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Optimization Of Carboxymethyl Cellulose (CMC) Synthesis In Production Of Hydrogel From Ananas comosus L. Leaves

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Abstrak. *Cellulose and its derivatives are important industrial raw materials because of their abundance, biodegradable properties, environmentally friendly, and have good mechanical and thermal properties. This study aims to determine the synthesis process and characteristics of carboxymethyl cellulose (CMC) in the manufacture of hydrogels from pineapple leaf waste. The stages of the CMC synthesis process from pineapple leaves are carried out through the process of delignification, bleaching, alkalization and carboxymethylation. Cellulose modification was done by alkalization method using 30% NaOH and variation of temperature and time on carboxymethylation with monocloroacetic acid (MCA) in 2-propanol solvent. In the manufacture of CMC hydrogel was made by using calcium chloride ($CaCl_2$) as a crosslink agent. The results showed that CMC from pineapple leaf waste had good quality with pH 6,0-7,5 and degree of substitution values ranging from 0,4-1,2. Carboxymethyl cellulose and hydrogel produced showed the presence of O-H, C-H and C=O functional groups. The presence of ATR-IR peak 1053-1104 cm^{-1} in the bleached product confirmed the presence of β-(1,4)-glycosidic bond of pure cellulose, while the peak at 1500-1700 cm^{-1} of the modified cellulose product confirmed the carbonyl group of carboxymethyl cellulose (CMC).*

Keywords: *Synthesis, Pineapple leaf, carboxymethyl cellulose, hydrogel.*

INTRODUCTION

Indonesia has abundant natural resources with vast agricultural land. However, despite its great potential, food production often faces challenges such as land degradation and climate change [1]. Prolonged dry seasons can reduce water availability for crops and have adverse effects on soil. One way to optimize water and nutrient supply for crops is through the application of hydrogel from CMC [2]. Hydrogel plays an important role in the agricultural sector as a soil conditioner that has the ability to retain water and nutrients, thereby enhancing plant resilience to drought conditions [3]. Hydrogel production can be made from natural or synthetic polymers. To enhance biocompatibility with the environment, the use of synthetic polymers is minimized and replaced with alternative materials such as natural polymers like cellulose. In the industrial sector, hydrogel is synthesized using synthetic polymers produced from acrylic monomers (including acrylic acid and acrylamide) as the primary material [4]. Further research is increasingly focused on using biodegradable natural polymers as the primary material [5]. Natural polymer-based hydrogels, particularly those derived from cellulose and its derivatives such as carboxymethyl cellulose (CMC), have gained increasing attention due to their biodegradability, non-toxicity, and renewable availability. CMC-based hydrogels not

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only exhibit excellent water absorption and retention capacity but also show potential for applications in agriculture, such as soil conditioners and water-retaining agents, to improve water use efficiency. Therefore, the utilization of CMC from abundant lignocellulosic biomass like pineapple leaves offers a promising strategy to develop sustainable hydrogels while simultaneously addressing agricultural waste management issues.

One of the primary materials in hydrogel production from natural polymers is carboxymethyl cellulose (CMC), a water-soluble cellulose derivative with high water retention capacity [6]. According to the Central Statistics Agency (BPS), the average consumption of CMC from 2018 to 2022 was 5,747 tons/year, and the average production of CMC in Indonesia was recorded at 5,000 tons/year. This indicates that the demand for CMC is very high, particularly in the food, pharmaceutical, textile, and cosmetic industries. CMC is obtained through an alkalization and carboxymethylation reaction between cellulose and monochloroacetic acid (MCA) in a basic environment. Its polymer structure consists of long glucose chains derived from cellulose, modified by substituting hydroxyl groups (-OH) with carboxymethyl groups ($-CH_2-COOH$) on the cellulose chain [7]. The success of CMC synthesis is significantly influenced by several process parameters, including temperature and reaction time. Optimizing the synthesis temperature and time aims to obtain CMC with an optimal degree of substitution (DS), thereby producing hydrogels with good absorption capacity and stability for agricultural applications.

Previous studies have shown that variations in reaction conditions, such as alkalization time, sodium monochloroacetate concentration, and solvent type, also play an essential role in determining the quality of CMC produced. However, most research has primarily focused on conventional cellulose sources, leaving limited exploration of pineapple leaf-derived cellulose as a sustainable raw material. In this context, investigating the influence of synthesis parameters on CMC production from pineapple leaf cellulose is crucial to ensure its performance meets industrial requirements, while simultaneously promoting waste valorization and environmental sustainability. Pineapple leaves, which are generally considered agricultural waste, contain a high proportion of cellulose that can be extracted and utilized as a potential raw material for CMC production. Utilizing pineapple leaf cellulose not only reduces environmental problems associated with agricultural residue disposal but also creates added value products with wide applications in food, pharmaceuticals, cosmetics, and other industries. Compared to conventional sources such as wood pulp or cotton, pineapple leaves offer a renewable and low-cost alternative, making them highly attractive for sustainable material development.

