Synthesis and Characterization of Alginate-Cellulose Xanthate Beads from Corn Stalk with Porogen Variation

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***Abstract*- Corn stalk has a high content of cellulose that has the potential to make the composition of alginate-cellulose xanthate beads. Alginate and cellulose are biodegradable, renewable and non-meltable polymers that have wide applications in various industry sectors. The purpose of this research is to know the difference of addition of porogenic agent of CaCO3 and NaCl which produce optimum beads based on functional group and swelling power. Furthermore, optimum beads are characterized to know the morphology, topology, and porosity. This research is experimental. The variation in the concentration of porogenic addition of CaCO3 and NaCl are 0; 0.5 and 1 gram. Characterization of alginate-cellulose xanthate beads using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). The result of synthesis obtained on beads of alginate-cellulose xanthate, are known bigger pore with little amount on addition of porogenic CaCO3, whereas with addition of porogen NaCl obtained by smaller pore with big amount.**

Keywords— corn stalks, beads, alginates-cellulose xanthate, CaCO3, and NaCl.

I. INTRODUCTION

The alginate-cellulose xantate beads are particles with diameters on a micro scale up to millimeters. Alginate-cellulose xantate beads can be applied in ion exchange chromatography on water and carrier materials in drugs (Gericke, et al., 2013). According to Boufi and Chaker (2016), corn stalk waste after harvest contains 69% cellulose. Based on Yulianti's research, et al., (2016), stem waste can be used as an ingredient in making alginate-cellulose xantate beads. Similarly, the research that has been conducted by Puspitasari (2017), bagasse which has cellulose content can also be used as an ingredient in making alginate-cellulose xantate beads. Based on high cellulose content, corn stalks have great potential as ingredients for making alginate-cellulose xantate beads.

Allah has said in Q.S Ali-Imran verse 191. Based on that verse mentioned, it can be seen that everything God created both in the heavens and on earth is nothing in vain but full of lessons for His thinking creatures. The verse explains that everything that God created has a noble lesson and purpose, it is impossible for God to make vain (Al-Jazairi, 2007). For example, the use of cellulose corn stalk waste as a composition of alginate-cellulose xantate beads.

According to Gericke, et al., (2013), the formation of cellulose xantate is easier, because the process is directly without having to be isolated from the mixture first. Puspitasari (2017) said, cellulose xantate has high crystallinity and thermal stability. The higher the thermal stability, so the more crystalline, and the high crystallinity can increase the binding power of the beads so that they are more easily formed. According to Swatloski, et al. (2002), cellulose xantate is produced by reacting natural cellulose and carbon disulfide (CS_2) using NaOH solvents. Based on research conducted by Puspitasari (2017), the best solvent concentration of viscose solution was 6% NaOH with a viscosity value of 0.024 Pa.s, so that in this study 6% NaOH solvent was used in the manufacture of viscose solution in cellulose extracted from corn stalks.

This study uses alginate and cellulose xantate as a composition for making beads. Alginate is preferred as a bioadsorbent because it has excess recyclability, is hydrophilic, and has a carboxylic group which can bind to cellulose. According to Sonmez, et al. (2016), alginate was able to form a gel in the presence of polyvalent cations through the interaction of ionic cellulose composition in making alginate-cellulose beads affect the adsorption power when applied. Cellulose composition is 10 and 25% gives adsorption power of 68 and 80%. While the composition of beads of alginate without cellulose, can only adsorb metal by 19%. Based on Puspitasari's research (2017), the best composition of alginate-cellulose xantate is 1: 3 with 63.8% swelling ability.

The adsorption ability of alginate-cellulose xantate beads can be increased by the addition of pore forming agents (porogen). According to Purnamasari (2011), porogens that can be used are calcium carbonate ($CaCO_3$), sodium bicarbonate ($NaHCO_3$), and sodium chloride (NaCl). Based on research conducted by Choi, et al., (2002), the addition of NaCl porogen can produce smaller pores and the addition of $CaCO_3$ porogen to produce a smoother product if both are compared with porogen $NaHCO_3$.

The process of making beads of alginate-cellulose xantate required the addition of crosslinking agents as crosslinking polymer chains. The crosslinking agent used is Zn^{2+} on zinc acetate ($C_6H_6O_4Zn$). As Sonmez's research, et al., (2016), the addition of $C_6H_6O_4Zn$ in the manufacture of alginate-cellulose beads, can increase the adsorption ability of heavy metals compared to the addition of calcium chloride ($CaCl_2$).

Based on this description, it is necessary to develop a research on the synthesis of alginate-cellulose xantate beads with variations of porogen $CaCO_3$ and NaCl to obtain optimum beads. The optimum beads were determined by measuring the highest swelling power. Furthermore, the characterization of functional groups using FTIR, morphological characterization and surface topology using SEM-EDX and pore size characterization of beads using porosity analysis.

