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PROVISION OF CARBOXYMETHYL CELULLOSE MATERIAL BASED ON DURIAN SEED POWDER

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ABSTRACT

Carboxymethyl Cellulose (CMC) is a water-soluble derivative compound. Synthesis of this CMC includes the stages of cellulose alkalinization and carboxymethylation reactions. Durian seed flour is reacted with sodium hydroxide in isopropanol and sodium chloroacetate as a solvent. This study aims to determine the effect of temperature, carboxymethylation reaction time, volume variation of sodium hydroxide, and weight of sodium chloroacetate on the degree of substitution of resulting CMC. The results are shown that the greater the volume of 20%NaOH solution added and the longer carboxymethylation reaction time, the higher the carboxymethylcellulose Substitution Degree (DS) was produced. The most significant degree of substitution was the addition of 10 ml of 20%NaO Hand the reaction time lasted for 2 hours, namely 0.61.

Keywords: alkalination, carboxymetylation, celullose, degree of substitution.

INTRODUCTION

Carboxymethyl Cellulose (CMC) is an anionic polysaccharide, linear long-chain, water-soluble cellulose derivate [1], [2]. CMC is prepared by the reaction of monochloroacetic acid (MCA) with alkali cellulose [2]. CMC productions are usually based on cellulose from raw cellulose, cotton linters, fibres, wood, and pulp [2], [3]. The study of the synthesis of CMC based on grain cellulose has not been carried out. Durian seeds contain cellulose so it has the potential to be used as the material for making CMC. CMC production based on durian seeds does not need to go through the delignification stage so the powder obtained is maximized and the process is shorter. Durian seeds contain about 10% of the lignin in the seed coat [4], so the seed coat will be separated first from the durian seed.

The properties of CMC are dependent on the manufacturing process. The manufacture of CMC involves the carboxymethylation reaction of cellulose. In the carboxymethylation process, the cellulose becomes increasingly coarse, increasing the surface area of the reaction. The increase in the surface area of the reaction results in monocloroacetate molecules colliding more frequently with cellulose so that the resulting DS Carboxymethyl Celluloses is higher [5]. The degree of substitution (DS) is the number of hydroxyl groups that are replaced by Carboxymethyl Ceullose synthesis. The DS value determines the use of CMC. Theoretically, the maximum DS obtained from the Carboxymethyl Cellulose production is 3. However, commercial CMC has a DS of 0.4-1.5. DS of Carboxymethyl Ceullose used in food products usually has a range of 0.2-1.5 [6]. Carboxymethyl Cellulose with DS above 0.7 will dissolve entirely in water [5].

Synthesis of CMC from durian seed powder involves alkalization and carboxymethylation reactions. In this process, cellulose is dissolved in isopropanol, and sodium hydroxide (NaOH) is added because it is more reactive than other alkalis. NaOH is a powerful solvent for cellulose and also a suitable homogeneous reaction medium for the etherification of cellulose [7]. In the carboxymethylation reaction, there is a substitution of the hydroxyl group in cellulose with carboxymethyl group of sodium monochloro acetate. Substituent groups are found at C_2, C_3, and C_6, of D-glucopyranosyl units [8]. In the carboxymethylation reaction, the reactivity of each C group on cellulose is different from one another. The C6 chains is the most reactive, while the C3 chains are the least reactive [7]. In addition to the alkalization reaction and the carboxymethylation reaction, the synthesis process of Carboxymethyl Cellulose also occurs due to the formation of sodium glycolate [2].

