Variation of Alginate: Carboxymethyl Cellulose on Making Beads CMC from Cellulose of Corn Stalk

Anggun Pertiwi¹,* Eny Yulianti², Lilik Miftahul Khoiroh², Febi Yusniyanti²

¹ chemistry department, Sains and technology Faculty, UIN Maulana Malik Ibrahim, Malang, Indonesia, 65144
² chemistry department, Sains and technology Faculty, UIN Maulana Malik Ibrahim, Malang, Indonesia, 65144
*Corresponding Author. Email: angguncahya19@gmail.com

ABSTRACT
Synthesize CMC uses cellulose extracted from cornstalk waste. FTIR and XRD characterize CMC synthesize. Alginate: CMC (AC) beads made by dropping technique through the ionic gelation method with crosslinking CaCl₂ 3%. Fourier Transform Infra-Red (FTIR) to know the AC's function group, swelling test to know the swelling power, and SEM-EDX to see the surface characteristics. The optimum composition of AC composite beads was 1:2 based on beads' formation, the highest swelling power value 175.5%, and the diameter was 26.64%. The data FTIR AC showed that wave number at 819 cm⁻¹ indicates the presence of Ca-alginate linkage. The SEM-EDX of AC without CMC 1:0 showed a smooth surface, while the suracfer character of AC 1:2 is rough.

Keywords: alginate-carboxymethyl cellulose, beads, cornstalk

1. INTRODUCTION
In Indonesia, corn requirements always increase year to year. Nationally, the agriculture ministry states that along 2012-2016, east Java is on the first rank of the biggest corn producer for about 32.06%. All this time, corn utilization focuses on the seeds, while the other part, as stalk and cob, does not utilize maximally. As a result, be agriculture waste. According to [1][2], corn stalk contain of 42.6% cellulose, 8.2% lignin, 21.3% hemicellulose, and 9-11% is water. By containing cornstalk has a high potency to be modified, increasing the utility and economy.

Biopolymer composite from alginate and carboxymethyl cellulose is more effective on bead than flake form. It causes bead form has higher adsorption capacity and diffusion character [3], faster adsorption kinetics[4], and a more significant surface area[5]. Adsorption power depends on the composition. One of the biopolymers used to form bead is sodium alginate. Sodium alginate is a biodegradable and biocompatible material. It has high hydrophilicity and has an active site to bond with the multivalent cation hydroxyl group [6]. However, alginate has low stability so that alginate easily degradation terminally [7]. Therefore, utilization alginate must react as copolymerization with other materials as CMC. CMC has high hydrophilicity; non-toxic, biodegradable, has viscosity for about 700-1500 mPa with DS 0.6-0.95 [8].

The composition ratio of alginate and cellulose on making beads is influential on adsorption power. Using cellulose 10-25% can increase adsorption from 68% by 80%, while the adsorption beads by using alginate 100% are just 19% [6]. Mentioned to [7] that beads with alginate 100% have low porosity and rough, then beads with alginate CMC 1:1 has a hard surface and high porosity. Too high CMC concentrations cause morphologically compact and influence swelling power. [9] state that too high CMC for forming beads can produce beads with morphologically compact and hinder diffusion.

Based on that information on making bead with composition alginate: CMC needs to know the optimum condition of beads. In this research, corn stalk will modify cellulose beads with a variation ratio of 1:0, 1:1, 1:2, and 1:3 with adding crosslink agent CaCl₂ 3%. Cellulose from extraction and CMC synthesize characterized with XRD and determination best composition beads based on swelling power gravimetrically and the optical microscope, FTIR characterization to know function group, and SEM-EDX to know surface morphology of beads.
2. MATERIALS AND METHOD

2.1. Material

Cornstalk waste, sodium hydroxide p.a (Merck), hydrochloric acid p.a (Merck), sodium monochloro acetic p.a (Merck), methanol p.a (Merck), calcium chloride p.a (Merck), sodium chlorite p.a (Merck), acetic acid p.a (Merck), sodium alginate (Phyto), methylene blue p.a (Merck), aqua demineralization, and distilling water.

2.2. Method

2.2.1 Extraction of Cellulose from Cornstalks

25-gram cornstalk powder was added 500 mL NaOH 20% at 80°C for 90 m then washed with distilled water. After that, samples bleach with 100 mL of NaClO2 1% and CH3COOH, 10% till pH five at 75°C for an hour, then washed with distilled water until pH neutral. Pulps were hydrolyzed with 5% hydrochloric acid under reflux at 95°C for an hour; then, the hydrolyzed pulps were washed with distilled water and dried at room temperature [10]. Then samples characterize with FTIR and XRD.

