THE USE OF CITRIC ACID MODIFIED BACTERIAL CELULLOSE AS AN ENVIROMENTALLY FRIENDLY ADSORBENT

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ABSTRACT
The use of nata de coco as an ester cellulose raw material through esterification using various of carboxylic acids has been widely conducted. In this study, it was used citric acid with three carboxyl groups. This aim research were to determine the optimum reactant composition and to compare the cellulose citrate properties toward bacterial cellulose and commercial ester cellulose. Esterification at mass ratio of nata : citric acid were 1 : 1 up to 1 : 9 were conducting at temperature of 150°C. The optimum ester cellulose produced, were then characterized based on the FTIR spectrophotometry, hydrophobicity and degree of crystallinity. Furthermore, the surface area has been determined in order to find out its potency as an adsorbent. The result revealed that reaction using citric acid has affect on chemical structure and hydrophobicity. The increase of hydrophobicity and degree of crystallinity was influenced by citric acid added. On the other hand, it was obtained that cellulose citrate could be develop as an adsorbent.

Keywords : cellulose, esterification, citric acid, adsorbent

1. INTRODUCTION
The use of nata cellulosic as an ester cellulose raw material has been widely conducted due to its advantages. Nata de coco cellulose has a high purity with density between 300 and 900 kg/m³ and has a high tensile strength. It is also elastic and biodegradable (Krystinowicz, 2005). Cellulose modification using acetic acid anhydrid, propionic acid and stearic acid into ester cellulose has been studied (Nagel and Heinze, 2012; Feng-Yuang Hang, 2012). It has also produced using citric acid, an acid which have three functional groups of carboxylic acid (Kamulyan, 2014). The ester functional groups, substituting hydroxyl groups of cellulose, could be changed the nata thin film properties was more hydrophobic. This could give advantages on cellulose application as an adsorbent. Comparing to nata de coco, it has less swelling degree, so, it could be used as a selective adsorbent. On the other hand, citric acid modified cellulose, has possibility formed a porous material due to crosslink formation.

In previous research, the use of citric acid was a crosslinking agent or crosslinker of starch derivate. It was produced a polymers with has more water resistant (Reddy and Yang, 2010). The crosslinking is bonding between a polymer bonds each other, both of covalent or ionic bonding. Cellulose citrate has a capability of metal ion adsorption (Thanh, D.H and Nhung, H.L., 2009).

It is well known that esterification of hydroxyl functional groups on carboxyl was condensation reaction which produced water as a by product. Thus, the backward reaction of ester hydrolysis could be occurred. In order to reduce the ester hydrolysis, the heterogeneous esterification using dibutyltin oxide as an organometallic catalyst has been investigated. In addition, the by product formation could be minimalized through solid state reaction. In fact, reactants used in this study i.e. nata cellulosic and citric acid were renewable and sustainable natural resources, thus it provides advantages.

Esterification condition such as the amount of citric acid could affect ester cellulose produced. Modification cellulose into cellulose citrate will change several properties, as well as chemical structure and hydrophilicity or hydrophobicity. The investigation done is to compare the nata cellulosic properties, before and after reacting with citric acid, also it was then compared against commercial cellulose ester. Furthermore, its possibility used as an adsorbent has been studied. That is, in order to produce a cellulose citrate matrix for enzyme
immobilize, modification at various reactant composition has been carried out.

2. METHODOLOGY

2.1. Experimental

The purified nata de coco gel was made into thin film using heat-pressed at temperature of 120°C for 5 minutes. It was then pulverized in order to enlarge the surface area. Esterification cellulose powder and citric acid by solid state reaction has been done. resulting ester and the reactant remain were separated and the yielding was determined. The optimum cellulose ester obtained, was then characterized for finding out the changes chemical and physical properties, the potency as an adsorbent was investigated based on surface area, determined through stearic acid adsorption in benzene solvent. Quantitative analysis was done volumetrically using alcoholic NaOH.

2.2. Material

Nata de coco, obtained from local producer, was purified and heat-pressed into thin film. Citric acid used was bought from Chemical store, while dibutyltin oxide (pro analysis) was obtained from Merck.

2.3. Equipment

The main equipment was closed stainless-steel reactor supporting by mechanical stirrer and heater (Figure 1).

![Figure 1. Esterification reactor](image)

Note:
1. Reactor
2. Heater connected with thermocouple
3. Heating regulator
4. Mechanical stirrer

Instrument used was FTIR Spectrophotometer (Shimadzu 8400S, Chemistry Department, Brawijaya University), X-Ray Diffraction (PANalytical Xpert PRO, State University of Malang).

