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Synthesis and Characterization of Beads Alginate Carboxymethyl Cellulose from Corn Stalk (*Zea Mays*) Using $BaCl_2$ As Crosslink with Variation Concentration

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ABSTRACT
This research aims to develop cellulose products extracted from corn stalk to use as cellulose beads. Cellulose has extracted using the best solvent, which is 10% NaOH. The extracted cellulose was modified to carboxymethyl cellulose using a monochloro acetate reagent with the best ratio of 5:5 and 3 hours of reaction time. Cellulose beads made from carboxymethyl cellulose and alginate with the best composition 1: 2. This study uses variations of BaCl2 crosslink 3%, 5%, and 10%. Fourier Transform Infra-Red (FTIR) characterization to determine functional groups of beads. Then geometry analysis of beads using optical microscopy, and surface morphological analysis using X-ray Scanning Electron Microscopy-Energy (SEM-EDX). The best cellulose beads are base on high swelling 97.1% at 5% crosslink concentration.

Keywords: *Cornstalk, Cellulose beads, Alginate, Crosslinked*

1. INTRODUCTION

Cornstalks are agricultural solid waste, which increases the production of 1.11% annually [1]. Cellulose contains cornstalk ± 40% [2][3], potentially used as a cellulose source. Cellulose is a type of polymer with the property of being renewable, degraded, and modified to increase its use [4].

Carboxymethyl cellulose (CMC) is a modification of cellulose that has a functional group CH_2COO^- and has a viscosity value of 7.574,67 cP [5] with a substitution degree value of 0,6-0,85 [6]; thus, CMC has high hydrophilic characteristics. CMC adsorption ability is higher when compared to cellulose [6].

Cellulose beads can use as fertilizer fixers, water treatment, drug carrier material, ion-exchange chromatography, and others. The CMC composition used in making beads affects the adsorption power produced. The use of 10% and 25% CMC will increase the adsorption power by 65% to 80%.

The method of making beads used is ionic gelation [7], which involves divalent or multivalent ions as crosslink agents like Ba^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+} dan Sr^{2+} [8], which serves to strengthen the mechanical strength of the particles formed.

$BaCl_2$ as a crosslink has advantages, including the swelling value of the beads produced is relatively stable because of the large ion size of Ba^{2+} (1,74 A^0), compared with $CaCl_2$ (1,14 A^0), and $Al(SO_4)_3$ (0,68 A^0) [9][10], so resulting in dense bead shape. A strong constituent composition [11][12] also said that the use of higher concentrations of crosslinks used would result in more hardened beads, resulting in decreased adsorption power from the beads.

Beads can adsorb methylene blue [13] as a waste absorber agent. Carboxymethyl groups in CMC can increase the absorption of methylene blue [14], so the use of CMC in beads making can also increase the ability to adsorption of methylene blue [15].

Based on this description, it is necessary to synthesize alginate-CMC beads from corn stems using variations in the concentration of BaCl2 crosslinks 3%, 5%, and 10% to get the best beads results. The characterization used was FTIR, swelling test, optical microscope, digital penetrometer, SEM-EDX, and UV-Vis.

2. MATERIAL AND METHODS

2.1 Material

Cornstalk waste from Kediri district, sodium hydroxide (NaOH) p.a, acetic acid (CH_3COOH) p.a, barium chloride ($BaCl_2$) p.a, sodium alginate $(C_6H_7O_6Na)_n$ p.a, aquademin, aquades, methanol (CH_3OH) p.a, asam klorida (HCl) 37% p.a, sodium chloride ($NaCl_2O$) p.a, dan sodium monochloroacetate ($CH_3ClCOONa$) p.a, nitric acid (HNO_3) p.a, pp indicator p.a dan *methylene blue* p.a.

2.2 Methods

2.2.1.Extraction and Modification Cellulose

Cellulose extract from cornstalk [16] and carboxymethyl cellulose is a modification of cellulose structure [17].

2.2.2 Making Carboxymethyl Cellulose Alginate Beads with Variation Concentration of $BaCl_2$

Making alginate-CMC beads using sodium alginate composition: CMC (w / w) 1: 2 dissolved in 25 mL demin water. Furthermore, the solution is homogenized and dropped into a $BaCl_2$ crosslink solution with variations in the concentration of 3%, 5%, and 10% using a syringe needle. Beads formed in the crosslink solution are allowed to stand for 24 hours. Furthermore, the beads are washed using demin water and dried in an oven at 36℃ 24 hours.

