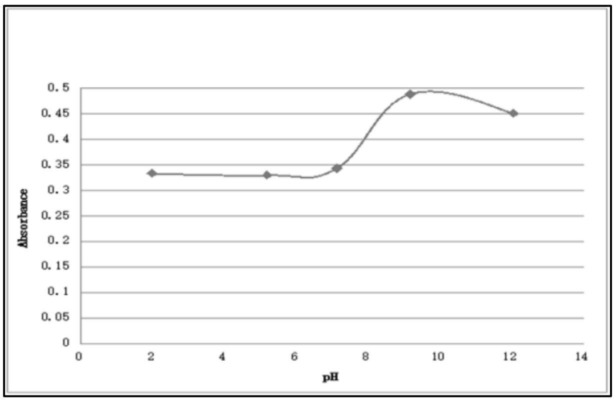


Figure 2. The effect of pH on the absorbance of Cs dye.

The stability of sappan colorant also studied in previous research on food and beverage. The results were recommended that extract of sappan wood could use as a natural colorant for foods and beverages in alkali pH [20]

The solution of Cs dye was measured over several days of storage to ensure the stability of the concentrations of the active substance. The result showed that after 8 days in storage, the absorption of the solution started to decrease, indicating a decrease in the concentration of the active substances. The optimal time to use this solution is within 0-8 days.

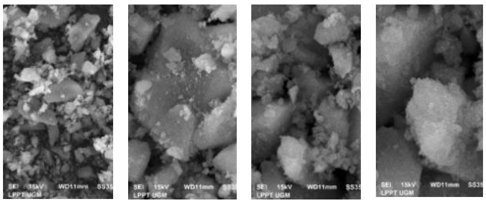
Analysis of the time stability of sappan dye was also conducted by Ngamwonglumlert that stated that the storage stability of the extract was assessed at 4°C for 7 days in the dark [21].

Silica Modifiied Sappan *Dye*

The silica is in the form of a white powder as shown in **Figure 3**.

Figure 3. Silica from rice husk ash.

Analysis of the morphology and elemental composition of silica particles was conducted using a Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) JSM-6510LA at four magnifications: 1,000x, 3,000x, 5,000x, and 10,000x. The morphology of rice husk silica is presented in **Figure 4**. The morphology of SiO_2 at 1,000x magnification showed that the particles have an irregular shape and no aggregation is observed. The morphology of silica is shown at magnifications of 3,000x, 5,000x, and 10,000x. This is consistent with the results of previous research, which stated that the morphology of rice husk ash silica exhibited various sizes and no aggregation [22].



(a) (b) (c) (d)

Figure 4. Morphology of rice husk ash SiO_2 at 1,000 (a), 3,000 (b), 5,000 (c), and 10.000 (d) magnifications.

Silica crystallinity was analyzed using an X-ray Diffractometer (XRD) Rigaku Miniplex 600. The obtained data were analyzed using Origin 6.1 software. The XRD pattern of rice husk silica is presented in **Figure 5**. Rice husk ash silica in this study is amorphous. The pattern widens and exhibits a peak at (2θ) = 20°-23.02°. Amorphous silica has a higher solubility compared to the crystalline phase. This result aligns with previous studies where amorphous silica produced a wide pattern at (2θ) = 20°-24°[22].

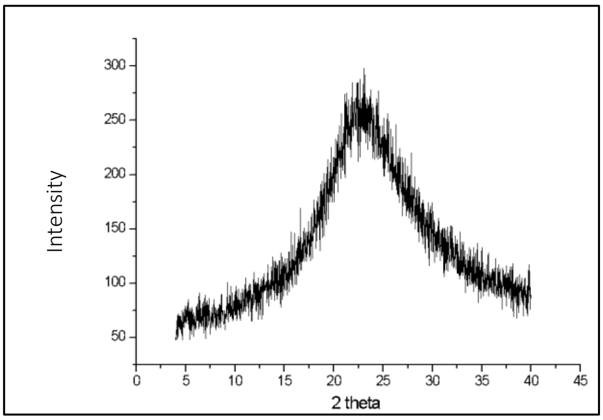


Figure 5. XRD pattern of rice husk ash silica.