In general, Carboxymethyl Cellulose synthesis research chooses isopropanol as a solvent because isopropanol provides a high DS value of 0.72 [9]. The synthesis process of Carboxymethyl Cellulose, reactant, and temperature of carboxymethylation reaction affect the degree of substitution of CarboxymethylCellulose produced [10]. In this study, sodium chloroacetate acts as a reactant in the carboxymethylation-reaction of Carboxymethyl Cellulose. The use of sodium chloroacetate and NaOH must be at an appropriate ratio to produce the optimal degree of substitution. Excess sodium chloroacetate resulted in a sodium chloroacetate reaction with NaOH to form sodium glycolate so that CM purity was reduced. In addition, the carboxymethylation temperature also has an influence on the degree of substitution of CMC. The higher the temperature of the carboxymethylation reaction, the higher the DS obtained. The increasing reaction temperature will be more reactive for sodium chloroacetate to attack cellulose. But at a certain point, with increasing temperature, the resulting degree of substitution of CMC decreases. This is because temperatures that are too high might be intermolecular elimination among hydroxyl groups of neighbouring chains giving rise to cross-linking by ether linkages, thus decreasing the sites of -OH groups for carboxymethylation [10].

MATERIAL AND METHODS

Durian seeds are obtained from durian that are on Glugur bypass Street, Medan. The chemicals used were Isopropanol, Acetic acid, 5% Calcium hydroxide, Sodium hydroxide, and Sodium chloroacetate, Methanol and Ethanolobtainedfrom CV Rudang Jaya Medan, Sodiummetabisulfitewasobtainedfrom T&T Chemical Bandung, Sodium chloroacetate was obtained from CVAneka Chemical Medan.

Raw Material Preparation

Durian seeds are rinsed with distilled water, removed from the skin, the soaked with 5% calcium hydroxide and 5% sodium metabisulfite solution for 24 hours. The durian seed meat is smoothed and dried in the sun, then sieved with a sieve size of 70-100 mesh[11].

Synthesis of CMC

The initial stage (Alkalination) of durian seed flour was treated with 20% sodium hydroxide with a ratio of 1: 3(w/v) in 1:20(g/v). Isopropanol solvent lasts for 1 hour [2], [3]. The carboxymethylation stage was reacted with sodium chloroacetate, which was varied for 1.5 hours. The solution was allowed to stand to form 2 phases, and the solid phase was dissolved in methanol and allowed to stand for 12 hours, then neutralized using acetic acid. The solid was filtered and washed using 96% ethanol and methanol [2], [3], then dried in an oven at 50°C for 5 hours and placed in a desiccator for 24 hours.

Degree of Substitution Analysis

CMC degree of substitution analysis was appointed to ASTM D 1439 and was controlled in the process of Chemical Industry Laboratory, Universitas Sumatera Utara. The degree of substitution is defined using:

$$A = \frac{BC - DE}{F} \quad (1)$$

$$\text{Degree of substitution} = \frac{0.162 \text{ x A}}{1 - (0.058 \text{ x A})} \quad (2)$$

Where:

A = mili-equivalent of acid consumption (mL.M.gram^{-1})
B = sodium hydroxide volume (mL)
C = Sodium hydroxide concentration (M)
D = hydrochloric acid volume (mL)
E = hydrochloric acid concentration (M)

Fourier Transform Infra-Red (FTIR)

FTIR analysis was finalized at the Belawan Custom Laboratory Office, Medan, using the 10th series Thermo Scientific Nicolet TM iS TM Spectrometer with a current of 3.2 A, a voltage of 100-240 VAC frequency of 47-63 Hz produced by Thermo Fisher Scientific.

Scanning Electron Microscopy-Energy Diffraction X-Ray (SEM-EDX)

SEM-EDX analysis was finalized at the Integral Laboratory, Dipenogoro University, using the JSM6510LA and JED2300 devices with a voltage of 20 kV and a magnification of 3000 times.

RESULTS AND DISCUSSIONS

Fourier Transform Infra-Red (FTIR)

The purpose of the characterization of Fourier Transform Infra-Red (FTIR) is to identify the functional groups of commercial CMC, CMC Durian seed powder before and after purification which can be seen in Figure-1.