Moreover, the global demand for biodegradable and environmentally friendly polymers continues to grow as industries shift toward greener alternatives. CMC derived from pineapple leaves has the potential to meet this demand by offering functional properties comparable to CMC from conventional sources while supporting circular economy principles. Therefore, optimizing the synthesis of CMC from pineapple leaf cellulose through careful adjustment of process variables is not only scientifically relevant but also strategically important to enhance economic and ecological value.

Indonesia has abundant biomass resources, one of which is pineapple leaves (Ananas comosus L.), which are often discarded as waste without added value. Pineapple leaves contain higher cellulose content compared to the skin and core, making them a promising alternative raw material for CMC production [8]. Pineapple leaf waste contains 13.05% lignin, 21.02% hemicellulose, and 41.15% cellulose [9]. The abundance of pineapple plantation areas in Indonesia in 2023 reached 58,322 hectares for planted area and 55,160 hectares for harvested area [10], indicating that the availability of pineapple leaf waste as a cellulose source is highly potential for sustainable utilization. Pineapple leaves account for approximately 90% of total pineapple harvest waste. Therefore, pineapple solid waste needs to be processed and reused to produce environmentally friendly products. The high cellulose content in pineapple leaves provides a great opportunity for their utilization as raw material in the production of carboxymethyl cellulose (CMC). CMC is a cellulose derivative widely applied in various industries such as food, pharmaceuticals, cosmetics, textiles, and paper due to its properties as a thickener, stabilizer, binder, and emulsifier. Conventionally, CMC production relies on wood-based or cotton-derived cellulose, which raises concerns regarding sustainability and deforestation. Therefore, the utilization of pineapple leaf waste not only offers an alternative cellulose source but also supports the concept of a circular economy by reducing agricultural waste and providing value-added products with environmental benefits.

In reducing organic waste, one approach is to utilize pineapple leaves in CMC production. Through the optimization of CMC synthesis, particularly in terms of temperature and reaction time variations, CMC of higher quality can be produced. This significantly affects the characteristics of the resulting hydrogel, as CMC quality determines water absorption capacity, gel structure stability, and its application in agricultural uses. Thus, this innovation not only reduces waste but also produces value-added products that support environmental conservation and sustainable resource utilization. Comprehensive studies on the utilization of pineapple leaf cellulose for CMC-based hydrogel production are still limited. Most existing works emphasize conventional cellulose sources or focus on single process parameters without systematically evaluating the combined effect of temperature and reaction time on product quality. Therefore, this study aims to investigate the optimization of CMC synthesis conditions from pineapple leaf cellulose and to evaluate the characteristics of the resulting hydrogel for potential agricultural applications. The findings are expected to provide scientific insights into waste valorization while contributing to the development of sustainable biomaterials.

MATERIALS AND METHOD

Preparation of raw materials

The pineapple leaves used in this study came from pineapple plantations in Belik District, Pemalang Regency, Central Java. The pineapple leaves were washed and dried to remove mud, soil, and sand. After that, the pineapple leaves were cut and ground into small pieces. Next, the pineapple leaves were dried to a moisture content of 10%. The solvent used was monochloroacetic acid,2-propanol, *monocloroacetic acid* (MCA). All chemicals used in this study were analytical grade. This research is divided into several processes, namely delignification, bleaching, alkalization, and carboxymethylation. The delignification process is carried out by mixing NaOH with the raw material used, namely pineapple leaves. Then, bleaching is carried out to increase the purity of the raw material for the production of carboxymethyl cellulose. Next, the alkali treatment process is carried out by reacting the bleached cellulose with a NaOH solution to make the hydroxyl groups in the cellulose more reactive so that they can react easily in the carboxymethylation stage. In the carboxymethylation stage, the hydrogen atoms in the cellulose hydroxyl groups are replaced with carboxymethyl groups ($-CH_2COOH$). In the final stage, namely hydrogel production, the CMC solution is reacted with calcium chloride ($CaCl_2$), where Ca^{2+} ions act as cross-linking agents that connect the CMC chains.

The samples from the research will then be analyzed, both qualitatively and quantitatively. Qualitative analysis is performed using pH testing and ATR-IR analysis. Quantitative analysis will be conducted using UV-Vis spectrophotometry, HPLC, and degree of substitution (DS). DS indicates the number of cellulose hydroxyl groups that have reacted with monochloroacetic acid (MCA) to form carboxymethyl groups. The higher the degree of substitution value, the greater the influence on the carboxymethyl groups present in CMC. For a clearer understanding of this research, please refer to the following flowchart:

Preparation of pulp

In the pulp processing stage, we use a method called Ethanol Multi Explosion (CHEMEX). This process begins with the preparation of 500 g of pineapple leaves that have been ground with a water content of 10%. Next, the pineapple leaves are pretreated using 250 L of 10% NaOH solution at a high temperature (140–145 °C) and high pressure (4–7 kg/cm^3) for 30 minutes using a mixer and an exploder with a capacity of 450 L. The reactor is then suddenly opened after optimum conditions are achieved and the pressure is suddenly reduced to atmospheric pressure. After the steam explosion process, the pineapple leaf pulp is then cleaned and neutralized using water to a pH of 7–9. Next, the neutralized pineapple leaves pulp is further processed by sterilization at 80 °C in a buffer tank. Finally, the sterilized pineapple leaves pulp is separated from the solution using pressure filtration. A schematic diagram of lignin extraction from pineapple leaves is presented in Figure 1.

