

Preparation of Cellulose-Citral Fiber from Fabric Waste Using the Encapsulation Method

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Abstract

The significant increase in fabric waste each year has the potential to become a source of environmentally friendly cellulose raw materials. Cellulose extracted from this textile waste can be utilized with active compounds found in essential oils. This study aims to synthesize cellulose-citral compounds based on cellulose extracted from textile waste and citral from lemongrass oil (*Cymbopogon citratus*) using an encapsulation method to enhance stability and extend the shelf life of citral with the assistance of environmentally friendly natural H-zeolite catalysts. The cellulose extraction process uses the acid hydrolysis method with a 1M HCl solution. Natural zeolite is activated using the acid method with HF, HCl, and NH_4Cl . Subsequently, cellulose-citral synthesis is performed using the reflux method at 70 °C for 10 hours. The synthesized product was encapsulated with gum arabic coating using the spray drying method to protect and extend the shelf life of citral. The results of cellulose-citral synthesis showed that the best synthesis was the 10-hour cellulose-citral synthesis, characterized by the formation of carbonyl bonds and C-O-C bonds in the synthesis product from the reaction of the hydroxyl group (-OH) of cellulose with the aldehyde group (-CHO) of citral at a peak of 1738,54 cm^{-1} with the lowest transmittance of 93.59% and a GC area of 1.5%. The particle size of cellulose-citral microcapsules increased to 3717.27 ± 416.84 nm. The encapsulation method using gum arabic was less effective in improving the stability and shelf life of cellulose-citral. Based on the characterization results, only a small amount of citral was encapsulated.

Keywords: Fabric waste, Extraction, Cellulose, Citral, Encapsulation

1. Introduction

The increasing demand for fast fashion in the modern era in the textile and fashion industry has led to a significant increase in textile waste every year. According to data from the National Waste Management Information System (SIPSN) in 2023, Indonesia generates 2.95% of its total annual waste of 38.6 million tons as textile/fabric waste, as shown in Figure 1 (Kementerian Lingkungan Hidup, 2023). Most of the unmanaged textile waste still ends up in landfills (TPA), causing environmental issues. Textile waste, one of the most common and voluminous types of waste, is cotton fiber textile waste. One potential approach to reduce the negative impact of textile waste is to process it into new, valuable raw materials as a source of cellulose fiber (Costa et al., 2022).

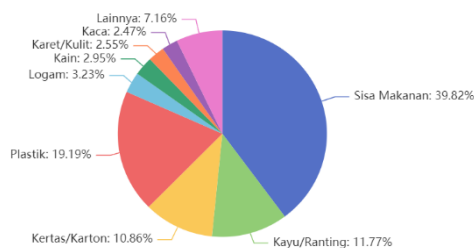


Figure 1. Types of waste in Indonesia
Source: <https://sipsn.menlhk.go.id/sipsn/>

Cotton is one of the main resources in various modern industries and the most widely consumed fiber after polyester (Lu et al., 2023). Discarded cotton textile waste still contains cellulose that can potentially be recycled into biopolymer composites or new fiber raw materials. Cellulose is one of the most abundant natural polysaccharides, consisting of repeating β -linked (1 $\rightarrow$ 4) D-glucose units (Do et al., 2023). Cellulose found in textiles made from cotton fibers is much purer, around 90% (Djayanti et al., 2021), making it easier and more cost-effective to obtain cellulose from these materials (Costa et al., 2022). Textile waste recycling methods include mechanical, chemical, and biological recycling. Chemical recycling uses various chemical processes to produce new materials (micro/nano materials, porous materials, functional materials) by decomposing waste cotton fibers (Lu et al., 2023). One of the commonly used chemical recycling processes is acid hydrolysis, which aims to remove contaminants present in textiles and separate cellulose from other fibers using chemical reagents such as strong acids.

The cellulose extracted from textile waste can be used for various applications. One of them is in the synthesis of cellulose composites with active compounds found in essential oils, namely citral. Citral has a distinctive lemon-like aroma and is known to have strong antibacterial properties against both gram-positive and gram-negative bacteria (Oladeji et al., 2019).

The synthesis of cellulose-citral involves cellulose extracted from citral isolated from lemongrass oil with the help of a natural zeolite catalyst. Cellulose contains many hydroxyl groups (-OH), while citral contains aldehyde groups (-CHO). The hydroxyl groups in cellulose react with the aldehyde groups in citral to form ester groups (RCOC). Citral has high volatility and is highly susceptible to degradation due to the presence of oxygen, light, and high temperatures, making it prone to evaporation and unstable under environmental changes. To address these issues, an alternative method is needed, namely encapsulation.

Encapsulation captures the active compound and releases it at a controlled rate under specific conditions, enhancing its bioavailability, stability, and applicability in different matrices (Ozdemir et al., 2021). The cellulose-citral encapsulation method using gum arabic as a coating will be applied to synthetic cellulose fibers. In this study, a catalyst will also be used to enhance reaction efficiency. The catalyst used is natural zeolite from Malang, activated with acid treatment to form H-natural zeolite catalyst. This activation process aims to enhance the catalytic properties of zeolite, enabling it to more effectively accelerate the reaction between cellulose and citral.

The use of the active ingredient citral in essential oils in this study aims to increase the value of cellulose extraction as a new raw material with broad application potential. This study aims to design a method for processing textile waste based on natural materials while utilizing cellulose and citral from lemongrass oil to produce aromatic fiber raw materials.

2. Methodology

2.1. Extraction of Cellulose from Fabric Waste

Textile waste is cut into small pieces (<1 cm²) and soaked in 1 mol L⁻¹ HCl with a soaking ratio of 1:15 (w/v). The mixture is then heated at reflux temperature for several hours until all the fibers turn into powder. The reaction is carried out for approximately 7 hours until all fibers have been converted into powder. The powder is then filtered and washed twice with 96% ethanol and acetone. The powder is then filtered and dried in an oven at 50°C, after which it is analyzed using FTIR and SEM (Costa et al., 2022).