2.3 Characterization of Carboxymethyl Cellulose Alginate Beads

FTIR characterization to determine functional groups from cornstalk powder, cellulose extracts, carboxymethyl cellulose, and CMC beads.

2.3.1 Swelling Power

A total of ± 40 mg of beads soaked in 10 mL distilled water at a time immersion variation at 3, 5, 8, 24, 29, and 31 hours. The swelling test gravimetrically based on the equation:

$$Swelling = \frac{Wt-Wo}{Wo} x100\% \quad (1)$$

Wt is the weight of the hydrated beads, and Wo is the dry weight [14].

2.3.2 Mechanical Strength Test

The mechanical strength test is to use a digital penetrometer. Measurements using a 3.5 mm probe needle. Repeated sample measurements three times.

2.3.3 Beads Activity Test in Methylene Blue

A total of ± 14 mg of beads soaked in 12 mL of methylene blue. The methylene blue solution determines absorbance on days 5, 11, 15, 20, and 22. Measurement of absorbance of methylene blue using UV-Vis spectroscopy with a wavelength of 665 nm. The calculation of the adsorption capacity of beads on equation [14] :

$$Qe = (Co - Ce) v/w \quad (2)$$

2.3.4 SEM-EDX Characterization

SEM characterization to determine the surface morphology of the beads. Furthermore, EDX is used to find out the elements contained in beads.

3. RESULT AND DISCUSSION

3.1 Cellulose Extraction from Cornstalk

FTIR characterization to determine functional group changes at the extraction stage. FTIR analysis in Figure 1.

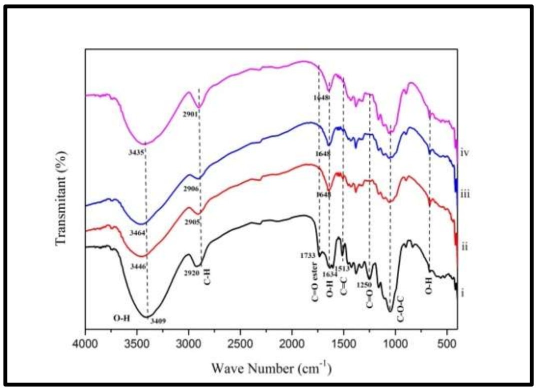

Figure 1. IR spectra of cellulose extraction stages

IR Spectra Figure 1 shows the different uptake at each stage of cellulose extraction from cornstalks. The IR spectra (i) shows the peaks showing O-H groups at wavelength 3409 cm^{-1} and saturated C-H at 2920 cm^{-1}. Absorption peaks also appear at 1733 cm^{-1} and 1250 cm^{-1}, which show C = O esters and C-O bonds indicating hemicellulose compounds. While the wave number 1634 $cm-^{1}$ shows the adsorbed water uptake in corn starch powder delignification, bleaching, and hydrolysis. The uptake of 1513 cm^{-1} indicates the presence of lignin compounds.

The yield of cellulose obtained from cellulose extraction from cornstalk is 30% so that the structure can convert into carboxymethyl cellulose as a result of research [17].

3.2 Variation Concentration of $BaCl_2$ as Crosslink in Making Carboxymethyl Cellulose Alginate Beads

Formation of beads occurs because of the bond between crosslink (Ba2+) and COO^- group on the block of glucuronic acid residues (sodium alginate) that forms a three-dimensional network (egg box) [10]. In comparison, CMC in beads formation is only a matrix that functions to increase beads' swelling power. Increased swelling power on beads is due to electrostatic interactions between the COO groups in the CMC.

The beads produced vary based on the concentration of the crosslink used. Beads made with a 5% concentration have a round shape [9], in Figure 2.

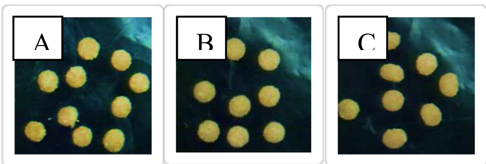

Figure 2. Beads (a) 3% (b) 5% (c) 10%

The swelling value also shows beads with a crosslink concentration of 5% having optimum results in soaking for 24 hours in Figure 3.