2.4. Synthesis of Cellulose Citrate

Nata cellulose powder was esterified using citric acid at variation of mass ratio nata : citric acid were 1 : 1, 1 : 3, 1 : 5, 1 : 7 and 1 : 9. It has been performed with added 1% catalyst, at temperature of 150°C for 3 hours. Product obtained was washed using aquadest. The solid was filtered, then was dried and last was weighed. Finally, it was calculated to find out the yield. Meanwhile, the filtrate was analyzed for determining the residual unreact-ting citric acid by titration alakalimetry. Thus, it was used for deciding the esterification rate.

2.5. Characterization of Cellulose Ester

The optimum cellulose ester produced was further characterized including chemical properties and physical properties i.e. hydrophobicity and degree of crystallinity.

Chemical structure was analyzed by FTIR spectrophotometry using KBr pellets at wave number of 4000-400 cm⁻¹. The spectrum was interpretated for identifying the changes of functional groups, before and after esterification. It was then compared with commercial cellulose ester.

In addition, the degree of substitution was also observed through saponification using alcoholic NaOH. The excess of NaOH was then reacted with HCl for 12 hours and was analyzed by titration alkaliometry.

On the other hand, hydrophobicity was measured based on degree of swelling. It has been done using aquadest for 1, 2, 3, 4 and 5 days. Moreover, degree of crystallinity was analyzed by X-ray diffraction using Cu Kα radiation (40 mA, 40 KV) at 20 of 5° to 75°. Similarly, the diffractogram pattern was compared between cellulose, cellulose citrate and commercial cellulose ester. Degree of crystallinity was calculated based on peak area and determined using approach methods gravimetrically.

2.6. Potency as Adsorbent

The potency of cellulose citrate as an adsorbent has been investigated through surface
area determination. It has been done using stearic acid at 0.005M; 0.01M; 0.025M; 0.05M; 0.075M and 0.1M of concentration. Furthermore, it was adsorbed for 180 minutes and filtered. The stearic acid remained was measured volumetrically using 0.05M alcoholic NaOH. The surface area, S, was calculated using following equation:

\[ S = \frac{C_m A_m N}{M} \]  

C_m = amount of adsorbate (g/g adsorbent)  
N = Avogadro number  
M = adsorbate molecular weight  
A_m = adsorbate cross sectional area

3. RESULT AND DISCUSSION

3.1. Yield and Esterification Rate

In order to purify the esterification product, unreacted citric acid and catalyst was removed. Thus, mass of purified cellulose ester and total mass of reactant was compared and was calculated as yield. The yield, before and after purification, was described on figure 2.

![Figure 2. Yield of cellulose citrate](image)

Unpurified product at ratio of 1 : 3 up to 1 : 7 has similar yield. In contrast, the lowest yield was the purified product at ratio of 1 : 5 (Fig. 2), thus, it was the highest mass lost. However, the mass lost will be inversely proportional to the reacting citric acid, therefore, the highest reaction rate will be established at mass ratio 1 : 3 or 1 : 7. Accordingly, the average rate of esterification has been determined. In fact, the number of hydroxyl functional groups was much more than the number of citric acid carboxyl, hence, esterification rate is assumed depend on citric acid amount. The average rate at various initial concentration was showed at figure 3.

![Figure 3. Average rate of cellulose esterification](image)

Although the highest average rate was obtained at mass ratio of 1 : 5, however it was the lowest yield of ester produced. This result showed that, even if the initial rate was the highest, however, this will decrease due to the increasing hydroxyl functional groups reacting with carboxyl functional groups. Meanwhile, the number of carboxyl functional groups reacting increase, this lead the further reaction will be more difficult due to the barrier effect, thus, will decrease the reaction rate. Although at mass ratio of 1 : 7 and 1 : 3 has similar product yield, however, cellulose ester obtained at ratio of 1 : 7 was sticky. Therefore the optimal mass ratio of esterification product was 1 : 3.

3.2. Chemical Structure and Degree of Substitution

Cellulose ester chemical structure was analyzed and interpreted based on FTIR spectrum (Fig. 4, 5 and 6).

![Figure 4. FTIR Spectrum of nata de coco cellulose](image)
The result of interpreted spectrum above was described as following table.