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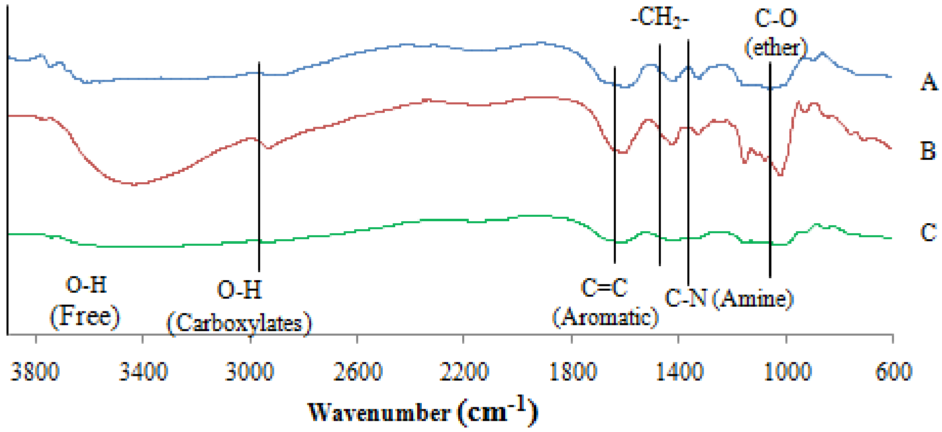

Functional Group	Description [12]	Wavenumber(cm^{-1})
3650-3600	O-H(free)	
3450-2400	O-H(Carboxylates)	
1680-1600	C=C(Aromatic)	
1450-1400	-CH2-	
1350-1000	C-N(Amine)	
1300-1000	C-O(Ether)	

Figure-1. FTIR analysis results for commercial CMC (A), CMC durian seed powder before (C), and after purification (C).

Commercial CMC has a degree of substitution of 1.12, and CMC of durian seeds has a degree of substitution of 0.61. Figure-1 shows there is an O-H group (free) wavenumber 3600.90 in the commercial CMC(A); O-H (carboxylate) group wavenumber 2921.59; group C=C (aromatic) wavenumber 1604.27; the -CH2-group wavenumber 1423.09; the C-O group (ether) wavenumber 1063.84. Aromatic groups and ether groups represent groups of cellulose. The carboxylate group and the -CH2-group represent a carboxymethyl group [13].

In Figure-1, it can be seen that the CMC of durian seeds before purification (B) also has an O-H (free) group which does not bind to any C atoms with wavenumber 3431.98; O-H (carboxylate) group wavenumber 2928.76; group C=C (aromatic) wavenumber 1606.27; the -CH2-group wavenumber 1423.27; the group C-N (Amine) wavenumber 1329.20 and the C-O group (ether) wavenumber 1156.60. Carboxylate groups, aromatic groups, -CH2- groups, and ether groups are the same group as commercial CMC. The presence of this group indicates that hath the power has been synthesized into CMC [13].

In Figure-1, it can be seen that the CMC of durian seeds after being purified (C) there is also has an anO-H (free) group which does not bind to any C atoms with wavenumber 3422.1; O-H (carboxylate) group wavenumber 2931.32; group C=C (aromatic) wavenumber 1607.77; the -CH2- group wavenumber 1422.19; and the C-O group (ether) wavenumber 1156.70. Carboxylate groups, aromatic group, -CH2- groups, and ether groups are the same group as commercial CMC. The presence of this group indicates that the power has been synthesized in to CMC [13].

O-H groups (free) found in commercial CMC (A) and CMC durian seed powder (B) showed that there was still water content. The difference between commercial CMC and CMC from durian seeds in the presence of C-N groups (amines), and the presence of amine group in CMC from durian seeds because durian seeds are a source of cellulose-containing protein [14]. Whereas in commercial CMC, the source of cellulose used is pulp so that there are no amine groups[2].