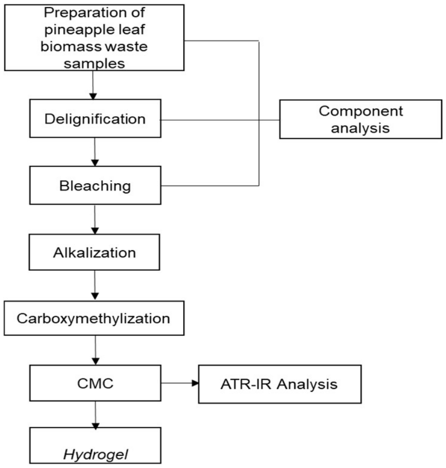

Figure 1 Research methods and design for hydrogel production

Bleaching

As much as 10 g pulps of pineapple leaves was subjected in to erlenmeyer flask and with 120 mL of H_2O_2 10% placed in a 60ºC water bath for 1.5 hours. After that, remove the sample from the water bath and filter it using a sieve to separate the liquid and solid components of the sample. Wash the solid sample until the pH of the sample is neutral (pH 7). After that, the solid bleaching product is oven-dried at 60°C for 5 hours until dry

Alkalization

In the alkalization process, 2.5 g of bleached sample was added to 5 mL of 30% w/v NaOH solution. It was mixed in an Erlenmeyer flask and 50 mL of 2-propanol was added. It was stirred with a magnetic stirrer at a temperature of 25ºC for 24 hours, then the alkalization results were filtered.

Carboxymethylation

In the carboxymethylation process, 3 g of MCA and 12 mL of 2-propanol were added to the alkalization product. Then, it was filtered and soaked in 150 mL of methanol. The carboxymethylation product is neutralized using CH_3COOH to a pH of 6–7. Next, it is washed with 96% ethanol three times and dried in an oven at 60°C for 24 hours. During the carboxymethylation stage, variations in temperature and time affect the DS of carboxymethyl cellulose. Variations of the carboxymethylation reactions are crucial to optimize the efficiency of substitution, since higher temperature and longer reaction time generally increase the reactivity of cellulose but may also lead to side reactions that reduce product quality. Therefore, determining the optimal conditions is essential to obtain CMC with a stable structure, high solubility, and desirable functional properties.

Table 1 Variations in Carboxymethylation reaction

Run	Content (%)	Temperature
1	2	35
2	2	45
3	2	55
4	3	35
5	3	45
6	3	55
7	4	35
8	4	45
9	4	55

Characterization

Analysis of chemical composition

The compositional analysis of the pineapple leaves feedstock was performed, using The National Renewable Energy Laboratory (NREL) method followed by monosaccharides analysis using High-performance liquid chromatography (HPLC). Pineapple leaves was sun-dried and washed to obtain 10% moisture content and then cut into 0.6–0.8 cm in length. For analytical analyses, pineapple leaves was ground to 40–60 mesh by a grinder. Cellulose, hemicellulose, and lignin of pineapple leaves were analyzed. The sulfuric acid hydrolysis process method was used to determine acid-insoluble lignin content. First, oven-dried 1.0 g OPEFB was reacted with 72% sulfuric acid for 2.5 hours and diluted with distilled water to 4%. It was then hydrolyzed at 121°C for 1 hour. Secondly, the residue was filtered and weighed, the solid was acid-insoluble lignin.

For acid-soluble lignin, it was determined using UV spectrophotometer at 205 nm of the filtrate. Cellulose and hemicellulose were determined from glucose and xylose contents by HPLC. Aminex HPX-87H as column and mobile phase 5 mM H_2SO_4 at a rate of 0.6 mL/min was used for HPLC. Furthermore, a Waters 2414 refractive index (RI) detector with a temperature oven set at 40 °C and 65 °C for the column input and output, respectively, was used.

RESULT AND DISCUSSION

Synthesis of Pineapple Leaf Cellulose

The process of synthesizing cellulose from pineapple leaves has been successfully carried out, which involves two stages, namely delignification and bleaching. In this study, the delignification method involves the use of chemicals such as alkali to break the lignin bonds and separate them from the cellulose fibers. Lignin is a non-cellulose component found in plant cell walls along with cellulose and hemicellulose. the pineapple leaf samples are reacted with a 10% NaOH solution. The 10% NaOH solution serves to reduce the lignin content attached to the cellulose fibers. Based on the delignification reaction mechanism using an alkali solution, ester bonds are broken due to the addition of NaOH. To break the ester bonds in lignin, NaOH is used as a nucleophile, and hydroxyl ions (OH^-) attack hydrogen atoms to form H_2O. This process causes the lignocellulose structure to be rearranged, with the release of cellulose. The composition of the pineapple leaves feedstock was analyzed using the NREL method, followed by monosaccharide analysis using HPLC. The chemical compositions of raw material pineapple leaves were 51.59%, 7.12%, and 6.56% for cellulose, hemicellulose, and total lignin, respectively is presented in Table 1.