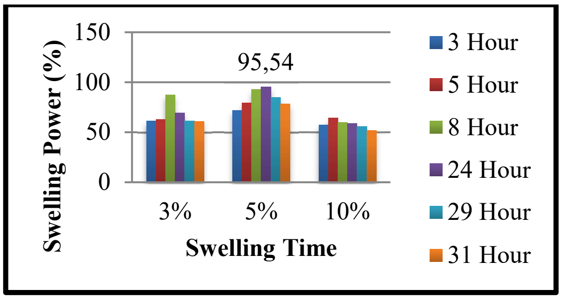

Figure 3. Graphs of swelling power analysis results

Based on Figure 3, the highest value of swelling power shown in beads with a concentration of $BaCl_2$ 5%, equal to 95.54%. It is possible due to the optimum crosslinking of beads so that the beads adsorption power is also optimum at that hour. This swelling result supported by a magnification of diameter beads data measured using an optical microscope, as shown in Figure 4.

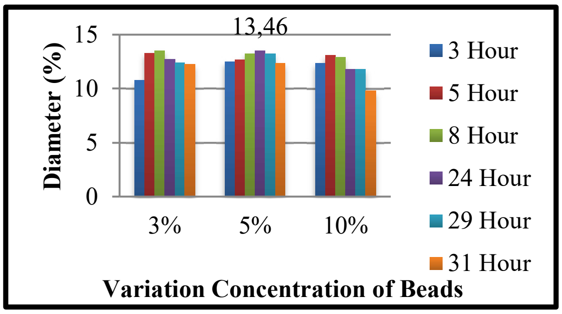

Figure 4. Graph from analysis of diameter beads

The figure shows the increase in the beads' diameter, which results are linear with the swelling value. The percentage value of diameter beads with 5% crosslink concentration increased from the immersion time of 3 hours to 24 hours, which is equal to 13.65%. It is happening because the greater the value of swelling, it will affect the beads' diameter swelling.

Increasing the concentration of crosslinks used will affect the level of hardness of the beads produced. The higher the concentration of crosslinks used, the level of hardness of beads will also increase by the measurement of violence presented in Figure 5.

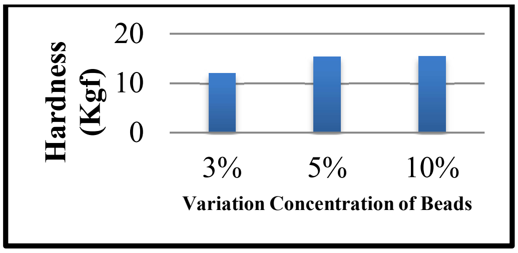

Figure 5. Graph of hardness level of beads

Figure 5 shows that the hardness value of beads increases at a concentration of 10%. It shows that 10% of swelling beads also produce low swelling. So it can be concluded that the high concentration of crosslinks used will affect the results of swelling and hardness on beads.

The success rate of beads formation being by the bond between COO^- and Ba^{2+} in Figure 6.

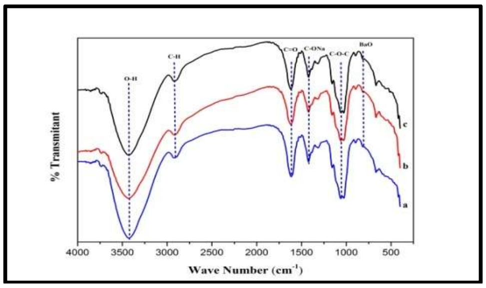

Figure 6. IR Spectra of beads in (a) 3% (b) 5% (c) 10%

The absorption shows the bond between CO^- and Ba^{2+} at a wavelength of 805 cm^{-1}. The absorption's intensity is getting sharper along with the high concentration of $BaCl_2$, although the difference is not too significant. Whereas the uptake that appeared at 1619 cm^{-1}, 1420 cm^{-1}, and 1059 cm^{-1}, respectively, were C = O, C-ONa, and C-O-C groups are indicating the presence of sodium alginate.