2.2. Preparation of Natural Zeolite Catalyst into H-ZA

Natural zeolite chunks are ground with a mortar and then in a grinder until homogeneous particles that pass through a 100 mesh sieve are obtained. The sieved material is dried from water by heating in an oven at 120°C for 3 hours. A total of 150 grams of 100-mesh dried natural zeolite is soaked in 175 mL of 1% HF for 15 minutes, then washed until neutral and dried at 50°C. A total of 136 grams of natural zeolite was soaked again in 566.6 mL of 6 M HCl for 30 minutes while heated at 50°C, then dried at 120°C. After that, 95 grams of activated natural zeolite was placed in 1187.5 mL of 3 M NH₄Cl solution. The mixture was stirred for 24 hours at room temperature. The mixture was then washed and filtered with running water until free of chloride ions (Cl⁻) (tested with AgNO₃ solution), indicated by the absence of white

precipitation. The sample was dried again in an oven at 120 °C for 3 hours, then the solid was calcined at 450 °C for 1 hour to remove NH₃ gas. The result of this process is called Natural H-Zeolite or H-ZA. The natural zeolite is then analyzed using FTIR, SAA, and XRD (A W Fadhilah, E Cahyono, 2018); (Cahyono et al., 2014).

2.3. Synthesis of Cellulose-Citral

The ratio used in this synthesis consists of cellulose, H-ZA, citral, and ethyl acetate (20 grams : 4 grams : 20 mL : 80 mL). 20 grams of cellulose were placed in a round-bottom flask. Then, 80 mL of ethyl acetate was added as a solvent. Next, 20 mL of citral was added, along with 4 g of natural H-zeolite catalyst, and the mixture was stirred with a magnetic stirrer and heated at 70 °C for 10 hours. Every 2.5 hours, the mixture is taken during the reaction process. After that, the cellulose-citral synthesis product is centrifuged for 10 minutes at a speed of 4000 rpm. After centrifugation, separate the cellulose and zeolite using a spatula. The obtained product is weighed and oven-dried, then analyzed using FTIR spectroscopy, GC, and SEM.

2.4. Cellulose-Citral Encapsulation

Encapsulation was performed by dissolving 3 grams of cellulose-citral in 60 mL of distilled water, 2 grams of gum arabic, 1.2 g of Tween 80, and 6 mL of epichlorohydrin. The mixture is then sonicated at a temperature of 30–35°C for 10–20 minutes. The sonication is then stopped, and the resulting emulsion is stored in a sealed glass bottle. The emulsion was then cooled in a freezer and subsequently freeze-dried to convert the cellulose-citral slurry into cellulose-citral microcapsule powder. The cellulose-citral microcapsules were stored in sealed glass bottles in a refrigerator until further analysis. The cellulose-citral microcapsules were then analyzed using FTIR, SEM, and GC.

3. Results and Discussion

3.1. Extraction of Cellulose from Fabric Waste

Cellulose extraction from textile waste in this study used the acid hydrolysis method, which aims to remove contaminants and separate cellulose from non-cellulose fibers found in textile fabrics. The textile fabric used was white fabric, which was then extracted with 1 mol/L HCl. The lower the concentration of HCl used, the higher the cellulose yield produced (Pratiwi & Lestari, 2022). This occurs because using HCl at high concentrations accelerates the hydrolysis process. As a result, during the washing process, a large amount of glucose monomers are formed, which can reduce the cellulose yield. This extraction produces white cellulose, as shown in Figure 2, with a yield of 80%, as presented in Table 1. This result is not significantly different from previous studies on cotton fabric samples, which also yielded relatively high yields of 80–90%. This indicates that the acid hydrolysis method used in this study is sufficiently effective for obtaining cellulose extract from textile waste.

Table 1. Cellulose extraction results

Cotton fabric mass (g)	Extracted mass (g)	Yield (%)
66,6	53,3	80

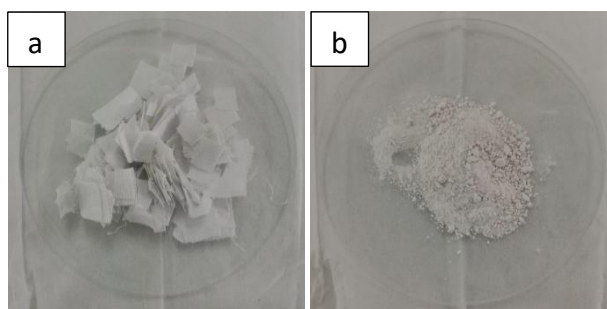


Figure 2. a) Fabric waste, b) Extracted cellulose

A comparison of the FTIR spectra of textile fabric, commercial cellulose, and extracted cellulose is shown in Figure 3. The FTIR spectra of the three samples show characteristic cellulose absorption bands. In the FTIR spectrum of extracted cellulose, there is a hydroxyl group (OH) at the absorption band of 3336 cm⁻¹, C-H group at 2899 cm⁻¹, CH₂ bending bond at the peak of 1428 cm⁻¹, and C-C and C-O-C bending bonds at 1161 cm⁻¹ and 1109 cm⁻¹, small peak at 1031 cm⁻¹ indicating C-O-C bonds from the pyranose ring, and 896 cm⁻¹ indicating β-glycosidic bonds, which are characteristic of cellulose. This is consistent with the FTIR spectra of textile fabrics and commercial cellulose. The FTIR results of the textile fabric sample show an ester group spectrum at the peak of 1735 cm⁻¹. This peak does not appear in the spectrum

of commercial cellulose and extracted cellulose, indicating that the extraction process successfully removed the C=O group from the ester or hemicellulose (Ruiz-Caldas *et al.*, 2023).