The compositional analysis was performed using Energy Dispersive X-Ray (EDX). The material composition in the sample is presented in **Figure 6** and **Table 2**. The highest element present is oxygen (57.83%), followed by silicone (27.08%) and carbon (15.09%). The amount of oxygen is twice that of silicon, corresponding to the composition of the SiO_2 compound, which requires Si and O in a ratio of 2:1.

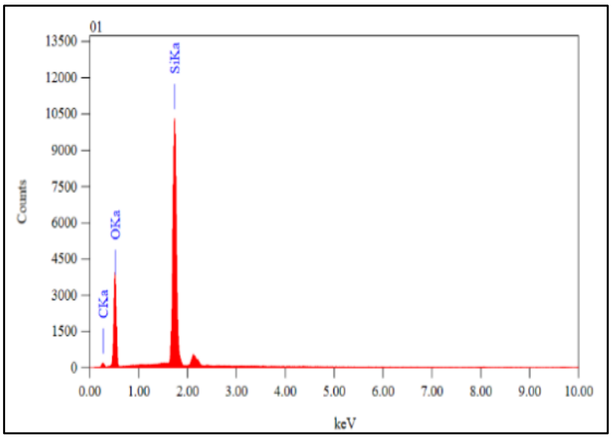


Figure 6. The EDX peaks of rice husk silica.

Table 2. Composition of rice husk silica.

Element	Percent (%)
O	57,83
Si	27,08
C	15,09

The size distribution of rice husk silica was analyzed using a Particle Size Analyzer LLPA-C10. The obtained data include the particle size distribution and accumulation (percent). The results are shown in **Figure 7**. The particle size distribution of silica in this research ranges from 0.2 to 2,000 µm. The size was calculated as the average diameter. The results showed that the average diameter of silica particles is 45.731 µm. In textile protection applications, micro-sized particles are usually utilized, with particle sizes ranging from 1 to 1000 mm. This indicates that the obtained particle size is still suitable for textile protection requirements. The silica obtained in this study was applied to silica-modified sappan dye to achieve textile protection against ultraviolet light.

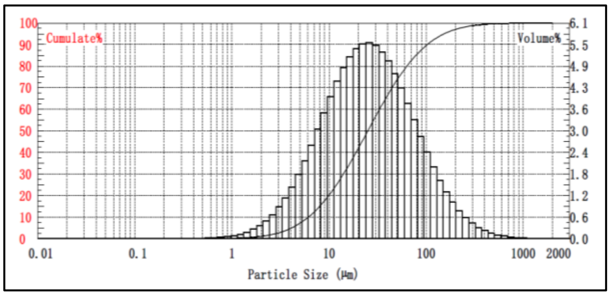


Figure 7. Particle size analysis of rice husk silica.

Application of Silica-modified Sappan (Si-Cs) Dye on Cotton Fabrics

Coloring product of standard sappan dye

The first experiment involved the optimal dyeing of fabrics. The samples were immersed 1 to 7 times in the Cs dye standard solution. The result was evaluated using a visual colorimetric method, as shown in **Figure 8**. The fabrics were examined with various mordant agents (M1-M6), where the mordants varied as follows: 0 = No Mordant, 1 = Alum sulfate, 2 = Ferrous sulfate, 3 = Lime, 4 = Alum acetate, 5= Ferrous acetate, 6= Acetic acid. A **mordant** or **dye fixative** is a substance used to bind dyes to fabrics by forming a complex with the dye, which then attaches to the fabric (or tissue). It may be used for dyeing fabrics or for intensifying stains in cell or tissue preparations. C represent the symbol of immersion.

Figure 8 shows the coloring product of standard (control) Cs dye with various mordant agents. From left to right, the yield of dyeing by M1, M2, M3, M4, M5, and M6 and M0 respectively, is displayed. The non-mordanted samples showed weak coloring products. The other mordant agents influenced the color direction of the product. The fabrics mordanted with iron mordant exhibited a stronger color. The higher the concentration of the mordant agent, the stronger the resulting color [23].

From top to bottom, the effect of immersion repetition is shown. The more frequent immersion, the more intense the color produced on the fabrics. After the 5th immersion, the color intensity becomes relatively constant, indicating that the absorption of the dye into the cotton fiber is maximized.

