World Journal of
Chemical and Pharmaceutical Sciences
Journal homepage: https://zealjournals.com/wjcps/
ISSN: 2945-3186 (Online)

(Research Article)

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Enhancing the light fastness of tannin from mangrove waste by encapsulation with chitosan nanoparticle

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World Journal of Chemical and Pharmaceutical Sciences, 2023, 02(01), 009–016

Publication history: Received on 23 November 2022; revised on 07 January 2023; accepted on 09 January 2023

Article DOI: https://doi.org/10.53346/wjcps.2023.2.1.0037

Abstract

Microwave assisted extraction is an environmentally friendly extraction method, which has been used to extract tannins from mangrove waste. Tannin is a natural dye which is easily oxidized, easily degraded and the color fades easily. To increase its color retention, tannin was encapsulated with chitosan nanoparticle. This study aims to determine the effect of volume tween 80 on particle size and physical and chemical characteristics of tannin extract from mangroves encapsulated with chitosan nanoparticle. The encapsulated tannin extract particle size was measured by Particle Size Analyzer and characterized by FTIR, SEM. The test results showed that the average particle diameter of the encapsulated tannin extract was in the range of 192.37 nm with a PDI of 0.1660 which was obtained by adding 0.5 mL of Tween 80. Encapsulation efficiency reaches 78.1%. The FTIR spectrum showed the presence of a cross-linked C=N stretching absorption band at wave number 1643.35 cm-1 in nano encapsulation of tannin extract.. The color fastness test of cotton cloth in hot water has a value of ΔE = 3, which means that the color fastness is moderate.

Keywords: Tannin; Mangrove waste; Chitosan nanoparticle; Light fastness

1. Introduction

Natural dyes can be obtained from plants, animals and microorganisms. When extracted, almost all parts of plants such as flowers, fruits, leaves, seeds, bark, stems and roots can produce dyes [1]. These dyes come from natural pigments contained in plants, which are secondary metabolites of plants such as bixin [2], catechins [3], anthocyanins [4], and henna [5]. The advantage of natural dyes is that they are safe for health because they contain antioxidant components, are anti-bacterial, and are easily biodegradable and non-toxic [6].

Research on natural dyes is more aimed at developing extraction techniques, increasing their stability at high temperatures, engineering their surfaces. Especially for the textile industry, materials are also developed for mordanting, exploring sources of natural dyes, improving the function of textiles, such as anti-bacterial textiles, and anti-UV textiles. Girl et al [7] modified the surface of the wool cloth by coating the surface of the wool cloth with chitosan which aims to inhibit bacterial growth and increase the absorption of Henna dye. Chitosan and carboxyl methyl chitosan were also used by Hong Pan et al [8] as surface coatings for cotton fabrics to increase absorption of cationic dyes and inhibit the growth of e.coli and S.Aureus bacteria. Alina et al [9] coated the surface of silk fabric with chitosan to improve mechanical properties, temperature resistance and UV resistance. Erdawati and Nurul (10) coated silk with chitosan to increase curcumin absorption in silk.

With the development of nanotechnology, textile industry players also use nanomaterials to improve the color quality of textile fabrics. Baki et al [11] studied the effect of coating the surface of silk cloth with TiO_2 nanoparticles on the mechanical properties, heat resistance and anti-UV. The results showed that the increased mechanical and physical

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properties of silk were due to the interaction between TiO_2 and the OH groups of serine on the surface of the silk. During the formation of TiO_2 interactions, TiO_2 interactions also occur with the OH groups of amino acids. The results of the TGA test showed that the heat resistance of silk cloth coated with CeO_2 nanoparticles was higher than that of silk cloth not coated with CeO_2 nanoparticles. Likewise, the color of silk cloth coated with CeO_2 has a value of b* = 12.76, while silk cloth that is not coated with CeO_2 has a b* value of only 2.74, meaning that silk cloth coated with CeO_2 nanoparticles has a brighter yellow color than silk cloth coated with CeO_2. not coated with CeO_2[5] . Anamika et al [13] studied the effect of the amount of ZnO nanoparticles used for coating silk cloth against the ability of silk cloth to absorb UV. The results showed that the more ZnO the more UV rays were absorbed. In addition to nanoparticles, some natural dyes also function as anti-UV. Yuyang et al [14] compared the anti-UV properties of Baicalin (herbal plant extract) and benzotriazole ultraviolet absorber (commercial UV absorber) against the UV anti-UV properties of silk fabrics treated with two uv absorbers. The results of his research showed that silk cloth treated with 2% Baicalin had anti-bacterial properties against e. coli, S. Aureus, antioxidants, and the resistance to UV rays was much better than silk cloth treated with commercial UV absorber. Camphor leaf extract which contains anthocyanins and catechins can also function as anti-UV, anti-bacterial and increase the color resistance of silk and wool fabrics [15]. Nattaya et al [16] studied the effects of temperature, time and on the process of dyeing nylon fabric with mangrove extracts. The results showed that pH 5, temperature 90^0C and 60 minutes were the optimum conditions to produce the desired nylon color. In another study, Nattaya et al [17] studied the effect of mordant on the color of silk dyed with mangrove extracts. Silk fabrics that were mordant with stannous chloride, aluminum potassium sulfate, and copper sulfate produced a variety of pale to dark reddish-brown color shades, while silk fabrics that were not mordant were of reddish-brown color. The optimum conditions for staining were obtained at pH 3, temperature 90^0C and 60 minutes.