Degree of Substitution

The purpose of the degree of substitution is to analyze the effect of the carboxymethylation reaction temperature on the degree of CMC substitution of durian seed, 2 g of sodium chloroacetate was used.

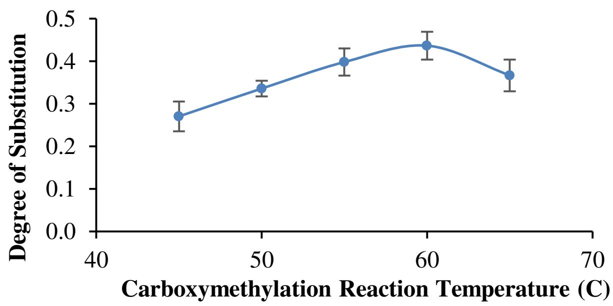

Figure-2. Effect of Carboxymethylation reaction on the degree of CMC substitution of durian seeds.

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In Figure-2, it can be seen that the higher the temperature of the carboxymethylation reaction, the degree of substitution will increase to the maximum and be reached at 60°C (0.44), after which the degree of substitution will decrease. The rise in the degree of substitution is due to the exchange of groups between Na-Cellulose and carboxymethyl groups of sodium chloroacetate. With the rising temperature, molecules will move faster so that sodium chloroacetate and cellulose molecules will rub against each other more often. The decrease in the degree of substitution is because when the temperature passes 60°C may be due to the cellulose degradation where the chemical elimination of water from cellulose originates primarily from an intramolecular elimination [2] In a study conducted by Jia *et al*. (2016), degree of substitution of CMC has increased with increasing temperature of carboxymethylation reaction. However, when the temperature of carboxymethylation reaction is above 65°C, the degree of substitution of CMC has decreased.

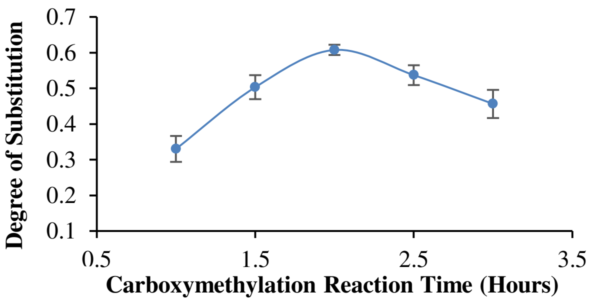

Figure-3. Effect of Carboxymethylation time on the degree of CMC substitution of durian seeds.

In Figure-3, it can be seen that the longer the carboxymethylation reaction time, the higher the degree of CMC substitution produced. The Maximum degree of substitution obtained at a reaction time of 2 hours is 0.61. According to the reaction mechanism, the higher degree of substitution is due to substitution reaction. The addition of the reaction time of 2.5 hours and 3 hours causes a decrease in the degree of substitution. According to the reaction mechanism, longer contact time causes saturated sodium chloroacetate to react with sodium cellulose resulting in d a decreasing degree of substitution. They were supported by previous research where Yeasmin and Ibrahim, 2015, varied the carboxymethylaton time from 1 to 6 hours. The best value for the degree of substitution is 2.5 hours.

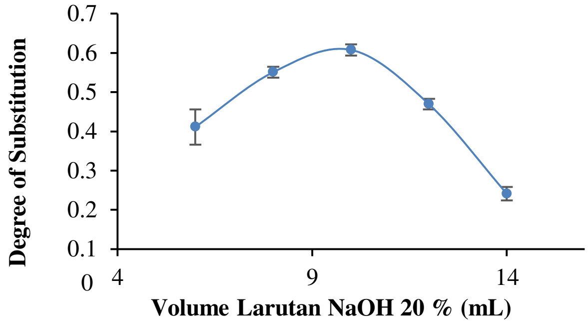

Figure-4. Effect of volume variation of 20% NaOH on the degree of CMC substitution of durian seeds.