II. EXPERIMENTAL

2.1 Cellulose Extraction from Corn Stems

The prepared corn stalk powder was weighed 50 grams and soaked in 1000 ml of 10% NaOH at 80°C for 90 minutes. Then, wash with distilled water and squeeze. 40 ml of acetic acid and 250 ml of sodium chlorite ($NaCl_2O$) 1% were added at a temperature of 75°C for 1 hour. After that, wash with distilled water until neutral and squeezed. Cellulose extract was hydrolyzed with 5% HCl (1:20) at 95°C for 1 hour and the functional group was analyzed.

2.2 Making Cellulose Xantat

Five grams of cellulose extract were soaked in 20% NaOH for 40 mL for 3 hours. Then squeezed and allowed to stand for 60 hours at room temperature for aging. Then, alkaline cellulose was reacted with 2.5 mL CS_2 and 6% NaOH as much as 10 mL in a shaker incubator at a speed of 150 rpm at 25°C for 3 hours. The cellulose xantate obtained was characterized by its functional group using FTIR.

2.3 Determination of the Best Concentration from the Variations of Porogen $CaCO_3$ and NaCl in the Formation of Pore Beads

One gram of sodium alginate is dissolved in 25 ml of aquademin by heating. Cellulose xantate was added by comparison of alginate-cellulose 1: 3. Then, variations of $CaCO_3$ and NaCl porogens were carried out, with $CaCO_3$ and NaCl variations 0; 0.5; 1; and 1.5. The solution formed was dripped using an 18G syringe needle into 5% $C_6H_6O_4Zn$ as much as 50 mL and allowed to stand for 24 hours. Beads formed are filtered and washed using aqua demineralization. Beads resulting from the addition of NaCl porogen were washed and soaked in a sterile glass container with aquademin at room temperature for 48 hours. The washing efficiency (NaCl) was checked by measuring the conductivity of washing water periodically to close to the conductivity value of water which is 1 µS / cm (Tas, 2008). Meanwhile, the results of beads addition of porogen $CaCO_3$ reacted with 10% CH_3COOH using magntic stirrer until no bubbles appeared. The resulting beads are washed to a neutral pH with aqua demineralization. The resulting wet beads were dried using 37 ° C for 9 hours. Then, the swelling power, the functional group, and the size of the porous were identified.

III. RESULT AND DISCUSSION

3.1 Cellulose Extraction

FTIR analysis is used to determine molecular vibrations. Molecular vibrations produced from corn stem powder and cellulose after hydrolysis are shown in Figures 4.1 and 4.2.

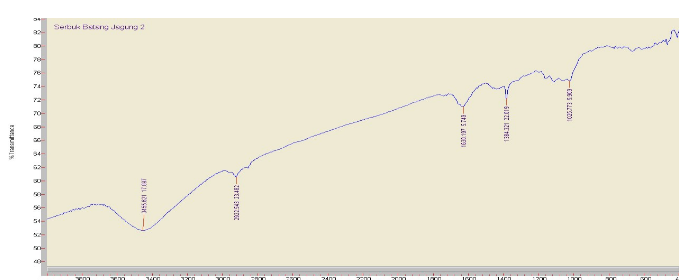

Figure 4.1 IR spectra of corn stalk powder

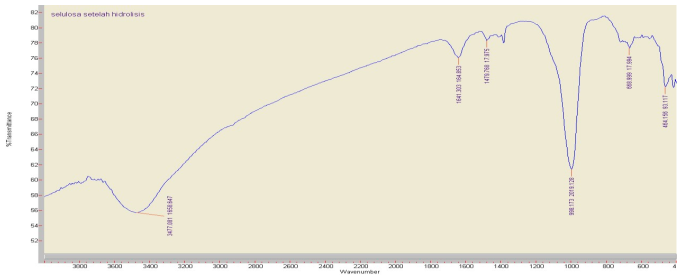

Figure 4.2 Cellulose IR spectra after hydrolysis

Wave number 3455 cm^1 shows the presence of –OH stretching bond, 2923 cm^1 shows C-H sp3 bond, 1630 cm^1 shows C = O stretching and 1384 cm^1 shows C-O-H bond, and wave number 1050 cm^1 shows the primary bond in C-OH. Based on the wave numbers produced in the spectra above, it indicates that corn stalk powder contains pure cellulose. Whereas in cellulose spectra after hydrolysis wave number 994 cm^1 appears which shows the presence of C-O and C-C bonds in glucose.

3.2 Making Cellulose Xantat

Viscose solution is made by reacting alkaline cellulose with CS2 dissolved with NaOH. The measurement results using FTIR produced wave numbers 3423 cm^1, 2807 cm^1, 1607 cm^1, 1393 cm^1, and 1050 cm^1 which indicated pure cellulose. In addition, wave number 666 cm^1 appears which indicates the reaction of -OH groups in the cellulose structure C-2, C-3, and C-6. Wave numbers 1161 cm^1, 1110 cm^1, and 1050 cm^1 indicate the -O-C (= S) -S group. Whereas the characteristic of the -O-C (= S) -S group is the wave number 1110 cm^1, shown in Figure 4.3.