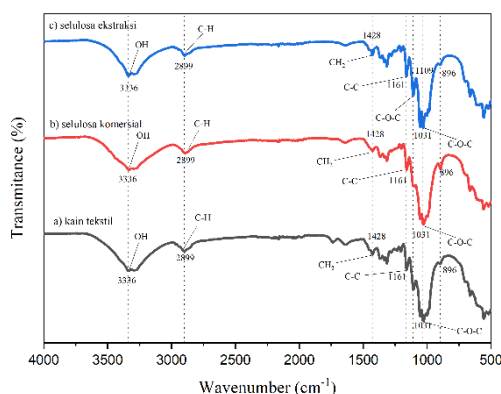


Figure 3. FTIR spectrum; a) textile fabric, b) commercial cellulose, and c) extracted cellulose

Morphological analysis and particle size analysis of commercial cellulose and extracted cellulose were performed using SEM on samples of extracted cellulose and commercial cellulose at magnifications ranging from 5,000 to 50,000 times. Morphologically, the commercial cellulose in Figure 4 exhibits a relatively rough, uniform surface with minimal agglomeration between particles. Meanwhile, the structure of the extracted cellulose in Figure 5 has a smooth, irregular surface with minimal agglomeration. This occurs because the acid hydrolysis process uses HCl, which is strong enough to hydrolyze the fabric. The visible and non-homogeneous fiber structure indicates that the extraction process is capable of removing non-cellulose components such as lignin and hemicellulose without damaging the original form of cellulose (Costa *et al.*, 2022). Additionally, commercial cellulose has a smaller and more uniform particle size than extracted cellulose. From the particle size distribution analysis, commercial cellulose has a dominant particle size of 3760.57 ± 46.29 nm, which is smaller than the extracted cellulose, which has a size of 6697.14 ± 92.68 nm, as shown in Figure 6.

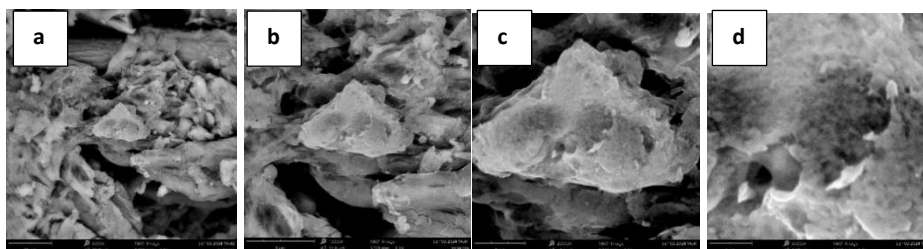


Figure 4. SEM of commercial cellulose; a) 5000x, b) 10000x, c) 20000x, d) 50000x

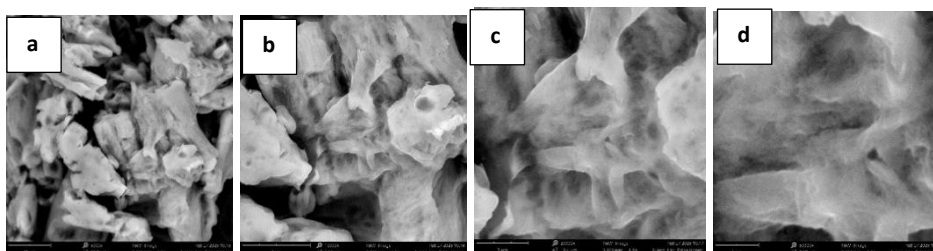


Figure 5. SEM cellulose extraction; a) 5000x, b) 10000x, c) 20000x, d) 50000x

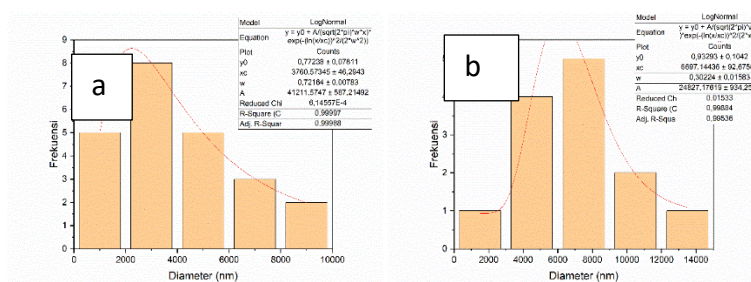
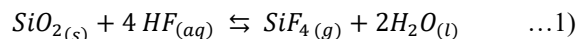


Figure 6. Graph of particle size distribution; a) commercial cellulose, b) extracted cellulose

3.2. Activation of Natural Zeolite into H-ZA

The activation of natural zeolite aims to expand the surface area of the catalyst by removing organic impurities, metal ions (M^{n+}) such as alkali and alkaline earth metals, as well as transition metals that undergo deionization found in natural zeolite (Setyowati et al., 2014). Based on this study, the preparation was carried out by grinding zeolite chunks until they passed through a 100-mesh sieve to ensure more uniform particle sizes of natural zeolite. The natural zeolite was then dried at 120 °C for 3 hours to remove the water contained in the natural zeolite and increase the number of pores and surface area of the natural zeolite (Asmorowati et al., 2023).

Natural zeolite is chemically activated by soaking it in a 1% HF solution, 6 M HCl, and 1 M NH_4Cl . Soaking natural zeolite in a 1% HF solution aims to remove impurities or free silica, thereby increasing the mesopore volume and crystallinity without damaging the crystal structure (Sholikah et al., 2023). This causes the silicon in natural zeolite to react with HF and form SiF_4 which is highly volatile. As shown in reaction equation 1) below.



Activation is continued with 6 M HCl solution which will increase the acidity and increase the Si/Al ratio due to dealumination in the natural zeolite structure. Charge-neutralizing ions (M^{n+}) (counter cation) will decrease because the aluminate group reacts with HCl (H^+) during the dealumination process. The activated natural zeolite (ZA) is then soaked in NH_4Cl and stirred for 24 hours to replace metal cations such as Na^+ and other cations with NH_4^+ . This process produces NH_4^+ZA after being washed with distilled water to remove Cl^- ions and dried for subsequent calcination (Setyowati et al., 2014). Calcination releases NH_3 gas, resulting in H-ZA as shown in the reaction in Figure 7.