Table 2 Chemical composition of pineapple leaves

Pineapple Leaves Sample	Cellulose (%)	Hemicellulose(%)	Lignin(%)
Raw Material	42.94	8.59	25.14
Delignification	42.10	7.74	18.45
Bleaching	51.59	7.12	6.56

In the component analysis, there was a significant decrease in lignin content during the bleaching process to 6.56%. The bleaching process was carried out to increase the purity of cellulose, which aimed to whiten the sample by removing the color pigments contained in the pineapple leaf sample by adding a bleaching agent in the form of H_2O_2. CMC is produced by modifying cellulose through two main stages alkalization and carboxymethylation. The alkalization process is carried out to activate the substitution of carboxymethylation reagents into the cellulose structure and develop the cellulose structure. The development of the cellulose structure occurs due to the breaking of hydrogen bonds. Carboxymethyl cellulose (CMC) synthesized from pineapple leaf cellulose produces a fine white powder.

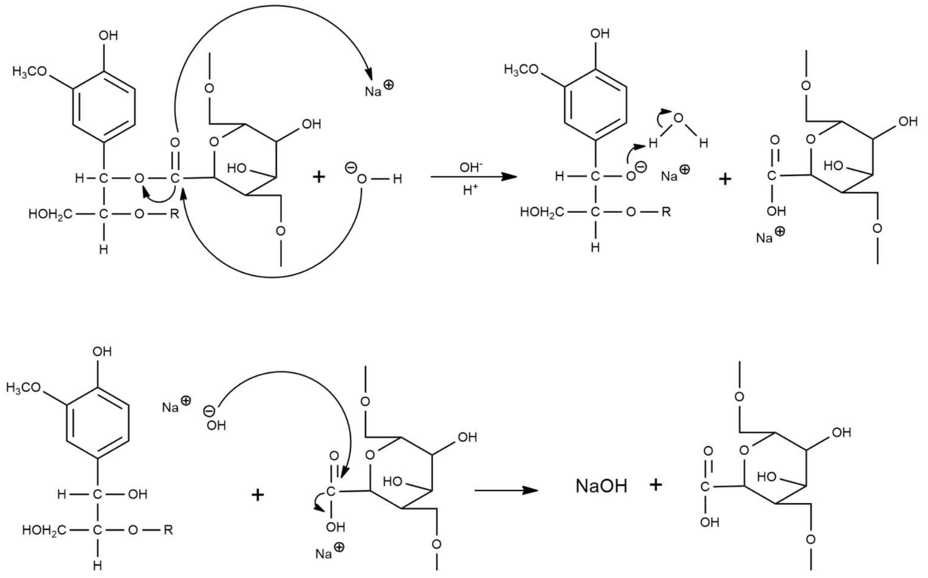

Figure 2 Mechanism of Breaking the Bond Between Lignin and Cellulose using NaOH

Based on the delignification reaction mechanism using an alkaline solution, ester bonds are broken due to the addition of NaOH. To break the ester bonds in lignin, NaOH is used as a nucleophile, and hydroxyl ions (OH-) attack hydrogen atoms to form H_2O. This process causes the lignocellulose structure to be rearranged, releasing cellulose. The bleaching process aims to dissolve and remove residual lignin compounds that can cause discoloration. This process uses H_2O_2 in a basic environment. The higher the pH of the solution, the more anion groups (HOO^-) are continuously formed. This can accelerate the reaction between the anion groups (HOO^-) and the chromophore groups in lignin, resulting in a faster bleaching process. The bleaching process using H_2O_2 can be seen in the following mechanism:

$$HOOH + HO^- \longleftrightarrow HOO^- + H_2O \quad (1)$$

The bleaching process causes lignin to be reduced and the size of the lignin structure to shrink. After bleaching, the cellulose is neutralized again to obtain a balanced pH before drying. This CMC is water-soluble, a characteristic that is important for ensuring its effectiveness as a thickening or stabilizing agent. The acidity level or pH greatly affects the stability and characteristics of CMC during storage. According to SNI 06-3736-1995, good-quality CMC has a pH standard of Grade I within the range of 6.0–8.0 and Grade II within 6.0–10.0. This pH testing is conducted by dissolving the CMC sample in distilled water, then measuring it using pH paper. A pH within the optimal range not only meets quality standards but also ensures product stability, consistent viscosity, and optimal gel-forming ability when applied in various products. The degree of purity and structural modification of cellulose strongly influences the functional quality of CMC. The successful reduction of lignin and hemicellulose not only improves the color and appearance of the final product but also enhances the accessibility of hydroxyl groups, which are the main reactive sites for carboxymethylation. A higher availability of these reactive sites increases the degree of substitution (DS), which directly correlates with the solubility, viscosity, and water-binding capacity of CMC. This characteristic is particularly important when CMC is intended for applications that demand high stability and uniform dispersion in aqueous systems.

