

PREPARATION OF CHITOSAN-CELLULOSE COMPOSITE BEADS USING CELLULOSE ISOLATED FROM SUGARCANE BAGASSE

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Abstract : Chitosan-cellulose composite beads had been prepared using cellulose isolated from sugarcane bagasse. Sugarcane bagasse was hydrolyzed with H_2SO_4 with various concentrations (30, 40, and 50%). Cellulose obtained was characterized using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). FTIR analysis results inform the existence of typical functional groups of cellulose in the sample. XRD patterns show H_2SO_4 concentration on the hydrolysis process influence the crystallinity of cellulose. Cellulose was used as a filler in the preparation of chitosan-cellulose composite beads. The results show that cellulose decrease the crystallinity of chitosan.

Keywords: Sugarcane bagasse, cellulose, chitosan, composite beads, H_2SO_4

I INTRODUCTION

Sugarcane bagasse is still considered as an invaluable waste which contains cellulose (38.9%) [1]. The use of sugarcane bagasse as a source of cellulose has not been widely reported. Cellulose has been used in some applications due to its wide availability in nature and low production cost [2,3]. Therefore, in order to increase the economic value of sugarcane bagasse, in this work we used cellulose isolated from sugarcane bagasse as a filler of chitosan polymer. Some methods to obtain pure cellulose from a materials has been developed, including chemical [4], mechanical [5], and biological [6] methods. This research employed chemical extraction method, which was acid hydrolysis. Cellulose extraction through hydrolysis with strong acid is the most common used method [2,4]. This process include the hydrolysis of the amorphous parts of cellulose and hemicellulose fibers [7,8]. Chitosan is a biopolymer obtained from deacetylation of chitin from the shell, such as of: shrimps, crabs, and insects [9]. In its development, chitosan is often utilized as an adsorbent biomaterial due to its possession of amine groups ($-NH_2$) which is effectively significant in the adsorption of heavy metal ions [10,11]. Nevertheless, chitosan has some drawbacks such as its weak durability and stability.[12].

In order to overcome this weakness, it is necessary to modify chitosan with other materials [6]. One material that can be used in modifying chitosan is cellulose. Modification of

chitosan using cellulose is expected to produce a new material that has better properties than its nature. The formation of a new material of chitosan-cellulose composite is expected to be used as an adsorbent which can improve the weaknesses of each material. Some researchers have reported the preparation of chitosan-cellulose composite. However, they used commercial cellulose which produced expensive composite. Meanwhile, it is known that sugarcane bagasse contains cellulose. It is easily found and inexpensive. Therefore, in this work we used cellulose from sugarcane bagasse for chitosan-cellulose composite beads preparation.

II METHODOLOGY

Isolation of cellulose from sugarcane bagasse

Sugarcane bagasse was washed with water and dried. Next, the dried sugarcane bagasse was cut to small piece, and crushed with blender. Hydrolysis was then conducted by dissolving the sample into H_2SO_4 solution with concentration variation of 30, 40, and 50% and stirred for 90 min. Afterwards, cold distilled water was added and left for 10 min. Next, the mixture was filled with distilled water until the neutral pH was reached. After filtered, the sample was then dried in an oven for 12 h at $40^\circ C$. The rough cellulose was bleached using 30% H_2O_2 for 90 min, and rewashed with distilled water. The bleaching procedure was conducted twice. The obtained cellulose, after that, was dried in an oven for 12 h at $40^\circ C$ [13].

Preparation of chitosan-cellulose composites

0.35 g chitosan (purchased from Tokyo Chemical Industry Co., Ltd. Japan) was dissolved in 20 mL of 2% acetic acid, stirred for 2 h. Then, 0.13 g cellulose was added, and stirred for the next 2 h. The mixture was dripped into 3M NaOH in order to form bead-shaped composite. Afterward, the composite beads were filtered and washed with distilled water until the neutral pH is reached. The beads were dried in an oven for 12 h. The extract was confirmed with FTIR spectrum and XRD diffractogram.

Characterization

FTIR

The FTIR spectrum was obtained by Cary 630 Fourier Transform Infrared Spectrometer (Agilent Technologies) in wavenumber range of 4000 – 600 cm^{-1} . The purpose of this analysis is to identify the functional groups of the sugarcane bagasse, hydrolyzed cellulose and chitosan-cellulose composite. Received spectrum exhibits the correlation between the wavenumber (cm^{-1}) and intensity.