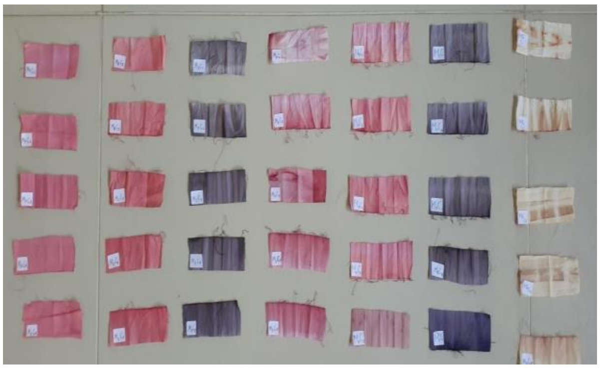


Figure 8. Coloring product of standard Cs dye (SiO_2=0) with various mordant agents. C = immersion repetition from top to bottom.

The variation of color trend also reported in other study of sappan dye application on silk. The performa of silk fabric against the secang wood colour using fixators produced a very sharp color [24]. In general, the dyeing on silk fabrics is stronger and more glowing than on cotton.

Coloring product of SiO_2 doped sappan dye (Si-Cs)

The experiment was conducted on Si-Cs dye. The standard Cs dye without SiO_2 modification was marked by S0 (Si = 0). As shown in **Figure 9**, the mordant agent had a certain effect on color formation. Alum mordant tended to produce a soft red color, while iron mordant led to a color tendency towards purple. Lime mordant affected the red color, making it tend towards pink. Acetic acid caused a decrease in pH, resulting in the Cs dye color tending towards orange. The non-mordanted samples exhibited a soft brownish red. This is consistent with another study on coloring fabrics with Caesapinia sappan dye combined with Curcuma longa, which showed variation in color trends depending on the fixer materials [4].

In the sample with SiO_2 addition (Si-Cs), visual observation showed that the color formation is stronger and brighter. It is in agreement with previous research that the addition of silica nanoparticles on the fabric surface imparts a very good and efficient Ultraviolet ray scattering due to the refractive index of SiO_2 [14]. The amount of SiO_2 affected the capability of the protection. The higher the amount, the better the protection.

Figure 9. Si-Cs dyeing on cotton, in various mordants and SiO_2 concentrations (0.1 mg/L (a); 0.2 mg/L (b); and, 0.3 mg/L (c)).

Determination of coloring quality based on fastness value

Colorfastness to washing and sunlight were measured on the dyed Fabrics. The fastness ratings of the dyed samples are presented in **Figure 10** and **Figure 11**. It can be seen that all the samples have excellent washing fastness with SiO_2 addition. The change in shade is almost equal to the values obtained on cationized fabrics dyed with commercial reactive dyes like *Caesalpinnia sappan*. The durability of the dyed fabrics to washing could be attributed to the formation of covalent linkages between the hydroxyl groups of SiO_2 and the hydroxyl groups of cotton fabric, as well as the ionic attraction between cationized cotton and the reactive dyes [16].

Fastness value indicates the resistance properties of fabrics under washing, ironing, and sun exposure. The higher the value, the better. The highest value was 5 indicating "very good" quality in dyeing and resistance, while 4 is good and 3 is fair. The results are shown in **Figure 10**.

This result indicates that the photocatalytic activity of SiO_2 did not show an adverse effect on the light fastness of the dyed fabrics. As reported previously, the photocatalytic activity of SiO_2 can be substantially affected by its structure, which depends on the heating temperature [25]. The amorphous SiO_2 produced in this research is a suitable material for pigment coating and photosensitive agents.

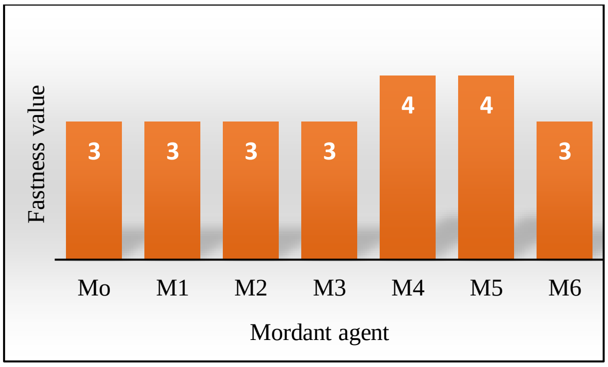


Figure 10. Fastness value of standard Cs dye (SiO_2=0) (0= No Mordant, 1 = Alum sulfate; 2 = Ferrous sulfate; 3 = Lime; 4 = Alum Acetate; 5= Ferrous acetate; 6= Acetic acid).