2.2.2. Preparation of Carboxymethyl Cellulose

Five grams of cellulose added with 100 mL water distillation and 10 mL sodium hydroxide 30% drop by drop for an hour under constant stirring—etherification with five-gram sodium monochloro acetic under continuous stirring and at 60°C for three hours. The product obtained was filtered and suspended with 100 mL methanol for 1 d. then the samples were neutralized with acetic acid and filtered to get residue products. After that, the product was dried by oven at 60°C until constant weight [11]. Finally, the product was characterized by FTIR and XRD.

2.2.3 Determination of the Best Composition of Alginate: CMC in Making Beads

Beads made by mixing sodium alginate and CMC with different compositions 0:1, 1:0, 1:1, 1:2, dan 1:3 (g/g) by combining two biopolymers under constant stirring at room temperature until the solution be homogeneous. The formation of beads uses a gelation technique using a syringe needle dropwise from a distance of 3 cm into CaCl2 3%. Beads were formed instantly and were left in contact with CaCl2 3% for 1 d to complete the gelation. The beads that formed rinsed gently with aqua demineralization and dried at 37°C [9], [12]. Finally, beads characterized swelling power gravimetrically and the optical microscope, FTIR, and surface morphology with SEM EDX.

2.2.4 Characterization

2.2.4.1 XRD

X-ray diffraction applied to observe changes in cellulose and CMC. X-ray diffraction of product cellulose and CMC synthesize measure with X-ray diffractometer X’pertPRO PANalytical and recorded with Cu Ka λ =1,54056 Å (40 kV, 30 mA). Samples scanned from 0°-60°

2.2.4.2 Characterization of Functional Groups

Determination function group of AC variation using FTIR (VARIAN type FT 1000). Approximately beads were grinded with KBr using mortar agate and pressed in a pellet. Then put in the sample holder and measure the wavenumber of the function group [13].

2.2.4.3 Swelling AC Beads Test

Monitoring the water sorption process use gravimetric procedure and optical microscope[14]. ± 50 mg beads alginate: CMC suspended with10 mL aqua demineralization for 1 d. The swollen beads weighed on a digital balance. calculating the swelling ratio and diameter using the following equation Swelling ratio (%) = (Wf-Wi) / Wi x 100%

\[
\text{Diameter} \% = \frac{(Df-Di)}{Di} \times 100\%
\]

Wf is the final weight, and Wi is the initial weight of AC

Df is the final diameter, and Di is the initial diameter of AC.

2.2.4.4 Methylene Blue Adsorption

AC has suspended with methylene blue solution 50 ppm for 17 d. Then measure the absorbance with spectrophotometer UV-Vis (VARIAN) on 665.0 nm.

2.2.4.1 Characterization of Surface Morphology

The study micrograph of AC uses a scanning electron microscope (JEOL JSM 6510LA). (Anggraeni, 2008). This analysis is for AC optimum and control.

3. RESULT AND DISCUSSION

3.1 Cellulose extraction

The first step of cellulose extraction is lignification using sodium hydroxide 10% solution to dissolve noncellulose. Lignification cannot remove lignin as a whole is characterized by pulp production, which is still brown. In contrast, the loss of lignin is from the presence of black liquor leachate—the results of the adsorption band from each extraction step in cellulose extraction as Figure 1. The loss of noncellulose components supports the absent peak at 1513 cm-1 containing aromatic C=C
groups from lignin. Reducing the intensity at 1733 cm\(^{-1}\) indicates that the amount of group hemicellulose decreased. The intensity of the wavenumber 896 cm\(^{-1}\) is the absorption character of β-glycosides. This information has similarities with standard cellulose in research [15].

3.2 Making Carboxymethyl Cellulose

There are two steps to making CMC, that is, alkalization and carboxymethylation. In alkalization, cellulose reacts with sodium hydroxide to form sodium cellulose. The Hydroxyl group attacks the H atom on OH C3, C6, or C2 cellulose by releasing H2O, which causes the OH group of cellulose to inactive and swell. So, the monochloro acetate easy to diffuse on the carboxymethylation process. Based on physical observations, the produces of CMC synthesis is not too different from cellulose extracted. The colour is yellowish-white to very young cream. However, the FTIR characterization shows a sharper absorption at the wavenumbers of 1596 and 1413 cm\(^{-1}\). That indicates the amount of carboxyl group at CMC synthesis increases after carboxymethylation of replacing the hydroxyl group in cellulose. FTIR synthesis CMC spectra profile has similarities with standard CMC as in the study [16].