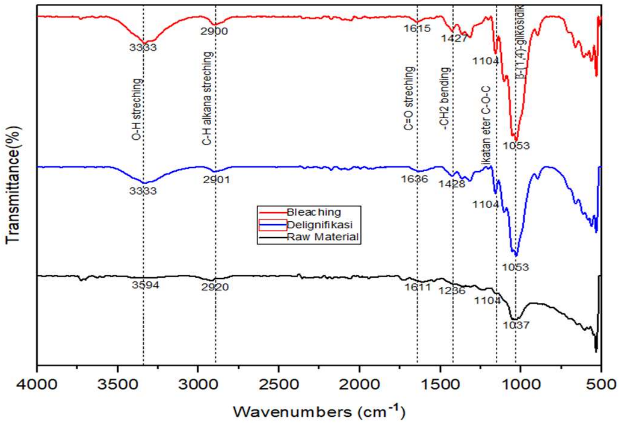

Figure 3 ATR-IR Spectrum of Raw Materials, Delignification and Bleaching

Based on the spectrum displayed, in the wavelength range of around 1000 cm^{-1} (1053-1104 cm^{-1}), there is a significant difference in peak intensity between the raw material, delignification, and bleaching samples. In this range, it is observed that the peaks in the samples after bleaching (red curve) and delignification (blue curve) have higher intensities compared to the raw material (black curve). The O-H, C-H, and C-O-C functional groups are the primary groups of cellulose[11]. This can be explained because the peaks in the 1053–1104 cm^{-1} range are characteristic of the C-O-C vibrations of the glycosidic bonds in cellulose[12].

Furthermore, the physicochemical properties of the synthesized CMC, such as viscosity, water-holding capacity, and pH stability, determine its suitability across different industrial applications. In the food industry, CMC functions as a stabilizer and thickener in beverages, sauces, and dairy products, while in pharmaceuticals it serves as a binder or disintegrant in tablet formulations. Its eco-friendly origin from pineapple leaf waste also adds value by supporting sustainable material development and reducing agricultural waste. Therefore, the optimization of bleaching, alkalization, and carboxymethylation processes is essential to produce CMC that not only complies with quality standards but also meets industrial demands for functionality and sustainability.

Synthesis of Carboxymethyl Cellulose (CMC)

Carboxymethyl cellulose is a modified cellulose compound that has been widely used in the food, pharmaceutical, textile, and cosmetics industries, indicating the potential for further development of CMC[13]. The physical and chemical properties of CMC differ significantly from those of native cellulose due to structural modifications through the carboxymethylation process. CMC production is the result of cellulose modification through two main stages of the process, namely alkalization and carboxymethylation. the alkali treatment process is carried out to activate the substitution of carboxymethylation reagents into the cellulose structure and to develop the cellulose structure. this development of the cellulose structure occurs due to the breaking of hydrogen bonds in the cellulose structure. if the alkali treatment is carried out properly, the carboxymethylation process will also proceed smoothly, as evidenced by the degree of substitution.

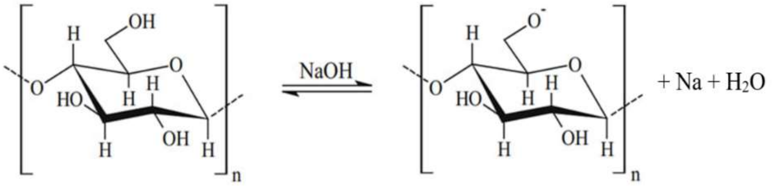

Figure 4 Alkalization Reaction

The hydroxyl groups (-OH) in cellulose are deprotonated to form alkoxides (O^-) with Na^+ ions from NaOH as counterions, producing water (H_2O) as a byproduct. This alkalization process is a crucial initial step in CMC synthesis because it enhances the nucleophilicity of the cellulose hydroxyl group, enabling the substitution reaction with monochloroacetic acid ($ClCH_2COOH$) in the subsequent carboxymethylation step. The hydroxyl groups (-OH) in cellulose are deprotonated to form alkoxides (O^-) with Na^+ ions from NaOH as counterions, producing water (H_2O) as a byproduct. This alkalization process is a crucial initial step in CMC synthesis because it enhances the nucleophilicity of the cellulose hydroxyl group, enabling the substitution reaction with monochloroacetic acid ($ClCH_2COOH$) in the subsequent carboxymethylation step. The efficiency of the alkalization step strongly influences the degree of substitution (DS) and overall yield of CMC. Insufficient alkalization may result in fewer reactive alkoxide sites, leading to incomplete substitution and lower solubility of the final product. On the other hand, excessive alkalinity can cause degradation of cellulose chains, reducing molecular weight and negatively impacting viscosity. Therefore, optimizing NaOH concentration, reaction time, and temperature during this stage is essential to ensure the formation of reactive intermediates while maintaining the structural integrity of cellulose for effective carboxymethylation.