The Effect of SiO_2 on the fastness value of dyed cotton

In this case, the effect of mordant was determined using five various mordant agents commonly used in the natural dye-based textile industry. Alum (in sulfate and acetate), iron (also in sulfate and acetate), lime (CaO), and acetic acid were administered in the preparation of the cotton fabric before the dyeing process. Mordant ions (Al, Fe, Ca) act as the central ion of complex compound formation with the active compound of Cs dye on the surface of the fiber. Acetic acid has no metal ion, so its action is quite different. It cannot form complex with the brazilein in the solution, resulting in no color formation on the fabrics. It is also consistent with other research that reported how mordant agents affect the color direction of the dyeing product [26].

Another research also explained that conjunction with certain metallic mordants by coordinative bonding is the reason for the attachment of the dye to fabric. In non-mordant dyeing, the attachment is formed by hydrogen bonding [27]. The hydrogen bond is weaker than the coordination bond, so dyeing with mordant makes the product stronger.

SiO_2 was added at 3 various concentrations: 0.1; 0.2; and 0.3 mg/L, to determine the effect of SiO_2 on the coloring process of Cs dye on cotton. The result of Cs-SiO2 dye on cotton with various SiO_2 addition on fastness value is shown in **Figure 11**.

Figure 11. Fastness value of Cs-SiO_2 with various mordants (M0 = No Mordant, 1 = Alum sulfate; 2 = Ferrous sulfate; 3 = Lime; 4 = Alum Acetate; 5= Ferrous acetate; 6= Acetic acid).

The non-mordant (M_0) group showed the lowest fastness value among all mordant groups, indicating that the mordant process affected the absorption of Cs dye into the fabric's fiber. Iron-based-mordants (ferrous sulfate=M_3 and ferrous acetate = M_5) had a stronger effect on dyeing, resulting in a higher fastness value compared to others. According to the role of mordant, iron (Fe) is the stronger ion that forms coordination bonds with the dye-active substances. Alum mordant showed a moderate fastness value, which resulted from the coordination bond of bidentate ligands via the ionized 10-hydroxyl group and 9-carbonyl oxygen to Al(III), with two water molecules acting as co-ligands to complete the octahedral arrangement [28].

Several studies also reported that the light fastness of the dyestuffs increased due to their incorporation into the sol-gel matrices, explained by the protection of organic molecules within the inorganic pores [29] [30] Pre-treatment with the ionizing reagent, as well as the doping of SiO_2 nanoparticles with reactive dyes, had no adverse effect on the fastness properties. The chromophore groups of the reactive dyes were not damaged, and the conjugated system was unaffected by SiO_2. This can be observed by the relatively constant color expression. The role of silica nanoparticles still requires further prospective study. As reported in another study, the coating of nano-silica on the surfaces of pigments could improve the wettability, acid, and alkali resistance, and wearability of the organic pigment [31].

CONCLUSION

The *Caesalpinnia sappan* L. Dyeing on cotton was affected by several factors: immersion frequency, mordant-fixation process, and the SiO_2 modification. Mordant-fixation agents influence the color trend of dyeing products. SiO_2-doped *Caesalpinnia sappan* L. natural dye on cotton fabrics showed a stronger red color expression and higher fastness value than the Cs standard dye.

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REFERENCES

[1] R. Mansour, "Natural dyes and pigments : extraction and applications", in *Handbook of Renewable Materials for Coloration and Finishing*, No. 1. September, M. Yusuf, Ed. Scrivener Publishing LLC, 75–102, 2018.

[2] A.W. Indrianingsih and C. Darsih, "Natural dyes from plants extract and its applications in Indonesian textile small-medium scale enterprise", *Eksergi*, **11**(1), 16–22, 2013, doi: 10.31315/e.v11i1.327.