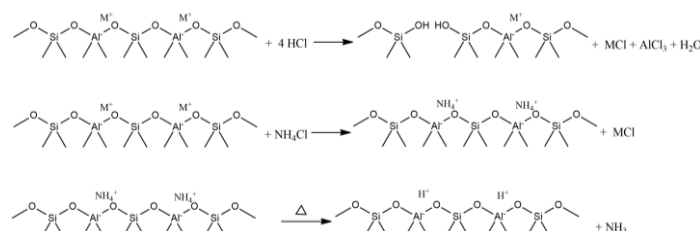


Figure 7. Activation reaction of natural zeolite

Source: Sholikah *et al.*, 2023

The H-ZA yield produced was 53.3% with the final color of H-ZA becoming bone white as shown in Table 2 and Figure 8. This mass reduction occurred due to a series of activation processes. During the activation stage, impurities such as organic impurities, metal ions (M^{n+}) like alkali and alkaline earth metals, and transition metals undergo deionization and dissolve as chloride salts. Additionally, the drying and calcination processes remove residual water and other volatile compounds, resulting in a decrease in natural zeolite.

Table 2. Yield results for H-ZA

Natural zeolite mass (g)	H-ZA Mass (g)	Yield (%)
150	80	53,3%

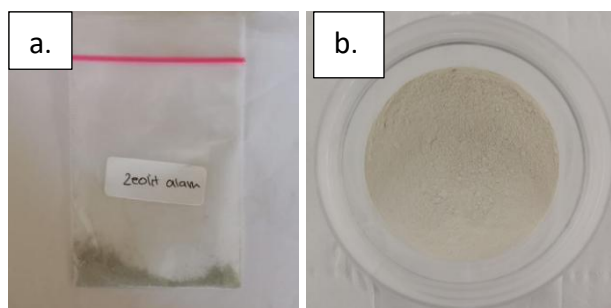
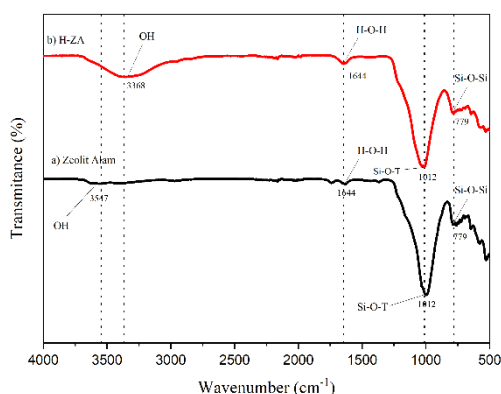


Figure 8. a) Natural zeolite, b) H-ZA

A comparison of the FTIR spectra of natural zeolite and H-ZA from this study is shown in Figure 9. The FTIR spectra of both samples show a shift in the band, indicating a change in the zeolite structure after activation. In natural zeolite, an absorption band appears at 3547 cm^{-1} which is the hydroxyl group ($-OH$) from water. This band shifts to 3368 cm^{-1} in H-ZA, indicating the Si-OH-Al group as a Bronsted acid site resulting from the exchange of metal cations with H^+ ions. Furthermore, in H-ZA, a vibration at 1644 cm^{-1} appears, which is not present in natural zeolite. This absorption band corresponds to the remaining H-O-H groups in H-ZA. A dominant peak at 1012 cm^{-1} represents the Si-O-T stretching

band of the aluminosilicate framework (T = Si or Al). The absorption band at 779 cm^{-1} is the symmetric stretching of Si-O-Si, indicating that the silica framework of the zeolite remains intact after acid activation.



Gambar 1. Spektrum FTIR; a) Zeolit Alam, b) H-ZA

The crystallinity patterns of natural zeolite and H-ZA obtained were analyzed using XRD, as shown in the graph in Figure 10. The data obtained showed several sharp peaks in the 2θ angle range between 10° and 70° . The peaks appear at $2\theta = 13,52^\circ, 19,69^\circ, 20,84^\circ, 22,31^\circ, 24,24^\circ, 25,75^\circ, 26,63^\circ, 27,88^\circ, 31,12^\circ, 36,57^\circ, 39,48^\circ, 42,46^\circ, 45,79^\circ, 50,13^\circ, 51,22^\circ, 55,01^\circ, 59,94^\circ$, dan $68,24^\circ$. These peaks indicate that there is no significant change in the diffraction pattern. This suggests that there is no damage to the zeolite structure after the activation and calcination process. The main components of natural zeolite and H-ZA are modernite minerals, as indicated by the similarity of the diffraction patterns in the Joint Committee on Powder Diffraction Standards (JCPDS No. 6-239) database. This is supported by the diffraction peaks of natural zeolite and H-ZA, which align with the findings of Sholikah *et al.* (2023), who concluded that the primary component of natural zeolite from Malang Regency is mordenite.

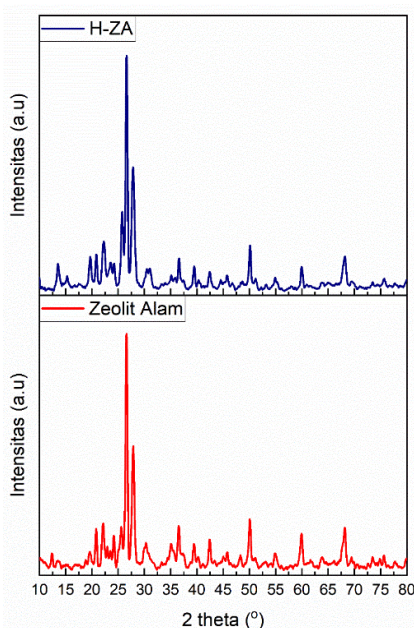


Figure 10. Diffractograms of natural zeolite and H-ZA

The surface area, diameter, and pore volume of natural zeolite in this study were determined using SAA characterization. Based on the results of surface area analysis using the BET method, the surface area of H-ZA was $365,477\text{ m}^2/\text{g}$. This surface area is larger than that reported in a previous study by Sholikah *et al.* (2023), which yielded a surface area of $137,8196\text{ m}^2/\text{g}$. The activation process results in a reduction in pore diameter and an increase in pore volume due to the removal of impurities that typically occupy the micropores. The adsorption-desorption graph is shown in Figure 11.