The carboxymethylation process is carried out to substitute the hydroxyl group in each anhydrous glucose unit using a carboxymethylation reagent in the form of monochloroacetic acid (MCA) to substitute the hydroxyl group. In this process, the hydroxyl group is replaced with a carboxymethyl group, resulting in the formation of CMC [14]. Factors that can influence the characteristics of CMC include the type and composition of reaction solvent, alkalinity, chloroacetate concentration, reaction time, and reaction temperature. The efficiency of the carboxymethylation process is generally evaluated based on the degree of substitution (DS), which indicates the average number of hydroxyl groups substituted by carboxymethyl groups in each anhydroglucose unit of cellulose. A higher DS value correlates with better solubility, increased viscosity, and improved performance of CMC in aqueous systems. Conversely, a low DS may result in poor water solubility and limited functional properties. Therefore, controlling reaction parameters such as NaOH concentration, MCA dosage, and temperature is critical to ensure an optimal balance between substitution efficiency and product quality.

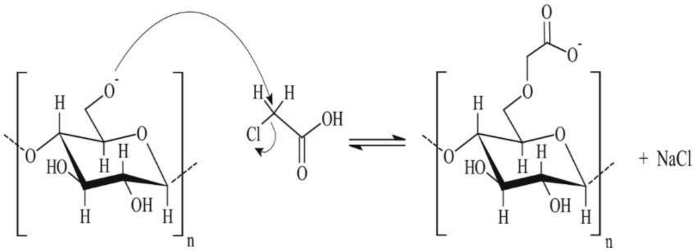

Figure 5 carboxymethylation Reaction

In addition to DS, the distribution of carboxymethyl groups along the cellulose chain also affects the final properties of CMC. A uniform substitution leads to stable viscosity and better gel-forming ability, while uneven substitution may cause phase separation or irregular dissolution behavior. Characterization methods such as Fourier Transform Infrared Spectroscopy commonly used to confirm structural modifications and evaluate morphological changes in the synthesized CMC. These analyses provide essential insights into the success of the reaction and the potential applicability of the product in food, pharmaceutical, and industrial formulations.

Structural characteristics

Functional group analysis of CMC is the result of a reaction between alkalized cellulose and NaOH, creating an alkaline environment, which is then reacted with MCA dissolved in 2-propanol at varying temperatures (35°C, 45°C, and 55°C) for 2, 3, and 4 hours, respectively. The samples are then soaked in 96% ethanol and dried. The resulting CMC is a white powder, In the ATR-IR analysis of the conversion of cellulose to CMC, changes in the spectrum can be observed through several characteristic peaks, indicated by the appearance of peaks from the C=O carboxyl group, peaks indicating C-O-C bonds from the ether chain ($-OCH_2COOH$), peaks indicating C-H vibrations, and peaks representing the -OH group. The results showed that the temperature and duration of the carboxymethylation process were two crucial factors in determining the optimal conditions and producing varying CMC characteristics. This substitution occurs at carbon atoms C-2, C-3, and C-6 of the glucose unit, which directly affects the chemical environment around the C-O-C bond.To discuss the changes of functional groups in lignin before and after modification, it was characterized by infrared spectroscopy. A typical lignin ATR-IR spectrum is presented in Figure 3. The ATR-IR analysis is used to record the change in chemical bonding after chemical modification. Figure 3 presents the chemical structure of lignin before and after modification It shows that unmodified lignin has three dominant peaks of the adsorption bands. The peaks at around 3300 cm^{-1}, 2900 cm^{-1}, and 1580 cm^{-1} were assigned to the stretching of hydroxyl group (O-H), symmetric and asymmetric C-H stretching vibration of methoxyl ($-OCH_3$), and aromatic ring skeleton stretching vibration, respectively.