[3] T. Juwitaningsih, N. Syahputra, E. Eddiyanto, N. Windayani, and Y. Rukayadi, "Antibacterial and anticancer activities of acetone extract *Caesalpinia sappan* L.," *al Kimiya: Jurnal Ilmu Kimia dan Terapan*, **9**(2), 82–88, 2022, doi: 10.15575/ak.v9i2.20966.

[4] N. Kusumawati, Samik, A.B. Santoso, and S. Muslim, "New natural dyes development: *Caesalpinia Sappan* L.-*Curcuma longa*",

Rasayan J. Chem., **13**(2), 991–999, 2020, doi: 10.31788/RJC.2020.1325410.

[5] O. Rina, S. Ibrahim, A. Dharma, Afrizal, C.U.W., and Y.R. Widodo, "Stabilities natural colorant of Sappan wood (*Caesalpinia sappan* L.) for food and beverages in various pH, temperature, and matrices of food", *International Journal of ChemTech* Research, **10**(1), 98–103, 2017.

[6] P. Ohama and N. Tumpat, "Textile dyeing with natural dye from sappan tree", *Int. J. Fash. Text. Eng.*, **8**(5), 432–434, 2014, doi: 10.5281/zenodo.1092830.

[7] I. Batubara *et al.*, "Brazilin content, antioxidative and lipase inhibition effects of sappanwood (*Caesalpinia Sappan*) from Indonesia", *J. Chem. Chem. Eng.*, **4**(10), 50-55, 2010.

[8] H.N. Lioe, D.R. Adawiyah, and R. Anggraeni, "Isolation and characterization of the major natural dyestuff component of Brazilwood (*Caesalpinia sappan* L.)," *Int. Food Res. J.*, **19**(2), 537–542, 2012.

[9] A.R. Widyasti, A. Lestari, K. Amri, F. Naufal, and K.S. Budiasih, "Pengembangan standarisasi pewarna alami batik dari kulit kayu secang (Caesalpinia sappan L.) dengan teknik spektroskopi", *Jurnal Penelitian Saintek*, **22**(1), 49–58, 2017, doi: 10.21831/jps.v22i1.14850.

[10] E. Rahayuningsih, W. Budhijanto, H.F. Prasasti, and M.T. Wahyuningrum, "Chemical modifications for intensity variation and spectrum extension of brazilein extract from sappanwood (*Caesalpinia sappan* L.)", *MATEC Web of Conference,* **156**, 01020, 2018, doi: 10.1051/matecconf/201815601020.

[11] I. Batubara, Z. Abidin, and M. Rahminiwati, "Ekstrak secang berukuran nano dengan kaolin", *J. Ilmu Pertan. Indones.*, **16**(2), 125–129, 2011.

[12] V.K. Nathan and M.E. Rani, "Natural dye from *Caesalpinia sappan* L. heartwood for eco-friendly coloring of recycled paper-based packing material and its in silico toxicity analysis", *Environ. Sci. Pollut. Res.*, **28**(22), 28713–28719, 2021.

[13] B. Wei, Q. Chen, G. Chen, R. Tang, and J. Zhang, "Adsorption properties of lac dyes on wool, silk, and nylon", *Journal of Chemistry*, 2013, 1–6, 2013, doi: 10.1155/2013/546839.

[14] N. Erdem, U.H. Erdogan, A.A. Cireli, and N. Onar, "Structural and ultraviolet-protective properties of nano-TiO_2-doped polypropylene filaments", *Journal of Applied Polymer Science*, **115**(1), 152-157, 2009, doi: 10.1002/app.30950.

[15] O.K. Alebeid, and T. Zhao, "Simultaneous dyeing and functional finishing of cotton fabric using reactive dyes doped with TiO_2 nano-sol", *J. Text. Inst.*, **107**(5), 625-635, 2016, doi: 10.1080/00405000.2015.1054209.

[16] T.M.A. Elmaaty and B. Mandour, "ZnO and TiO_2 nanoparticles as textile protecting agents against UV radiation: A review", *Asian Journal of Chemical Sciences*, **4**(1), 1-14, 2018, doi: 10.9734/AJOCS/2018/40329.