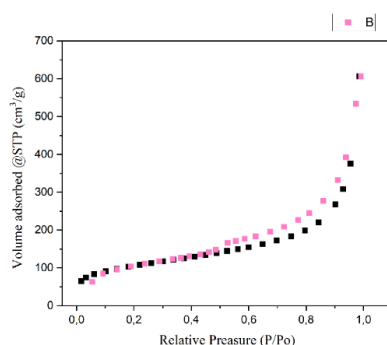


Figure 11. H-ZA adsorption and desorption graph

Based on the results of analysis using the BJH (Barret-Joyner-Halenda) method, the pore diameter of H-ZA is 3.77–3.88 nm. According to the IUPAC (International Union of Pure and Applied Chemistry), there are three categories of materials based on pore diameter: micropores (< 2 nm), mesopores (2–50 nm), and macropores (> 50 nm). Based on the data obtained, natural zeolite from Malang falls into the mesopore category (Sholikah *et al.*, 2023). The results of the BJH method analysis are presented in Table 3 below.

Table 3. Surface area of H-ZA using the BJH method

Parameters	H-ZA
Adsorpsi	
Surface Area (m ² /g)	147,336
Pore Diameter (cm ³ /g)	0,815292
Pore Diameter (nm)	3,77047
Desorpsi	
Surface Area (m ² /g)	357,894
Pore Diameter (cm ³ /g)	0.866312
Pore Diameter (nm)	3.86925

3.3. Cellulose-Citral Synthesis

This synthesis produces white cellulose-citral with a distinctive and pungent citral odor, as shown in Figure 18. The white color of the product indicates that no thermal degradation occurred during the synthesis process. The detected citral aroma indicates that a small amount of citral was physically adsorbed onto the cellulose surface.

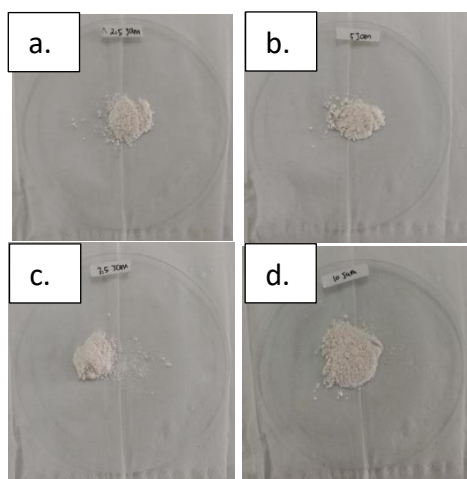


Figure 12. Synthesis of cellulose-citral; a) 2.5 hours, b) 5 hours, c) 7.5 hours, d) 10 hours

The reaction mechanism between cellulose and citral occurs through a hemiacetal condensation mechanism catalyzed by acid from H-ZA. The reaction begins with the activation of the carbonyl group (C=O) in the citral aldehyde unit by the H-Zeolit Alam acid catalyst. The H-Zeolite Natural catalyst acts as a proton donor (acid site) and absorbs the water produced by the reaction. The carbonyl group of citral undergoes protonation by the Bronsted acid on H-Zeolite Natural. Subsequently, citral is activated by the acid through the formation of a stable resonance carbocation on the carbonyl carbon. The hydroxyl group of cellulose then attacks the carbonyl group of citral. After that, the oxonium ion in cellulose transfers a proton to the carbonyl oxygen atom, forming an unstable intermediate. The intermediate then releases H⁺ and forms a stable ester bond between cellulose and citral (Fessenden R. J. and Fessenden Joan S, 1982). As shown in the cellulose-citral synthesis reaction mechanism illustrated in Figure 4.18.

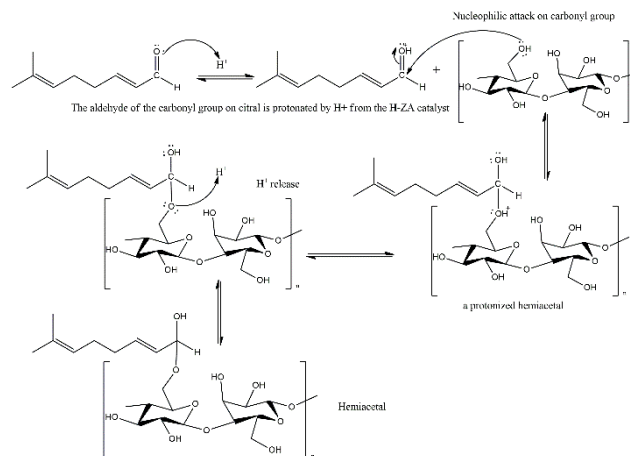


Figure 13. Mechanism of cellulose-citral synthesis

Analysis of the functional group characteristics of the cellulose-citral synthesis was carried out using FTIR. The FTIR spectra of citral, extracted cellulose, and cellulose-citral show significant differences as shown in Figure 20. Hydroxyl groups are seen in the $3200\text{--}3500\text{ cm}^{-1}$ region which is the stretching vibration of the O-H group in cellulose and citral. There is a peak that appears in the $3336,89\text{ cm}^{-1}$ absorption band with a transmittance of 81.36% on cellulose which indicates the presence of hydrogen bonds between cellulose molecules. These peaks are the stretching vibrations of the O-H of the cellulose hydroxyl group and the rest of the unreacted free O-H. The best O-H group peak is in the 10-hour cellulose-citral spectrum, the results are not much different, namely the peak appears at 3337.86 cm^{-1} absorption band with a lower transmittance value of 80%.