Figure-4 showed that the more volume of 20% NaOH solution added, the higher the degree of substitution of CMC is produced. The maximum degree of substitution obtained at the addition of 10 ml 20% NaOH is 0.61. This is because the concentration of NaOH plays a vital role in the synthesis of CMC and its by-products. According to the reaction mechanism, by increasing the volume of 20% NaOH, more OH groups can be substituted with sodium chloroacetate and produce higher degree of substitution.

Then the degree of substitution decreased after the increase of 12 ml and 14 ml of 20% NaOH. High alkaline concentration is not better where higher concentrations of NaOH react with mono-chloroacetic acid and form sodium glycolic, according to reaction, resulting in the inactivity of mono-chloroacetic acid [2]. In previous research, where Jia *et al*. (2016) varied the NaOH dosage between 4g to 14g. The degree of substitution increases significantly when NaOH concentration is increased to 10g, after which it decreases slowly.

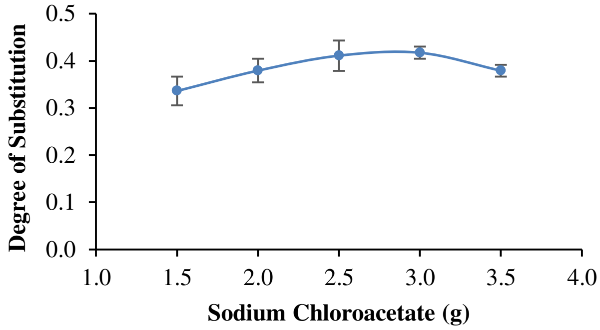

Figure-5. Effect of sodium chloroacetate wight variation on the degree of CMC substitution of durian seeds.

To analyze the weight variation of sodium chloroacetate against a degree of substitution of CMC from durian seeds, the carboxymethylation reaction was carried out at 55°C. As seed in Figure-5, the degree of CMC substitution of durian seed has raised (maximum 0.42) along with the addition of sodium chloroacetate by 1.5 to 3 g. at the rise of 3.5 g of sodium chloroacetate, the degree of substitution of CMC decreased [13]. The rise in degree of substitution occurs due to the exchange of groups between Na-cellulose that are substituted by the carboxymethyl group of sodium chloroacetate. More

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hydroxyl group in cellulose that is substituted by the carboxymethyl group of sodium chloroacetate, the degree of substitution increases. The addition of 3.5gr of sodium chloroacetate was caused by our action between NaOH and sodium chloroacetate to form sodium glycolate. According to Rachtanapun *et al.* (2012), in addition to the reaction of CMC formation during the CMC synthesis process, there is also a reaction to the formation of sodium glycolateand NaCl salts. This reaction occurs between NaOH, which is used during alkylation reaction with sodium chloroacetate [5].

XRD Characterization

The results of crystallinity testing using XRD on Commercial CMC and CMC from Durian Seed can be shown in Figure-6.