Encapsulation technique is one technique to engineer natural dyes. Various encapsulant materials have been used to encapsulate natural dyes. Ana et al [18] compared the ability of encapsulant types to maintain anthocyanin stability against pH and temperature. The results of his research showed that polymer composites containing alginate-protein-chitosan were better able to withstand loss of anthocyanins at 25^0C and at pH 4. Jingxin et al [19] studied encapsulant formulations for their ability to encapsulate anthocyanins from purple corn and blueberries. The results of his research showed that the chemical structure of anthocyanins and the compatibility between anthocyanins and alginate-pectin affect encapsulation efficiency. Besides that, pH, alginate pectin ratio, anthocyanin concentration, gum concentration also affects encapsulation efficiency. To improve the compatibility between curcumin and alginate, Jardim et al [20] made an encapsulant using a layered technique between chitosan and alginate to coat curcumin. The results of his research indicated that the layered technique would increase the amount of encapsulated curcumin. In this study, tannin extract from mangrove waste was encapsulated with chitosan nanoparticles to color cotton fabrics.

2. Material and methods

2.1 Material

Mangrove waste in the form of skins, stems obtained from Surabaya, cut with a chopper, dried in the sun for 3 days, and then milled with a disk mill.

2.2 Chemical reagent

Ethyl acetate, methanol, dichloromethane, distilled water, Tween 80, solution 0.15% chitosan in 1% acetic acid, 25% glutaraldehyde, $Na_2S_2O_5$, Na_2SO_4.

Analytical balance apparatus, glassware, rotavapor, hot plater magnetic stirrer, microwave assisted extraction (MAE) , Particle Size, Analyzer (PSA), FTIR,

Adobe Photoshop CS4 Retrieval of L*a*b* data on cloth using the Adobe Photoshop CS4 software application by opening the software, selecting the file menu > open file > selecting the image menu > mode > Lab Color, selecting the sampler tool, selecting sample size 5 by 5 average.

2.3 Extraction of mangrove waste

As much as 10 grams of mangrove waste powder was put into a three neck flask which was filled with 75 mL of ethyl acetate and 10 mL of distilled water. Then the mixture was refluxed by heating using a microwave for 15 minutes. The extract was filtered using filter paper and the ethyl acetate phase was taken. The ethyl acetate phase was then added with anhydrous Na_2SO_4 and allowed to stand for a while. Then filtered and concentrated by evaporation at 40^oC.

2.4 Encapsulation of tannins with chitosan nanoparticles

Tween 80 surfactant with various volumes (0.3 mL; 0.5 mL; and 1.0 mL) was added to 20 mL of 0.15% chitosan solution in 1% acetic acid. The mixture was then stirred with a magnetic stirrer at 1650 rpm for 1 hour. Then 250 µL of tannin solution (10 mg/mL in chloroform) was added to the mixture drop by drop (~20 µL/drop). The solution was stirred again for 1 hour to form an emulsion, after which 0.5 mL of 20% sodium sulfate solution was added drop by drop while stirring for 30 minutes. Add 0.1 mL of 25% glutaraldehyde and stirring was continued for 30 minutes. Finally, add 1 mL of 10% sodium metabisulfite solution and stir for 30 minutes to form a solid or powder.