In the spectrum of the synthesis results, alkyl groups appeared at wave numbers $2900\text{--}3000\text{ cm}^{-1}$ which are vibrations of aliphatic C-H groups. In the cellulose spectrum, the peak appeared at $2899,67\text{ cm}^{-1}$ with a transmittance of 90.11% indicating the presence of methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) groups. Whereas in the citral spectrum, the peak is sharper at $2917,90\text{ cm}^{-1}$ and $2857,82\text{ cm}^{-1}$ absorption bands with transmittance of 84.89% and 87.21% which show CH_3 dan CH_2 stretching vibrations, respectively (Tian *et al.*, 2018). In the spectrum of cellulose-citral 10 hours appeared at a peak of 2901.18 cm^{-1} with a transmittance of 90.31%.

The carbonyl group on citral appears in the 1671 cm^{-1} absorption band which is the $\text{C}=\text{O}$ stretching vibration of the aldehyde group. In the spectrum of the cellulose-citral synthesis, the $\text{C}=\text{O}$ peak of citral decreased or disappeared in intensity. This analysis is supported by the appearance of a new peak in the form of a carbonyl group in the synthesis with a wave number around 1738 cm^{-1} (Kusuma *et al.*, 2021). The peak is characteristic of the $\text{C}=\text{O}$ ester group resulting from the reaction between the hydroxyl group (O-H) of cellulose and the aldehyde group ($-\text{COOH}$) of citral. The best ester peak appeared in the 10-hour cellulose-citral synthesis at $1738,54\text{ cm}^{-1}$ with an intensity of 93.59%.

The ether group in the FTIR spectrum of cellulose and cellulose-citral shown in Figure 29 appears in the region of 1050 cm^{-1} to 1150 cm^{-1} . The peak is the stretching vibration of the C-O-C group in the cellulose glycosidic bond and the C-O ester. In the cellulose spectrum, ether groups appeared at $1109,63\text{ cm}^{-1}$ and $1054,88\text{ cm}^{-1}$ dengan nilai transmittansi sebesar 72,73% serta 59,43%. with transmittance values of 72.73% and 59.43%. The ether peak in each synthesis appeared at $1109,63\text{ cm}^{-1}$ and $1055,01\text{ cm}^{-1}$ with transmittance of 70.10% and 52.11%. The ether peak remained stable in all reaction spectra indicating that the cellulose polysaccharide skeleton was not degraded during the reaction process.

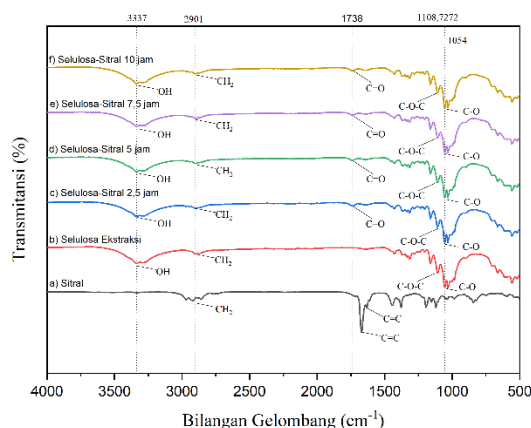


Figure 2. FTIR spectra; a) Citral, b) Extracted cellulose, Cellulose-Sitral: c) 2.5 hours, d) 5 hours, e) 7.5 hours, f) 10 hours

The results of the previous characterization were supported by surface morphology analysis using SEM to observe changes in the structure of cellulose-citral after the synthesis process. The morphological comparison of extracted cellulose and cellulose-citral can be observed in Figure 21. The structure of extracted cellulose has a rough, irregular surface, and there appears to be an agglomerated structure. And the extracted cellulose still shows relatively large, fine, and regularly arranged pores. These structures indicate the natural characteristics of cellulose. After the synthesis process, the SEM morphology shows a rougher and denser surface. In the SEM morphology of cellulose-citral there are also no free crystals or unreacted particles on the surface. The morphology shows that the product of the synthesis does not experience clumping or agglomeration. It also indicates that chemical bond formation occurs as a result of the reaction of the -OH group from cellulose with the -CHO group from citral which produces a hemi-acetal group. These morphological changes are in accordance with the research conducted by Tariq *et al.* (2022). The particle size of cellulose extracted from cellulose extraction has a size of 6697.14 ± 92.68 nm. After being reacted with citral in the synthesis process, the particle size of cellulose-citral decreased to 2983.49 ± 260.92 nm.

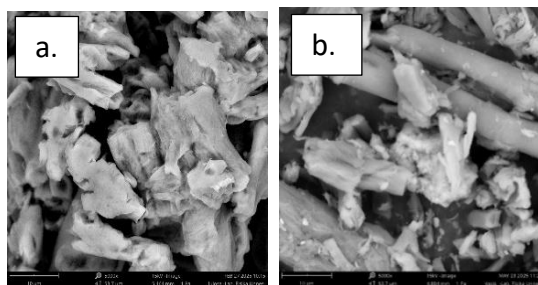


Figure 15. SEM Morphology; a) Extracted cellulose, b) 10 hours cellulose-citral

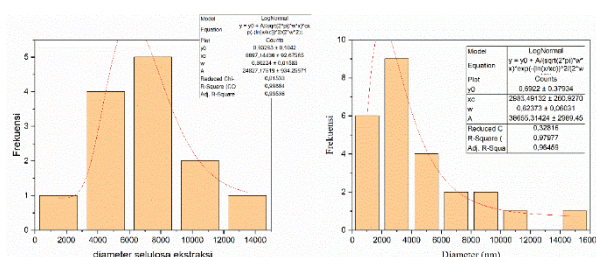


Figure 16. Particle Size Distribution; a) Extracted Cellulose, b) Cellulose-citral 10 hours

Gas Chromatography (GC) analysis was used to determine the presence of citral in the cellulose-citral product. The chromatogram results identified 2 main peaks at retention times of 8.960 min and 17.665 min which are shown in Figure 4.22. The peak with the largest area of 98.49% at retention time of 8.960 min was identified as n-hexane which was used as a solvent for citral. The solvent still dominates in large quantities in the mixture because it has not evaporated completely when flowed with N₂ gas. Then, the second peak that appeared at a retention time of 17.665 minutes with an area of 1.5% was citral. The relatively small citral peak indicates that only a small amount of free citral remains in the mixture after the synthesis process. Most of the citral has reacted and bonded with cellulose only physically bound, so some of the citral so that the citral is easy and becomes free citral. The GC analysis results support the data from FTIR spectroscopy and SEM morphology which show the modification of cellulose structure.