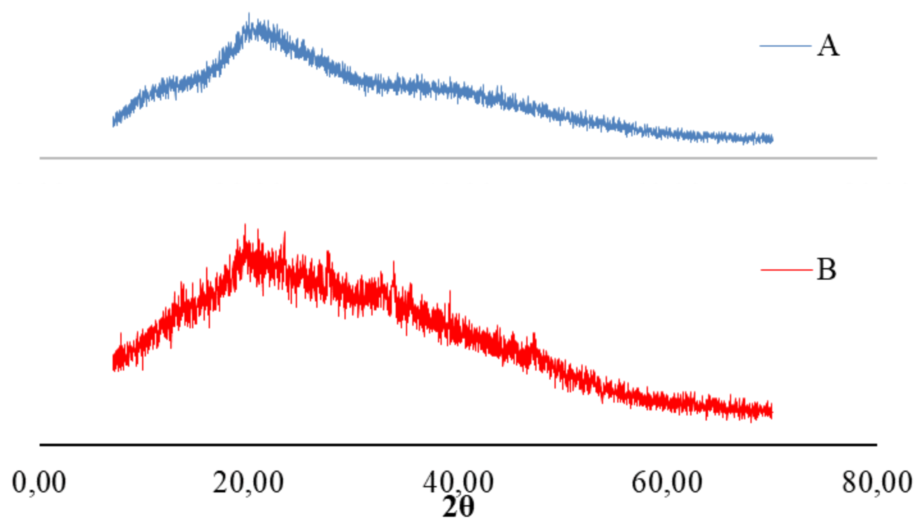


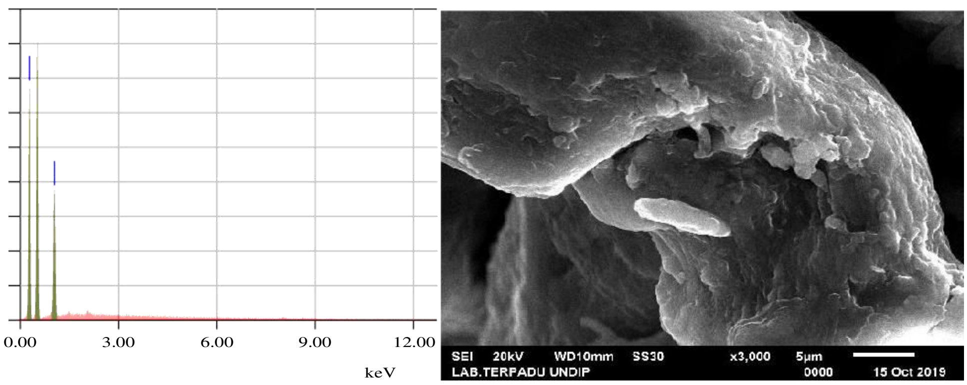
Figure-6. X-Ray (XRD) test result for commercial CMC (A) and CMC form durian seed (B).

Figure-6 shows that for commercial CMC (A) with a degree of substitution of 1.12, the crystallinity index of commercial CMC was 23.7%. For CMC with a degree of substitution of 0.61, the crystallinity index is 16.6%. The CMC crystallinity index can be calculated using the Segal method. According to Segal (1959), the crystallinity index can be calculated by comparing the intensity of the crystalline compound with the amorphous mixture of material [15]. The crystalline intensity (1002¬) of material can be seen from the highest peak in the XRD test result graph, while for the amorphous group, it is deenat2θ=18°C.

Commercial CMC has a greater crystallinity index than CMC from durian seeds. The carboxymethyl groups have a straighter structure than the O-H group. The carboxymethyl group is a hydrocarbon chain, and a straight hydrocarbon chain will increase the crystallinity index of the material [16]. The degree of substitution of CMC from durian seeds is more minor than commercial CMC. This indicates that there are fewer carboxymethyl group in CMC from durian seeds. The CMC crystallinity of durian seeds is lower because the CMC form durian seeds are fewer of carboxymethyl groups.

Scanning Electron Microscope Energy Dispersive X-Ray (SEM EDX) Characterization

The purpose of the characterization of Scanning Electron Microscope (SEM) is to find out how the morphology of Commercial CMC. The characteristics of SEM EDX from chicken eggshell powder can be seen in Figure-7.