2.5 Analysis of encapsulation efficiency

As much as 0.1000 grams of nano encapsulated powder was washed with ethyl acetate. Three times washing was carried out to separate tannins that were not encapsulated. After washing, it is then dried and weighed. The encapsulation efficiency is calculated by the equation

$$\%EE = \frac{Encapsulated\ tannin\ weight}{Tannin\ weight} \text{x}100\%$$

2.6 Characterization of tannin encapsulation

Tannins encapsulated with chitosan nanoparticles were characterized by SEM, FTIR, particle size and polydispersity index (PDI) were measured by PSA,

2.7 Cotton fabric dyeing

Cotton cloth is washed clean using distilled water, drained for 24 hours and cut with a size of 10 x 10 cm. Before the cotton cloth is dyed, it is mordant by boiling the cloth with 3 L of water containing 6 grams of alum and heating it to 85^{0}C-90°C until it boils, leaving it for 45 minutes while stirring. After that the stove was turned off and the cloth was left to soak for 24 hours. Then the cloth is washed with clean water and drained while aerated or dried in the shade until dry.

The cotton cloth is soaked in a tannin solution that has been encapsulated for 24 hours, then removed, drained, and dried. The fixing agent is alum which is dissolved in distilled water with a ratio of 1:20 (w/v), until the solution precipitates. The clear solution is taken and used to soak cotton cloth that has been dyed for 10 minutes, after which the cotton cloth is washed with water, drained, and allowed to dry.

2.8 Hot Water Color Fastness Test

Testing the color fastness of fabrics is carried out by boiling water with an initial temperature of ±38^{o}C and then placing a cotton cloth in a pot for 1 hour under low heat. The fabrics were then removed and air-dried for 24 hours. Assessment of the color of cotton cloth, qualitatively measured with the Canon MG3670 Scanner in Adobe Photoshop CS4 software which will produce L*, a*, and b*

2.9 Cold watercolor fastness test

Put ice cubes into the container and leave it until it melts. The dyed cloth is put into the container and soaked for 24 hours. The fabrics were then removed and air-dried for 24 hours. Assessment of the color of cotton cloth, qualitatively measured with the Canon MG3670 Scanner in Adobe Photoshop CS4 software which will produce L*, a*, and b*

The amount of color change before and after soaking in hot water or cold water is calculated by the formula:

Information:

ΔE = Color Difference
ΔL* = Brightness difference = L*after test- L*before test
Δa* = Red or green difference = a*after test -a*before test
Δb* = Yellow or blue difference = b*after test -b* before test

3. Results and discussion

3.1 Encapsulation Efficiency (%EE)

Encapsulation efficiency (EE) describes how much tannin is absorbed in chitosan. The higher the value of encapsulation efficiency, the more tannin trapped in chitosan and the better the quality of tannin. The test results showed that 1 gram of tannin encapsulated, after being washed and dried, the weight was 0.781 gram. This shows that as much as 78.1% of the tannin is absorbed in the chitosan nanoparticle

3.2 Particle size

Figure 1 shows the effect of Tween 80 volume on the average particle size and PDI values of tannin encapsulated with chitosan

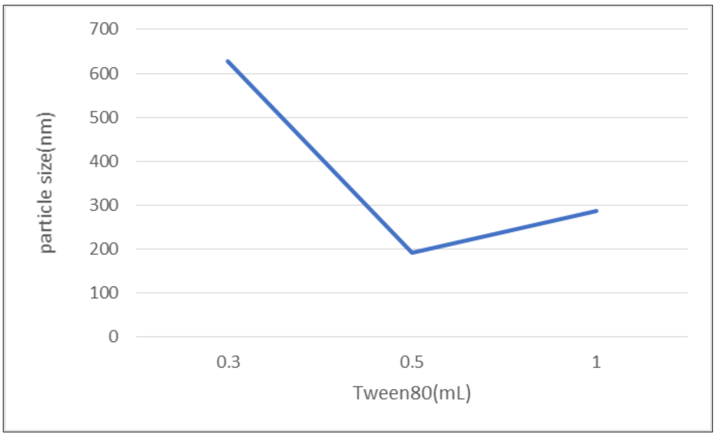

Figure 1 Effect of Tween 80 volume on particle size tannins encapsulated with chitosan nanoparticles

From Figure 1 it can be seen that the encapsulated tannin particle size decreased with the addition of Tween 80 but increased when 1 mL of Tween 80 was added. Where the interfacial surface becomes saturated, micelles are formed so that the adsorption of Tween 80 on the surface does not occur anymore. This causes the tannins to agglomerate and the particle size increases.Likewise, with the PDI value, the addition of 1 mL Twen 80 has a value of 0.1660, while the addition of 0.5 mL of Tween 80 has a PDI value of 0.3280.