[17] M.E. El-Naggar, Th.I. Shaheen, S. Zaghloul, M.H. El-rafie, and A. Hebeish, "Antibacterial activities and UV-protection of the in-situ synthesized titanium oxide nanoparticles on cotton fabrics", *Ind. Eng. Chem.* Res., **55**(10), 2661-2668, 2016, doi: 10.1021/acs.iecr.5b04315.

[18] R. Ghafarzadeh, A. Shams-Nateri, and A.F. Shojaie, "Effect of TiO_2 nanoparticle on light fastness and degradation of dyed fabric with direct dye", *Indian Journal of Fibre and Textile Research*, **43**(3), 363–368, 2018.

[19] A.M. Al-Etaibi and M.A. El-Apasery, "Nano TiO_2 imparting multifunctional performance on dyed polyester fabrics with some dispersed dyes using high-temperature dyeing as an environmentally benign method", *Int J Environ Res Public Health*, **17**(4), 1377, 2020.

[20] O. Rina, S. Ibrahim, A. Dharma, Afrizal, Chandra Utami W, Y.R. Widodo, "Stabilities natural colorant of Sappan wood (*Caesalpinia sappan*. L) for food and beverages in various pH, temperature, and matrices of food", *International Journal of ChemTech Research*, **10**(1), 098-103, 2017.

[21] L. Ngamwonglumlert, S. Devahastin, and N. Chiewchan, "Color and storage stabilities of natural colorant produced from sappan wood", *18th TSAE National Conference*, 2021.

[22] A.B.D. Nandiyanto, R. Ragadhita, and I. Istadi, "Techno-economic analysis for the production of silica particles from agricultural wastes", *Moroccan J. Chem.*, **8**(4), 801–818, 2020, doi: 10.48317/IMIST.PRSM/morjchem-v8i4.21637.

[23] P. Ohama and N.Tumpat, "Textile dyeing with natural dye from sappan tree (*Caesalpinia sappan* Linn.) extract",

International Journal of Fashion and Textile Engineering, **8**(5), 432-434, 2014, doi: doi: 10.5281/zenodo.1092830.

[24] Kurniati *et al.*, “Natural dyes from Secang (*Biancaea sappan*) wood in Sutera”, *J. Phys.: Conf. Ser.* **1387,** 012001, 2019, doi: 10.1088/1742-6596/1387/1/012001.

[25] D.K. Maharani, I. Kartini, and N.H. Aprilita, “Nanosilica-chitosan composite coating on cotton fabrics”, *AIP Conference Proceedings*, **1284**, 87-91, 2010, doi: 10.1063/1.3515570.

[26] K. Kannathasan and P. Kokila, “Dyeing of cotton fabric by *Caesalpinia sappan* aqueous extract at different temperatures and mordants”, *Current Botany*, **12**, 188-191, 2021, doi: 10.25081/cb.2021.v12.7277.

[27] R.W Dapson and C.L. Bain, “Brazilwood, and sappanwood, brazilin and the red dye brazilein: from textile dyeing and folk medicine to biological staining and musical instruments”, *Biotechnic & Histochemistry*, **90**(6): 401–423, 2015.

[28] K. Wongsooksin, S. Rattanaphani, M.T. Kulchai, V. Rattanaphani, and J.B. Bremner, “Study of an Al(III) complex with the plant dye brazilein from *Ceasalpinia sappan* linn”, *Suranaree J. Sci. Technol*., **15**(2), 159-165, 2008,

[29] R.C. Harsito, A.R. Prabowo, S.D. Prasetyo, and Z. Arifin, “Enhancement stability and color fastness of natural dye: A review”, *Open Engineering*, **11**(1), 548-555, 2021, 10.1515/eng-2021-0055.

[30] Md.A. Sufian, Md.A. Hannan, Md.M. Rana, and M.Z. Huq, “Comparative study of fastness properties and color absorbance criteria of conventional and avitera reactive dyeing on cotton knit fabric”, *European Scientific Journal*, **12**(15), 1857-1881, 2016, doi: 10.19044/esj.2016.v12n15p352.

[31] J. Yuan, W. Xing, G. Gu, and L. Wu, "The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique”, *Dyes and pigments*, **76**(2), 463-469, 2008, doi: 10.1016/j.dyepig.2006.10.002.