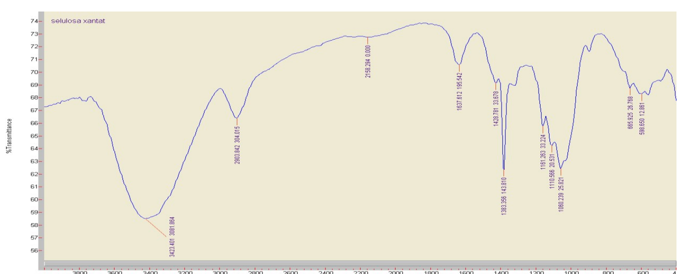

Figure 4.3 Cellulose xantate IR spectra

3.3 Making Xanthate Alginate-Cellulose Beads with Porogen Variations CaCO3 and NaCl

Cellulose alginate beads are made from a solution of cellulose xantate, alginate, and porogen variation by dropping process in zinc acetate solution. Zink acetate functions to form cross linkages between zinc and alginate so that the resulting beads are rigid. Then the beads are washed until neutral, and dried in an oven until they are constant which produces dry beads.

3.3.1 Analysis of Beads using Optical Microscopes

Variation of CaCO3 porogen is used because according to Choi, et al. (2002), the addition of CaCO3 porogen to the process of making beads, producing smoother products and high mechanical strength. While Research Peretz, et al. (2015) using porch NaCl in calcium alginate beads, produced flat round beads and had a rough surface. Beads without the addition of NaCl are almost round in shape and have a smooth surface with slight protrusions and hollows.

3.3.1.1 Porogen concentration of CaCO3 and NaCl 0.5 grams

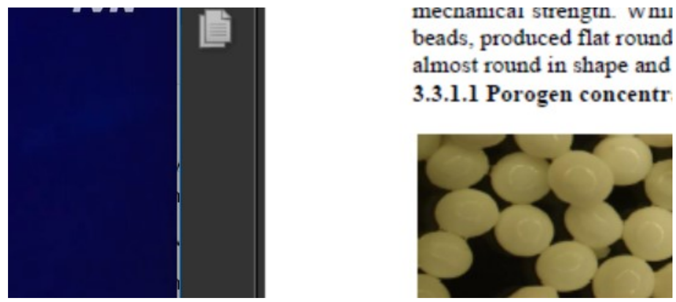

Figure 4.4 Results of beads with an optical microscope (a) adding CaCO3 0.5 grams magnification
of 0.75 x 10 (b) magnification of 2.5 x 10 (c) magnification of 10 x 10 (d) addition of
NaCl 0.5 grams magnification 0, 75 x 10 (e) magnification 2 x 10 (f) magnification
11.25 x 10

3.3.1.2 Porogen concentration of 1 gram CaCO3 and NaCl

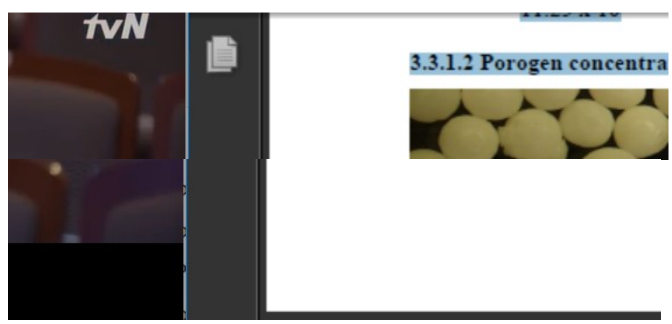

Figure 4.5 CaCO3 1 gram (a) magnification of 0.75 x 10 (b) magnification of 2.5 x 10 (c) magnification of 10 x 10, and addition of NaCl 1 gram (a) magnification of 0.75 x 10 (b) magnification 1 , 5 x 10 (c) magnification 11.25 x 10.

3.3.1.3 Porogen concentration of CaCO3 and NaCl 1.5 grams

Figure 4.6 The results of the addition of CaCO3 1.5 gram porogen (a) 0.75 x 10 (b) magnification 2.5 x 10 (c) magnification 10 x 10 and 1.5 grams NaCl (a) 0.75 x 10 magnification (b) magnification of 1.5 x 10 (c) magnification 11.25 x 10.

CONCLUSION

Based on the results of the research described in the discussion it can be concluded, that the synthesis results obtained in alginate-cellulose xantate beads, obtained a larger pore with a small amount on the addition of CaCO3 porogen, whereas with the addition of NaCl porogen obtained a smaller number of pores.

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