3.3 Characterization of Tannins with FT-IR

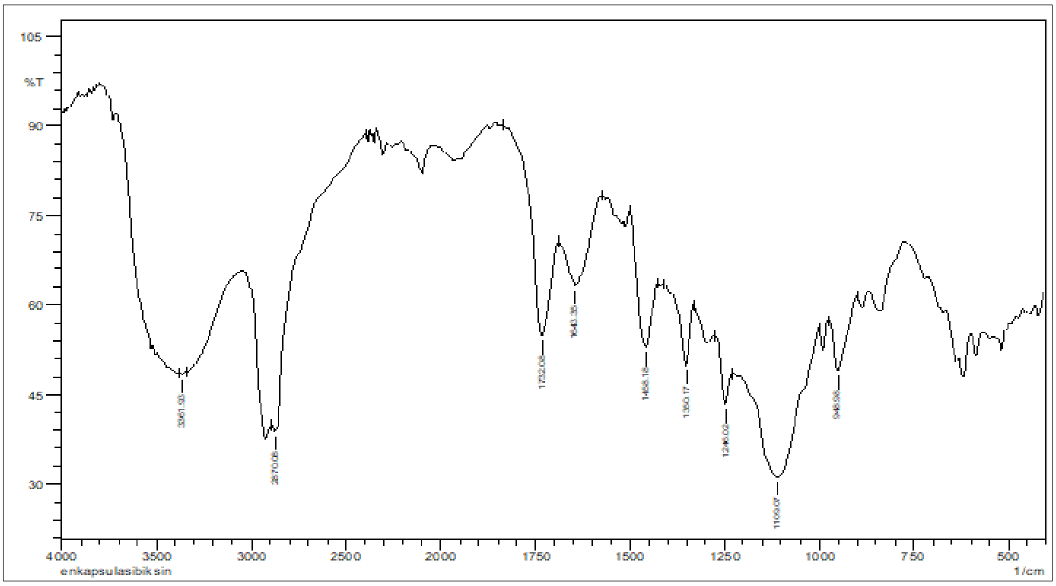

Figure 2 FTIR spectrums of tannins

The results of the analysis of the FTIR absorption pattern, at wave number 3186.54 cm^{-1} indicate the presence of O-H strain from the carboxylate group. The absorption band at that wave number is sharp and not wide enough due to the absence of intermolecular hydrogen bonds. Absorption at wave number 1708.04 cm^{-1} shows the C=O strain on the carbonyl group. The C=C alkene group in the unsaturated aliphatic structure is indicated by an absorption band at wave number 1605.81 cm^{-1}, while absorption at wave numbers 1275 cm^{-1} & 1158.30 cm^{-1} shows C-O vibrations and C-O-C stretching in the ester group at tannins.

Table 1 Functional group FTIR tannin, chitosan and tannin encapsulation wth chitosan nanoparticle

No	Functional group	Wave number (cm^{-1})	literature
1	Stretching C-H	3186.54	3750-3000
2	Stretching =C-H	3020.66	3300 – 3000
3	Stretching C-H	2929.03	3000-2700
4	Stretching C=O	1708.04	1900 – 1650
5	Stretching C=C	1605.81	1675 – 1500
6	Stretching C-H	1437.04	1470-1300
7	Stretching C-O	1275.00	~1250
8	Stretching C-O-C	1158.30	1050 – 1150
9	Vibration =C-H	967.34	1000 – 650

3.4 Color fastness test

The fastness test on cotton cloth using hot water can be seen in Table 2

Table 2 Results of Color Fastness in Hot Water of Cotton Fabrics

No	Coordinate	Before testing	After testing	ΔE
1	L	63.75	68.25	4.50
2	A	5.5	6.25	0.70
3	b	8,75	12.5	3.75