XRD

The diffractogram pattern was obtained with Shimadzu XRD-700 Series X-Ray. Diffractometer operates at 40kV and 30mA produces Cu K α with $\lambda = 0.154 \text{ nm}$ in the range $2\theta = 10\text{-}70^\circ$ uses a step size of $0.02^\circ/\text{min}$.

SEM

Micrograph was obtained by JSM-6510A/JSM-6510LA (Analytical/Analytical low vacuum SEM). The SEM images were taken with 100x and 500x magnification.

III RESULT AND DISCUSSION

Cellulose Isolation from Sugarcane Bagasse

Extraction of cellulose from sugarcane bagasse using H_2SO_4 with a concentration variation of 30, 40, and 50%, comparable to Cen et al. [14]. The different yields were stemmed from the different concentration of H_2SO_4 used for extraction where the addition of acid concentration decreased cellulose yield. This might be due to the ability of strong acid to degrade cellulose polymeric chain [15]. Figure 1 shows the FTIR spectra of initial sugarcane bagasse and isolated cellulose where the difference in the wavenumber and intensity confirm the isolated cellulose. Figure 1(a) exhibits absorption bands at 2900.94 cm^{-1} and 1068.92 cm^{-1} correspond to -CH and -CO vibrations, respectively. Absorption band at wave number 3410.15 cm^{-1} corresponds to OH vibration. A shift to the lower wave number can be observed in the isolated cellulose FTIR spectrum at 3367.71 cm^{-1} (Figure 1(b))

attributed to the depolymerization of hemicellulose and delignification.

Absorption band of raw sugarcane bagasse spectrum at around 1750 cm^{-1} which attributed to acetyl group (C=O) of hemicellulose ester or carbonyl ester of the *p*-coumaric monomeric lignin unit is not exhibited in the isolated cellulose spectrum. The sharper peak at around $1000\text{-}1240 \text{ cm}^{-1}$ is observed in the isolated cellulose spectra, compared to the one in raw sugarcane bagasse spectrum, attributing to cellulose characteristics. This signifies the increase of cellulose concentration, thus confirming the success of the hydrolysis.

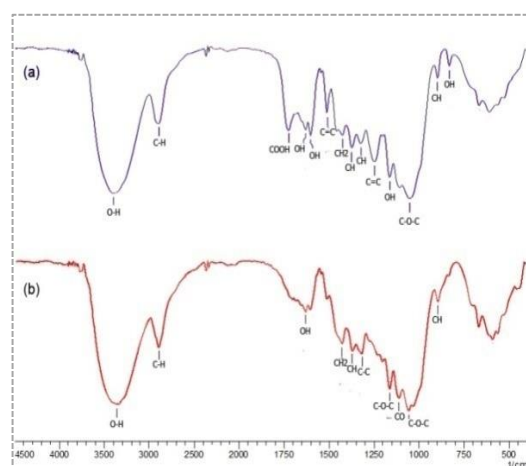


Figure 1 FTIR spectra of (a) sugarcane bagasse and (b) Isolated cellulose

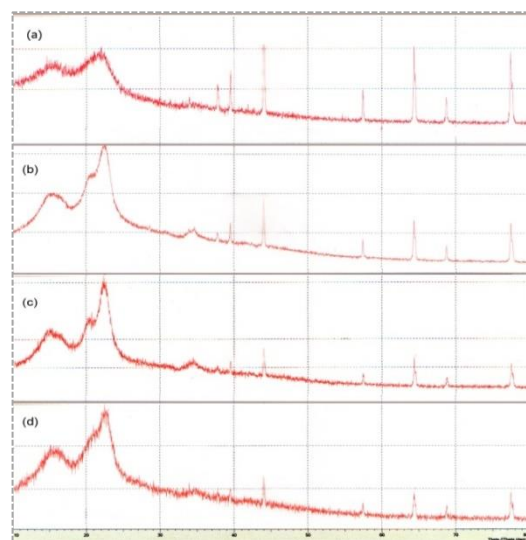


Figure 2 XRD patterns of (a) sugarcane bagasse, and cellulose isolated from sugarcane bagasse using (b) H_2SO_4 30%, (c) H_2SO_4 40% and (d) H_2SO_4 50%