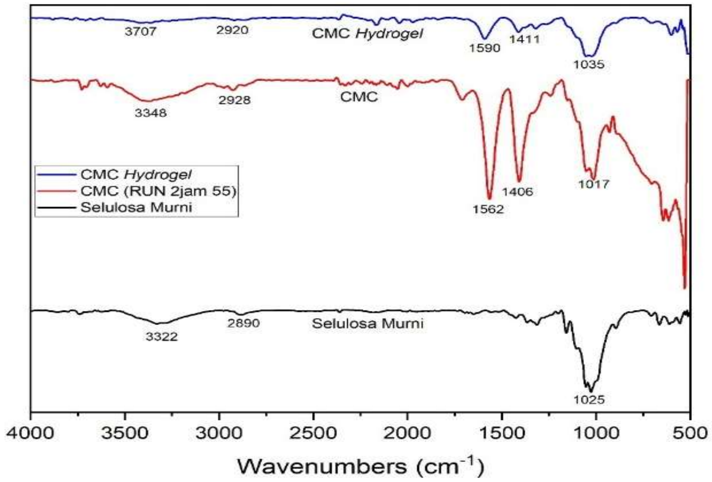

Figure 6 ATR-IR spectrum of pure cellulose, CMC, and CMC hydrogel

Factors influencing the decrease in transmittance in CMC hydrogel include the presence of water bound to hydrophilic groups (-OH and -COO-). These hydrogen bonds cause changes in the vibration of functional groups, resulting in increased absorption of IR light and a decrease in transmittance, which makes the peak appear smaller. The presence of crosslinking forms a 3D network structure. This structure affects IR radiation absorption and causes shifts or weakening of specific peaks [15]. Water molecules can disrupt the original functional group vibrations of CMC, causing the spectrum to change and transmittance to decrease. The decrease in transmittance also indicates successful incorporation of water molecules within the hydrogel matrix, which is closely related to its swelling behavior. Hydrophilic functional groups, particularly carboxymethyl and hydroxyl groups, attract and retain water molecules through hydrogen bonding. This interaction not only influences the IR spectrum but also plays a key role in determining the water absorption capacity, gel stability, and mechanical properties of the hydrogel. A higher degree of substitution (DS) generally results in more hydrophilic sites available, thereby enhancing water uptake and further contributing to spectral changes observed in ATR-IR analysis.

Additionally, the crosslinked 3D network structure enhances the hydrogel's mechanical strength and stability but at the same time restricts the mobility of polymer chains. This restriction modifies the vibrational modes of functional groups, which may be observed as shifts or broadening of characteristic peaks in the IR spectrum. Such spectral modifications provide indirect evidence of the formation of intermolecular interactions between CMC chains and the crosslinking agent, validating the success of the hydrogel formation process.

Furthermore, the reduction in transmittance can serve as a useful analytical marker for evaluating hydrogel quality and performance. By correlating IR spectral changes with swelling ratio, gel fraction, and mechanical stability, a comprehensive understanding of structure–property relationships in CMC hydrogels can be achieved. This correlation is essential for tailoring hydrogel properties according to specific applications, such as drug delivery, wound dressing, or agricultural water-retention agents, where both structural integrity and functional responsiveness to water are critical.

Determination of Degree of Substitution (DS)

Degree of Substitution (DS) is a measure that indicates how much a particular functional group has replaced hydrogen atoms in a polymer molecule. In ATR-IR analysis, DS is used to measure how much the carboxymethyl (COO-) group has replaced hydrogen atoms in cellulose. The higher the DS value, the more carboxymethyl groups are bound to cellulose, thereby increasing its hydrophilic properties. The equation used to calculate DS is:

$$\text{DS} = \frac{C{=}O\ group\ absorption\ intensity}{C{-}H\ group\ absorption\ intensity}$$

Degree of substitution is an important parameter in the characterization of polymers, especially modified cellulose polymers. ATR-IR analysis is an effective method for determining DS, as it provides both qualitative and quantitative information about the functional groups present in the sample. The optimal DS for hydrogel production ranges from 0.4 to 1.2, according to SNI 06-3726-1995. The degree of substitution is a major factor in the formation and solubility of CMC in water[16]. The DS value of CMC is influenced by several factors, including the alkalization process, temperature variations, and the duration of carboxymethylation, which all affect the DS of CMC. The higher the temperature used during the carboxymethylation process, the higher the DS. However, when the reaction temperature is too high, some of the hydroxyl groups that should react with the carboxymethylation reagent instead interact with the released water molecules, forming H_2O. As a result, the number of -OH groups available for substitution with carboxymethyl groups decreases, leading to a reduction in the degree of substitution (DS) in the CMC product[17]. The degree of substitution in organic molecules is related to the number of hydrogen atoms replaced by other groups in the main structure. This has a significant effect on the ATR-IR spectrum, particularly on the intensity and peak area of the C=O and C-H absorption groups.

This reaction explains the initial stage of CMC reacting with monochloroacetic acid under basic conditions (NaOH) and 2-propanol solvent. CMC, which has excess hydroxyl (-OH) groups, reacts with $CaCl_2$ solution at room temperature. Calcium ions (Ca^{2+}) in the $CaCl_2$ solution interact with the carboxyl groups (-COO-) on the CMC chains. Each Ca^{2+} ion can bond with two or more carboxyl groups, forming cross-links between CMC chains. The more cross-links formed, the more stable the structure becomes. The interaction between Ca^{2+} ions and the carboxyl groups of CMC results in the formation of ionic bridges that connect adjacent polymer chains. This crosslinking mechanism reduces the mobility of individual CMC chains, thereby enhancing the rigidity and mechanical stability of the resulting material. Such ionic crosslinks are nature meaning that they can be disrupted in the presence of strong chelating agents or competing cations. This property is advantageous for applications where controlled swelling or degradation of the material is desired, such as in drug delivery or biomedical hydrogels.