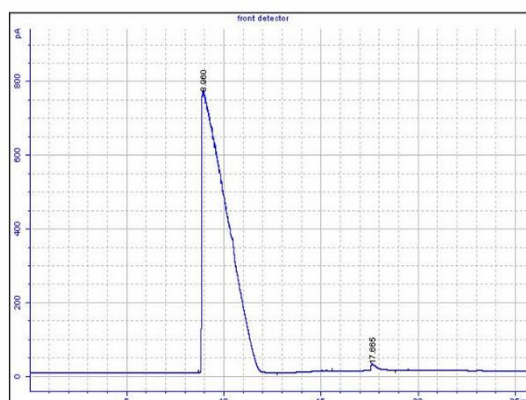


Figure 17. GC chromatogram of cellulose-citral synthesis 10 hours

3.4. Cellulose-Citral Encapsulation

Based on the results of the synthesis that has been carried out, cellulose-citral then enters the next stage, namely the encapsulation process. Encapsulation aims to increase the stability of citral compounds that have been bound to the cellulose matrix, while controlling the release of these active compounds. The dressing used is gum arabic because it is often used as a dressing, soluble, biodegradable, and non-toxic when used as a protective layer (de Souza *et al.*, 2020). Gum arabic has carboxylic groups ($-\text{COO}^-$) in water (Yang *et al.*, 2015). Gum arabic was emulsified in a mixture of water, cellulose-citral synthesis (time variation of 2.5 hours; 5 hours; 7.5 hours; 10 hours), tween 80, and epychlorohydrin. Based on the results of the emulsification process, the 10-hour cellulose-citral synthesis showed the most optimal emulsion stability results. The 10-hour cellulose-citral emulsion successfully maintained the dispersed phase for 24 hours and no phase separation was observed after freezing in the freezer. Encapsulation was carried out using the freeze drying method. The process and results of encapsulation can be seen in Figure 24 which shows a white fine powder.



Figure 18: Cellulose-citral encapsulation process and results

The encapsulated results were then analyzed for functional groups with FTIR spectroscopy. The FTIR spectrum shows the comparison of citral, extracted cellulose, synthesized results, and cellulose-citral encapsulation results. In the FTIR spectrum presented in Figure 4.24, there is a significant difference between the synthesis and encapsulation results. The hydroxyl group ($-\text{OH}$) appears at the peak of $3200\text{--}3500\text{ cm}^{-1}$ which is the stretching vibration of the O-H group on cellulose and citral. The best microcapsule spectrum results are in the 10-hour cellulose-citral microcapsule, the results are not much different, namely the peak appears at 3338.99 cm^{-1} absorption band with a lower transmittance value of 61.33%.

In the spectrum of the synthesized results, alkyl groups appear at wave numbers $2900\text{--}3000\text{ cm}^{-1}$ which are vibrations of aliphatic C-H groups. In the spectrum of 10-hour cellulose-citral microcapsules, a peak of 2922.43 cm^{-1} appeared with a transmittance of 80.24%. These results show a stable pattern and indicate that during the encapsulation process the carbon chains of cellulose and citral are maintained.

The carbonyl group in the encapsulation results appeared at a peak of 1736 cm^{-1} which is the $\text{C}=\text{O}$ stretching vibration of the aldehyde group. The result of 10 hours cellulose-citral encapsulation appeared at a peak of 1736.76 cm^{-1} with an intensity of 92.01%. The presence of this peak indicates that the ester group ($\text{C}=\text{O}$) resulting from the reaction between the hydroxyl group (O-H) of cellulose and the aldehyde group ($-\text{COOH}$) of citral was not damaged during the encapsulation process. The presence of the peak also indicates that some citral is still detected in the form of cellulose-citral microcapsules although the intensity is small.

The ether group in the FTIR spectrum of cellulose-citral microcapsules shown in Figure 25 appeared in the region of 1050 cm^{-1} to 1300 cm^{-1} . The ether peaks in 10-hour cellulose-citral were at 1314.99 cm^{-1} and 1054.46 cm^{-1} with transmittance values of 76.77% and 76.14%. The ether peak decreased in all spectra of cellulose-citral microcapsules indicating that the weakening of the cellulose polysaccharide skeleton and hemi-acetal bonds due to the encapsulation process.

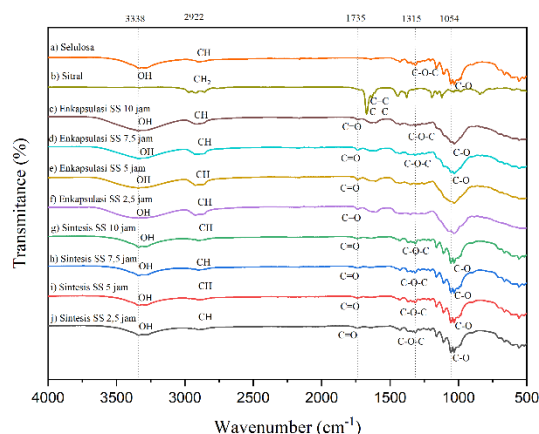


Figure 19: FTIR spectra of citral, cellulose, synthesized, and cellulose-citral encapsulation.