Characterization using XRD was also carried out on sugarcane bagasse which was hydrolyzed using H_2SO_4 with different concentration variations to determine the effect of its

concentration on the XRD pattern produced. The results of characterization using XRD can be seen in Figure 2. XRD patterns of sugarcane bagasse (Figure 2(a)) and hydrolyzed sugarcane bagasse (Figure 2(b)-(d)) show typical peaks of cellulose at $2\theta = 16^\circ$ and 23° . However, XRD pattern of sugarcane bagasse shows lower intensity and broader peaks than XRD patterns of cellulose isolated from sugarcane bagasse with various concentration of H_2SO_4 . It indicates the crystallinity of sugarcane bagasse was lower than isolated cellulose. This low crystallinity was contributed by noncellulose compounds in the sample such as lignin and hemicellulose. After hydrolysis process, noncellulose compounds content decreased and resulting relatively pure cellulose with higher crystallinity. The highest crystallinity was obtained at concentration of H_2SO_4 40%. At concentration 50% of H_2SO_4 , the crystallinity of the obtained cellulose was decrease. It was due to some crystalline part of cellulose starts to decompose.

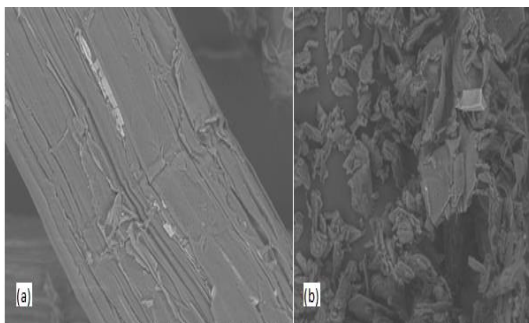


Figure 3 SEM images of (a) sugarcane bagasse and (b) cellulose isolated from sugarcane bagasse

Morphological observation was conducted with Scanning Electron Microscope (SEM), as shown by Figure 3. The surface morphology of raw sugarcane bagasse, as shown by Figure 3 (a), has a solid surface and well-ordered patterns. Meanwhile the surface morphology of isolated cellulose, as shown by Figure 3 (b), has an uneven particle distribution and incompact structure. This morphological change might suggest the successful hydrolysis. The determination of crystalline size was conducted to identify the average particle diameter size. As reported by and Mohan, et. al.[16] and Mahmood, et. al. [17], that the increase of acid concentration used in hydrolysis affects the particle size to be smaller. The average particle size of the isolated cellulose (Figure 3 (b)) is around 30-50 μm .

Preparation of chitosan-cellulose composite beads.

Characterization using FTIR instruments was conducted to observe the differences in

functional groups between chitosan, cellulose and chitosan-cellulose composite beads. The results of FTIR analysis are shown in Figure 4. The FTIR spectrum of chitosan shows the existence of a typical functional group of -NH at wave number 3443 cm^{-1} and bending vibration of amide groups is shown at wave number 1586 cm^{-1} . In addition, there are also other absorption bands of some functional groups such as C-O, C=O, C-H, and O-H at wave numbers 1700 cm^{-1} , 1658 cm^{-1} , 2866 cm^{-1} , and 3009 cm^{-1} , respectively.

Chitosan-cellulose composite beads FTIR spectrum shows absorption band of -NH vibration appears at lower wave number (3320 cm^{-1}). It is due to hydrogen bonding between chitosan and cellulose. It also shows the presence of C-H and C=O functional groups at wave numbers 2788 cm^{-1} and 1570 cm^{-1} , respectively. The chitosan-cellulose composite beads spectrum shows constituent functional groups of chitosan and cellulose. These results indicate the formation of chitosan-cellulose composite beads. This result is similar to the reports from Yang et. al. [18] and Lin, et. al. [19]

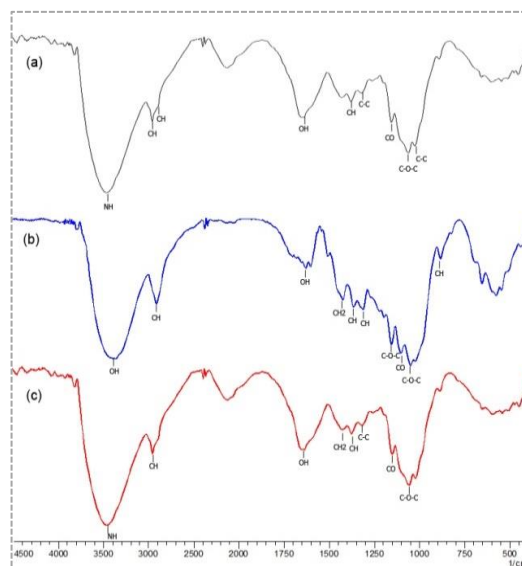


Figure 4 FTIR spectra of (a) chitosan, (b) cellulose isolated from sugarcane bagasse and (c) chitosan-cellulose composite beads