3.3 Beads Activity Test in Methylene Blue

Figure 7 shows that beads with a crosslink concentration of 3% have a high level of adsorption compared to 5% and 10%. Because of the higher concentration level of the crosslink, the adsorption power will decrease. The decrease in beads' adsorption is due to a large number of crosslinks between the crosslink and alginate [18].

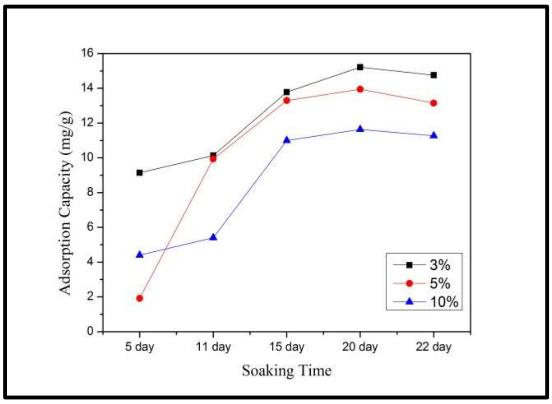

Figure 7. Graph of methylene blue adsorption capacity

3.4 SEM-EDX Characterization of Carboxymethyl Cellulose Alginate Beads

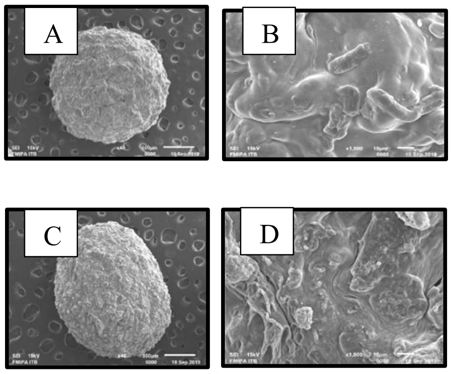

Figure 8. SEM characterization results (a) beads 5% 40x magnification, (b) beads 5% 1000x magnification, (c) beads 10% 40x magnification, and (d) beads 10% 1000x magnification

Figure 8 shows the morphology of beads in 5% and 10% using SEM characterization. Based on these images, beads with a crosslink concentration of 5% has a smooth morphology that forms like a cavity and is round-shaped, which is also supported by image-J analysis data. In comparison, beads with a crosslink concentration of 10% have a rough and uneven morphology and an uneven shape, which is supported by the results of the image-J analysis. The result is that the higher the concentration of crosslinks will affect the surface of beads. Increased crosslink concentration causes the surface of the beads to become more rough and uneven.

EDX characterization shows that 5% of beads contain elements including C, O, Na, Cl, and Ba. In comparison, 10% of beads contain elements of C, O, Cl, and Ba. Beads 10% have a higher percentage of Ba by the concentration contained in the beads. Increasing the percentage of Ba causes beads morphology to become smoother because of fewer cavities due to the increased interaction between alginate and Ba crosslink. The higher the crosslink concentration will affect the particle's shape, the less agglomeration level the results of the EDX characterization in Table 1.

Table 1. Per cent weight of each element of CMC alginate beads with crosslink concentrations of 5 and 10%.

Sample	Weight of each element (%)				
	C	**O**	**Na**	**Cl**	**Ba**
Beads 5%	50,08	42,18	0,63	2,63	4,43
Beads 10%	51,57	38,58		4,73	5,12

4. CONCLUSION

Variations concentrations of $BaCl_2$ as crosslink affect the shape, swelling power, diameter increase, and beads' mechanical strength. Cellulose compounds at wavelengths of 1021 cm^{-1}, 889 cm^{-1}, 1036 cm^{-1}. A wavelength of 805 cm-1 indicates the bond between COO^- and Ba^{2+}. Beads indicate the high adsorption capacity of beads against methylene blue with a 3% concentration, 14.75 mg / g.

AUTHORS' CONTRIBUTIONS

Eny Yulianti has given a literature tracker on the potential of cornstalk as adsorbent. Laila Nihayatul Khusna has done sample preparation and data collector in the laboratory. Lilik Miftahul Khoiroh discussed of determining the best concentration of $BaCl_2$ and data analysis of SEM-EDX. All authors provided their responses to the result analysis and scriptwriter.

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