Based on the data in Table 2, the value can be calculated. ΔE,that is

$$\Delta E = V\ (4{,}50)^2 + (0.70)^2 + (3.75)^2$$

$$= 5.94$$

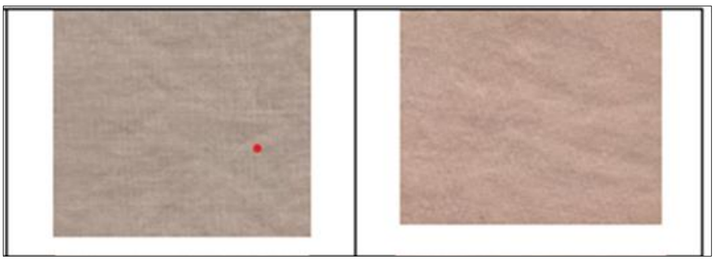

Figure 3 Color of cotton cloth .a) color before test, b) color after test with hot water

The results of the fastness test on cotton cloth using hot water can be seen in the Figure 3, the color of the cotton cloth fades to become lighter or brighter. Prior to the fastness test, cotton fabrics with Grayish Yellow 2.5 Y 6/2 color after being tested became Dull Yellow Orange 10YR 7/4. The process that occurs when heated, the fibers in the cotton cloth are opened, so that these fibers will react with ferrous sulfate ($FeSO_4$) to become ferric sulfate ($Fe_2SO_4)_3$.

The fastness test on cotton cloth using cold water can be seen in Table 3

Table 3 Results of Color Fastness in Cold Water of Cotton Fabrics

No	Coordinat	Before testing	After testing	ΔE
1	L	65	64.25	0.75
2	A	5,25	6.00	0.75
3	b	9	10.75	0,25

Based on the data in Table 3, the value can be calculated. ΔE,that is

$$\Delta E = V\ (-0.75)^2 + (0.75)^2 + (0.25)^2$$

$$\Delta E = 2.04$$

The results of the fastness test of cotton fabrics using cold water are shown in Fig. 4. It can be seen that the color of the cloth has changed slightly from the original Grayish Yellow 2.5 Y 6/2, and after being tested with cold water the color of the cloth has changed to Grayish Yellow 2.5Y 7/2. The color fastness of cotton cloth in cold water has a value that is included in the very good category. Well. This shows that in the fixation process there is a strong bond between the dye and the cellulose fiber through the formation of a complex. which causes the dyes released when in cold water to be very small.

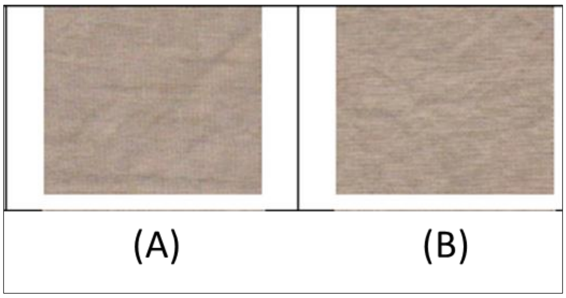

Figure 4 Color of cotton cloth .a) color before test, b) color after test with cold water

According to Hunter [21], the color fastness of encapsulated tannins is moderate. If the value of ΔE = 3 to 6.Changes in the ΔE value indicate the magnitude of the color fading value. The higher the ΔE value, the greater the fading, conversely, the lower the ΔE value, the smaller the fading. According to Widowati & Sutapa[22], the strength and weakness of the bond that occurs between the fabric fiber and the dye determines the fastness properties of the color retained in the fabric fiber which will strengthen the color fastness, that hydrogen bonds are formed between cellulose and dyes which make it difficult for the dyes to come out of the fiber.

4. Conclusion

Leaf litter, bark, and propagule waste from mangroves produce a natural brown dye. The brown color of the natural dye extract from mangrove waste is a type of condensed tannin consisting of hydroxyl, carbonyl and chromophore groups. The compounds contained are polyphenols and tannins. Dyeing quality on fabrics dyed with waste mangrove natural dyes ranges from 3 (adequate) to 4 (good) and meets SNI standards. The color fastness test in hot water has a value of ΔE = 5.94, which is included in the good category, and tests with water cold has a value of ΔE = 2.04 which is included in the very good category.

Compliance with ethical standards

Acknowledgments

This research was financially supported by University of Soetomo grant No.24/PEN/8/2021. I would like to thank my student Rizky Amelia and Randy Muhammad for collecting mangrove extract tannin and dyeing cotton.

Disclosure of conflict of interest

Authors have declared that there was no conflict of interest.

Statement of ethical approval

This research was financially supported by Universitas Suetomo grant no. 24/PEN/8/2021. I would like to thank my student Rizky Amelia and Randy Muhammad for collecting mangroves, extract tannin and dyeing cotton.

Statement of informed consent

Informed consent was obtained from all individual participants included in the study.

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