Characterization using X-Ray Diffraction (XRD) was conducted to determine the diffraction pattern materials before and after the synthesis of chitosan-cellulose composite beads. The result is shown in Figure 5. Figure 5(a) shows typical diffractogram of chitosan at $2\theta = 20^\circ$. Figure 5(b) is XRD pattern of cellulose isolated from sugarcane bagasse which shows typical diffractogram of cellulose at $2\theta = 16^\circ$ and 23° . Figure 5(c) is XRD pattern of chitosan-cellulose composite beads which

exhibits different XRD pattern compared with its initial materials (chitosan and cellulose).

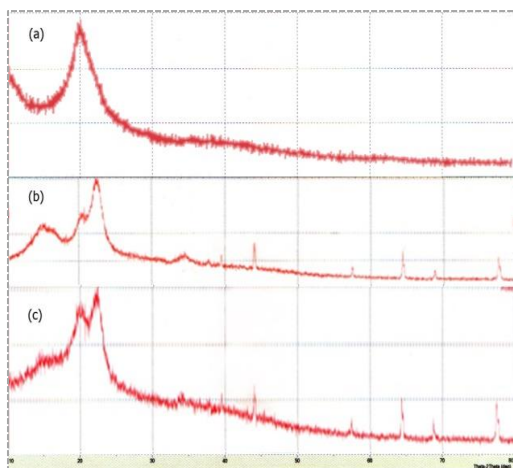


Figure 5 XRD patterns of (a) chitosan, (b) cellulose and (c) chitosan-cellulose composite beads

Diffractiongram of chitosan-cellulose composite beads shows combination of XRD patterns of chitosan and cellulose, where peaks appear at $2\theta = 15^\circ$, 20° and 23° with lower intensity and broader peaks than chitosan and cellulose. The similar results have also been reported by Lin et al. [19] and Dong et al. [20]. In addition, the decrease in intensity is due to cellulose chain binds to immobilized chitosan. Therefore the structure of chitosan is less organized and causes more amorphous properties. It indicates that chitosan has been successfully modified with cellulose.

The surface morphology of chitosan-cellulose composite was obtained with SEM analysis. It is shown in Figure (6). SEM image at 100 times magnification displays the formation of bead shape of chitosan-cellulose composite. The aim of having the bead-shaped composite is to increase the practical use as an adsorbent.

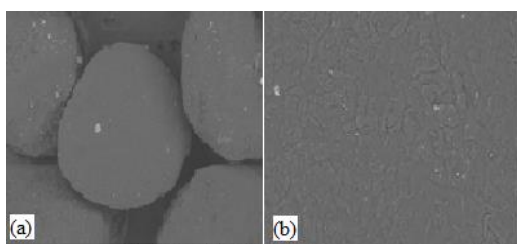


Figure 6 SEM images of chitosan-cellulose composite beads at (a) 100 x magnification and (b) 500 x magnification

Bead shape helps the adsorption process due to its compact material compared to powder adsorbents. Therefore, the adsorption can be more efficient in adsorbing the dissolved the metal ions due to its gravitational force, thus

can reach the bottom part of the solution. In comparison, powder adsorbent unable to reach the bottom part due to their tendency to float at the solution surface.

The SEM characterization at 500 times magnification suggests the surface morphology of the chitosan-cellulose composite beads. According to the image, it can be observed the even distribution of cellulose and chitosan indicated by the smooth structure of the composite surface. This confirms that the composite has been successfully prepared.

CONCLUSION

Cellulose has been successfully isolated from sugarcane bagasse using H_2SO_4 . The XRD analysis showed that cellulose crystallinity was influenced by the concentration of H_2SO_4 used in the hydrolysis process. The highest crystallinity was found at 40% H_2SO_4 concentration. SEM confirmed the morphological picture of cellulose isolated from bagasse with different particle sizes because of the hydrolysis process. This result shows that sugarcane bagasse can be used as a potential source of cellulose. Cellulose isolated from sugarcane bagasse has been used as filler in chitosan-cellulose composite beads preparation. The existence of cellulose in the composite causes the decrease of chitosan crystallinity.

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