The cellulose and CMC X-ray diffraction showed that cellulose has high crystallinity. That is because the extraction cellulose step can remove amorphous compounds as lignin and hemicellulose. That is an agreement with research [15] and [17]. The CMC diffractogram is almost the same as the cellulose peak with additional peaks at positions 32° and 45°, which show the CMC character. These results are similar to the previous research of [18][19][20][21].

3.3 Optimum Composition of Alginate: CMC in Making Beads

| Table 1. Optical microscope dry and wet beads with magnification 0,75 X 10 |
|-----------------------------------------------|
| Dry | Wet |
| AC 1:0 |          |
| AC 1:1 |          |
| AC 1:2 |          |
| AC 1:3 |          |

It was making Alginate: CMC (AC) beads by dropping technique through the ionic gelation method with crosslinking CaCl\(_2\) 3%. Determining the optimum
composition of AC is based on the formation of beads, power swelling calculated gravimetrically, and optical microscopy with ImageJ application's help to measure the increase in diameter and the adsorption of methylene blue dyes. In the composition of beads, 0:1 is not able to form beads formation. The composition consists only of a CMC matrix, while the fibre that acts as a bead formation that is alginate does not exist. Therefore, it cannot form spherical as bead formation when dropping the viscose solution into a crosslink solution.

AC beads 1:2 have a more spherical shape. Besides, the composition also has the highest swelling, and diameter increases with increasing time. Methylene blue adsorption result reinforces that result. For eleven and sixteen days, the AC 1:2 adsorption beads had the highest adsorption ability. On the day after that, the adsorption was almost constant, and there was no significant difference. In the five-day immersion, the adsorption process was slow, so that the number of MB adsorbed in beads was only slightly. That is because, at the beginning of the MB adsorption process, it only reaches the beads limiting screen, and the longer the immersion time, the MB successfully diffuses on the surface and pore structure of the beads. Finally, the active site of the AC beads is the negatively charged carboxylic group capable of binding to cations in MB. The determination of methylene blue adsorption concentration uses a standard curve in the equation $y = 0.5384x - 0.0075$ with a maximum wavelength of 665.0 nm.

### 3.3.3 Methylene Blue Adsorption Activity

![Figure 4. Graph of methylene blue adsorption](image)

The observation of swelling and adsorption of methylene blue in AC explained that swelling power and adsorption ability increased with CMC. CMC is hydrophilic and has a carboxylic group. Suppose the concentration increases in AC, enhanced repulsion between carboxylic group ion causes the network chains to undergo a more considerable relaxation, resulting in a more considerable swelling and methylene blue adsorption. However, when CMC's concentration becomes high, the increased number of carboxyl group chains produces a dense network and causes retention of mobility, and slow the diffusion process [22][23]. The analysis results using FTIR showed that the higher CMC concentrations used in the AC composite resulted in sharper peaks in the wavenumber region of 1400-1600 cm$^{-1}$, the C=O asymmetric symmetrical character the CMC.

![Figure 5. IR spectra of 1:0, 1:1, 1:2, and 1:3 beads](image)

In contrast, the other groups in each AC composition not significantly different. The other groups that appear are in the region of wave number 3412-3426 cm$^{-1}$, the OH group's character, the CH vibration at 2917-2932 cm$^{-1}$, 1027-1032 cm$^{-1}$ CO stretch 1315-1318 cm$^{-1}$ character OH stretch as well. The success of the bond between the crosslink Ca2+ and alginate seen at wavenumber that appears in the region 819 cm$^{-1}$. 

Figure 3. % swelling and diameter AC swollen beads graph

Figure 4. Graph of methylene blue adsorption

Figure 5. IR spectra of 1:0, 1:1, 1:2, and 1:3 beads
4. CONCLUSION

IR spectra of CMC synthesis showed sharper peaks at 1596 cm⁻¹ than peaks in cellulose also XRD cellulose and CMC diffractograms almost equal to the addition of 32 and 45 peaks in CMC. The best AC composition is 1:2 with the most considerable weight and diameter of 175.5% and 26.64%, respectively, in which the characterization of the surface is rough.

AUTHORS’ CONTRIBUTIONS

Eny Yulianti provided ideas and explored the literature on the potential of corn stalks as bio adsorbents. Anggun Cahyaning Pertiwi conducted sample preparation and collected research data. Lilik Miftakhul Khoiroh discussed the analysis of the XRD characterization results and determining the optimum composition of the beads making, as well as Febi Yusniyanti analyzed the results of the characterization of FTIR and SEM-EDX. All authors provided feedback on the results of the research analysis and scriptwriting.

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