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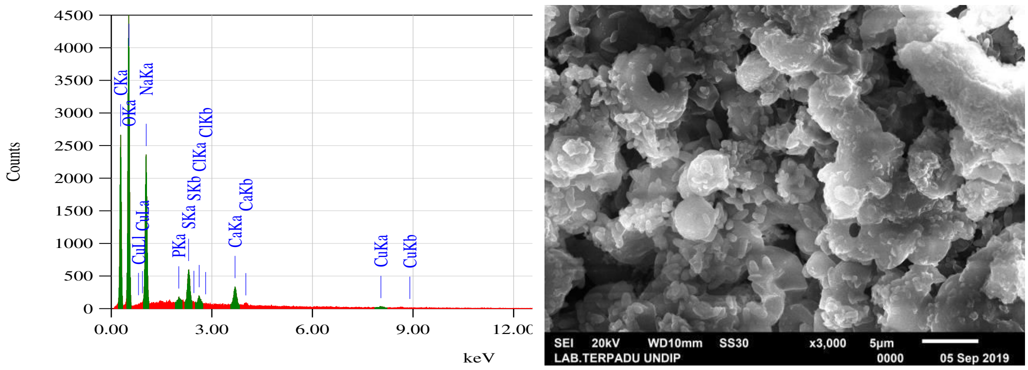
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.5250

Element	(keV)	Mass%	Sigma	Mol%	Compound	Mass%	Cation	K
C K	0.277	85.23	0.08	96.75	C	85.23	0.00	84.0412
O	3.81							
Na K	1.041	10.96	0.10	3.25	Na_2O	14.77	48.00	15.9588
Total		100.00		100.00				

Figure-7. Morphology and chemical composition of commercial CMC with a magnification of 3000times.

Figure-7. This shows that commercial CMC has irregularly shaped molecules, but some are cylindrical with a length of 7 μm. In Figure-7, it is also seen that the composition of commercial CMC consisting of elements commercial CMC is 85.23% carbon (C), 3.81 oxygen (O), and 10.96 sodium (Na). The presence of carbon (C) and oxygen (O) groups in the sample is because CMC is a cellulose derivative where cellulose is composed of the element carbon (C), oxygen (O), and hydrogen (H). Meanwhile, the presence of sodium (Na) group in form of an alkaline oxide (Na2O) is thought to have originated form NaOH, which is used in the CMC synthesis process.



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.5250

Element	(keV)	Mass%	SigmaMol%	Compound	Mass%	Cation	K	
C K	0.277	75.91	0.38	94.43	C	75.91 0.00	68.4292	
O		8.02						
Na K	1.041	10.94	0.16	3.56	Na_2O	14.7522.7820.4317		
PK	2.0130.23	0.05	0.06	P_2O_5	0.53 0.360.4633			
SK	2.3072.07	0.11	0.96	SO_3	5.17	3.09	4.4964	
Cl K	2.621	0.53	0.03	0.22	Cl	0.53	0.00	1.2764
Ca K	3.690	1.64	0.06	0.61	CaO	2.30	1.96	3.6835
Cu K	8.04 0.650.08 0.15	CuO	0.81	0.49	1.2196			
Total		100.00		100.00		100.00	28.68	

Figure-8. Morphology and chemical composition of CMC from durian seeds DS 0.61 Purity 99.99% with a magnification of 3000 times.

Figure-8 showed that the shape of the CMC molecule from durian seed is irregular, and there is a round shape. In Figure-8, it can be seen the CMC composition of durian seeds consists of 75.91% carbon elements, 8.02% oxygen, and 10.94% sodium. The presence of carbon (C) and oxygen (O) groups is because CMC is a cellulose derivative compound. Where cellulose is composed of the elements carbon (C), oxygen (O), and hydrogen (H). The presence of sodium (Na) atoms in the form Na2O is because the CMC synthesis process uses excess sodium hydroxide (NaOH). The element phosphorus (O) is 0.23% because durian seeds contain phosphorus (P). Calcium (Ca) held in CMC from durian seeds is also influenced by the use of calcium hydroxide(Ca(OH)2)in the durian seed pre-treatment stage [13].

CONCLUSIONS

The more volume of 20% NaOH solution added, the higher degree of substitution of carboxymethyl cellulose produced. The maximum degree of substitution obtained at the addition of 10 ml of 20% NaOH is 0.61. The longer the carboxymethylation reaction time, the higher the substitution degree of carboxymethyl cellulose produced. The highest degree of substitution lasted for a reaction time of 2 hours.

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