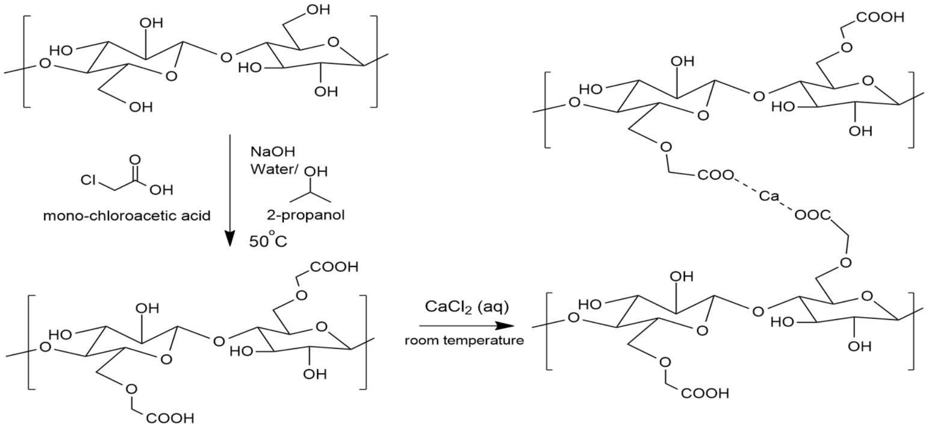

Figure 7 Crosslink $CaCl_2$

Furthermore, the degree of crosslinking directly influences the physicochemical characteristics of CMC, including water absorption, swelling capacity, and gel strength. A higher concentration of $CaCl_2$ typically results in denser crosslinking, producing a hydrogel with lower swelling capacity but greater mechanical integrity. Conversely, a lower crosslinking density provides higher swelling ability but reduced structural stability. Therefore, optimization of Ca^{2+} concentration is essential to balance flexibility, water retention, and strength according to the intended application of the CMC-based material. In addition, the crosslinking process significantly affects the spectroscopic and structural features of CMC. Fourier Transform Infrared analysis usually shows peak shifts or intensity changes in the carboxylate region, indicating ionic interactions with Ca^{2+}.

The C=O group represents the carboxyl group in CMC, while the C-H group represents the methyl group in CMC. Both ratios indicate the efficiency of carboxymethyl substitution in the cellulose structure, which are important indicators of the quality and characteristics of the resulting CMC. The results of the degree of substitution (DS) for carboxymethylation variations in Table 4.5 show that the interaction between temperature and carboxymethylation time affects the DS of CMC. The results indicate that the optimal time for the carboxymethylation process is 2 hours, yielding the highest DS value compared to other time variations. At a duration of 2 hours, the DS values ranged from (1.06–1.24), which were consistently higher than those at 3 hours (DS 0.56–0.74) and 4 hours (DS 0.48–0.85). The DS results for the 3-hour and 4-hour time variations were not significantly different. In terms of temperature variation, there is a tendency for DS values to increase at 45°C and 55°C. Meanwhile, at 3-hour and 4-hour durations, increasing the temperature from 35°C to 45°C results in a significant increase in DS. This indicates that 45°C could be an optimal point for certain process conditions. DS value set for CMC products is 0.4-1.2. The DS produced in the chemical modification process can be adjusted to suit specific application requirements. Precise control of the DS value results in materials with optimal characteristics for a wide range of applications, from agriculture, pharmaceuticals, textiles, and food to advanced biomaterials

CONCLUSION

This research results successfully synthesized cellulose from pineapple leaf waste through the processes of delignification, bleaching, alkalization, and carboxymethylation. The delignification and bleaching stages were effective in increasing the purity of cellulose to 51.59%. Furthermore, the alkali treatment process and variations in time (2 hours, 3 hours, 4 hours) and temperature (35°C, 45°C, 55°C) variations in the carboxymethylation process produced ATR-IR peaks of carboxymethyl cellulose, with the presence of carbonyl groups (C=O) detected at wavenumbers 1562–1604 cm^{-1}, which are the main characteristics of CMC, confirming the success of the carboxymethylation process. The highest peak intensity was obtained from the 2-hour 55°C variation, indicating that the basic cellulose structure had been influenced by MCA, with some hydroxyl (-OH) groups in the cellulose structure replaced by carboxymethyl (-CH_2COOH) groups. Based on the research results, hydrogel characterization showed that samples with variations in temperature and carboxymethylation time produced hydrogels in the form of transparent to bluish-white granules. Significant differences were observed in the hydrogel results. Pure cellulose without carboxymethylation treatment cannot form hydrogels because the structure of pure cellulose has strong hydrogen bonds between molecules and is hydrophilic, making it difficult to expand and absorb water. When pure cellulose is dripped into a crosslinking agent such as CaCl2 without carboxymethylation, pure cellulose has limitations in forming hydrogels. ATR-IR analysis results confirm the success of the carboxymethylation process and the formation of crosslinks in the hydrogel structure.

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