The SEM morphology of the cellulose-citral microcapsules showed a smoother and more coated surface. The particles appear more homogeneous and distributed in a relatively uniform size. This indicates that the encapsulation process went well, with the formation of a protective layer around the cellulose-citral complex. The dense surface structure indicates that the citral molecules are successfully protected within the encapsulant matrix. These results indicate that encapsulation not only maintains the morphological shape of the particles, but also improves surface stability and protection against the external environment. It was also observed in the morphology of cellulose-citral microcapsules that there were some small blobs which were slurries of cellulose-citral microcapsules. The spheres were few in number indicating that the encapsulation process successfully retained the citral compound albeit with low intensity. These results show agreement with previous research conducted by Tariq *et al.* (2022) and Bouaziz *et al.* (2021).

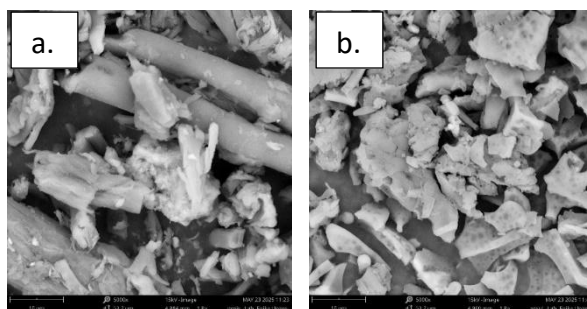


Figure 20. SEM morphology; a) cellulose-citral, b) cellulose-citral microcapsules

The particle size of cellulose-citral was 2983.49 ± 260.92 nm. After the encapsulation process, the particle size of cellulose-citral microcapsules increased to 3717.27 ± 416.84 nm. This increase is due to the formation of a protective layer around the surface of the cellulose-citral microcapsule particles. The encapsulation process involves the cellulose-citral polymer matrix with gum arabic which forms a solid capsule structure thereby increasing the particle size. The coating encapsulates the particles resulting in larger particles than before encapsulation.

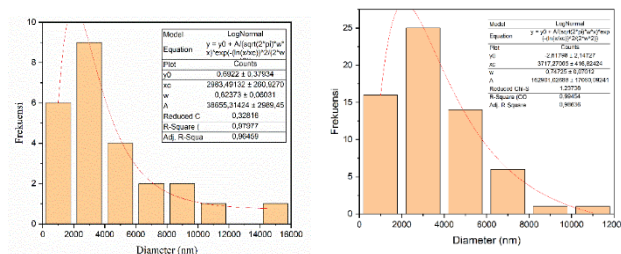


Figure 21: Particle size distribution, a) cellulose-citral, b) cellulose-citral microcapsules

The results of FTIR and SEM analysis were then confirmed by Gas Chromatography (GC) analysis used to determine the presence of citral in the cellulose-citral microcapsule product. The chromatogram results identified only 1 main peak at a retention time of 9.116 minutes with the largest peak area of 100% in Figure 4.27. The peak was identified as n-hexane which was used as a solvent for citral. The solvent still dominates in large quantities in the mixture because it has not evaporated completely when flowed with N₂ gas. In addition, confirmation from the previous analysis also identified that the citral content contained in the cellulose-citral microcapsules was very low. This is thought to be due to the reversible nature of the glycosidic bond in the cellulose-citral structure, making it easy to damage or release citral from

the cellulose matrix. Thus, the GC data provided the final confirmation that the encapsulation was not effective enough but there was still a low content of citral compounds in the cellulose-citral microcapsules.

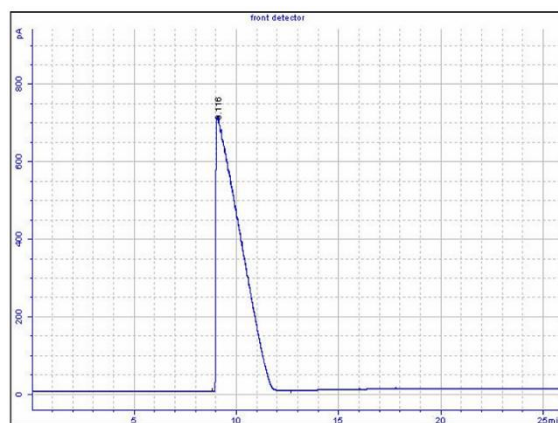


Figure 3. GC chromatogram of cellulose-citral microcapsules

4. Conclusion

Based on the results of the research that has been carried out, the following conclusions are obtained.

1. The yield of cellulose produced from the extraction of fabric waste is 83.3% which shows good efficiency through the acid hydrolysis method with optimal parameters using HCl solution with a concentration of 1 M at a temperature of 70 °C for 7 hours.
2. The effect of cellulose-citral synthesis reaction time has a significant effect with the most optimal cellulose-citral composite results at the 10th hour with the highest ester (C=O) peak intensity with a peak of 1738.54 cm⁻¹ with a transmittance of 93.59%.
3. The characteristics of the extracted cellulose in this study showed white results with a smooth, irregular surface, and minimal agglomeration with a size of 6697.14 ± 92.68 nm based on SEM morphology results. The characteristics of the cellulose-citral synthesis results show that there is a layer of citral covering the cellulose surface. Then, the characteristics of cellulose-citral microcapsules showed that the surface of cellulose was coated by the coating and there were small spheres indicated as encapsulated citral by gum arabic.

Encapsulation formulation affects the stability of cellulose-citral composite with the most optimal emulsion stability result is cellulose-citral 10 hours which successfully maintains the dispersed phase for 24 hours without phase separation. The encapsulation formulation does not increase the effectiveness of citral in cellulose-citral composites with parameter results in FTIR results with the highest ester peak intensity (C=O) with a peak of 1736.76 cm⁻¹ with a transmittance of 92.01% in 10-hour cellulose-citral microcapsules.

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