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Wave number (cm(^{-1}))</th>
<th>cellulose</th>
<th>Cellulose citrate</th>
<th>Cellulose ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH stretch</td>
<td>3328.76</td>
<td>3348.70</td>
<td>3455.84</td>
<td></td>
</tr>
<tr>
<td>-CH stretch</td>
<td>2926.01</td>
<td>2838.81</td>
<td>2822.56</td>
<td></td>
</tr>
<tr>
<td>-C=O stretch</td>
<td>-</td>
<td>1747.39</td>
<td>1751.01</td>
<td></td>
</tr>
<tr>
<td>-OH bending</td>
<td>1655.21</td>
<td>-</td>
<td>1650.12</td>
<td></td>
</tr>
<tr>
<td>-C-H bending</td>
<td>1437.22</td>
<td>1469.28</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>-N-O stretch</td>
<td>-</td>
<td>-</td>
<td>1284.50</td>
<td></td>
</tr>
<tr>
<td>-C-O stretch</td>
<td>1111.24</td>
<td>-</td>
<td>1052.36</td>
<td></td>
</tr>
</tbody>
</table>

In comparison, the different FTIR spectrum of cellulose and cellulose citrate was mainly performed at wave number of 1700 cm\(^{-1}\). It was indicated the specific vibration of ester carbonyl functional groups. Meanwhile, the intensity FTIR spectra on hydroxyl functional groups was almost high. This phenomenon can be explained that there were many unreacted cellulose hydroxyl functional groups. In contrast, the hydroxyl peak of commercial cellulose ester spectra was stronger than others, where as, it were wider than commercial cellulose ester. The presence of different peak pattern indicated that there were different on degree of substitution. In addition, it was showed that the wave number of hydroxyl functional groups were slightly shifted into higher position, by comparison cellulose spectra than others. It can confirm the presence of hydrogen bonding between hydroxyl and carbonyl functional groups, both inter and intra molecular. There was limited hydrogen bonding on cellulose, otherwise it were many of two others molecules.

The carbonyl functional groups of commercial cellulose ester was more dominant than others. This indicated there was different in degree of substitution. Degree of substitution was equal with the average number of substituent for every unit of glucose anhydride. There were 3 hydroxyl functional groups of cellulose monomer that could be substituted, i.e. C\(_2\), C\(_3\) and C\(_6\) positions. Thus, there were maximum 3 hydroxyl functional groups can be substituted. (Van de Burg, et. al., 2000). The analysis result showed that the cellulose citrate has degree of substitution of 0.314. Therefore, there were many hydroxyl functional groups unesterified.

3.3. Swelling Index and Hydrophobicity

Hydrophobicity was inversely proportional with the ability of water attracting. Therefore, in order to predict the hydrophobicity, degree of swelling on water as an approach methods has been conducted, as shown at Figure 7.
The trendline of curve could be used to determine the equilibrium time of swelling phenomenon. This can be calculated as turning point.

Table 2. The equilibrium time and degree of swelling

<table>
<thead>
<tr>
<th>Material</th>
<th>Equation</th>
<th>Time (days)</th>
<th>Degree of swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>$y = -0.8645x^3 + 9.5838x^2 + 32.748x$</td>
<td>3.7</td>
<td>208.26</td>
</tr>
<tr>
<td>Cellulose citrate</td>
<td>$y = -5.5583x^3 + 38.307x^2 - 9.985$</td>
<td>2.3</td>
<td>111.84</td>
</tr>
<tr>
<td>Commercial cellulose ester</td>
<td>$y = 1.0778x^3 - 3.775x^2 + 39.046x$</td>
<td>1.2</td>
<td>49.02</td>
</tr>
</tbody>
</table>

Cellulose degree of swelling (table 2) was higher than others. It was also showed, time of equilibrium was longer, thus, confirmed that it was more hydrophilic. The presence of citric functional groups cause in changing its properties was more hydrophobic. Where as, compared with commercial cellulose ester, the hydrophobicity was increasing, in accordance with degree of substitution.

It was well known that nata cellulose structure has amorphous phase. Hence, the ability on water attracting was higher than others. Therefore, water diffusion into cellulose molecule, through permeation mechanism, was higher although with slower rate. As a result, the cellulose equilibrium time was longer than the others. Due to many unreacted hydroxyl functional groups of cellulose, its degree of swelling was high. In contrast, water was entering cellulose citrate was obtained through porous diffusion mechanism; hence, diffusion rate was faster and also in equilibrium time obtained. However, the degree of swelling was lower (Reddy, N., dan Yang, Y., 2010).

3.4. Degree of Crystallinity

Accordingly, the change of structure could affect on degree of regularity, so it will affect on degree of crystallinity. Therefore it is important to measure it by X-ray diffraction methods.

It was showed on figure 8 that diffractogram has similar pattern, indicating the similarly crystal structure. However, two specific peaks have a slightly different intensity. One of specific area of cellulose was of 200 region at 20 was 22-25°.

![Figure 8. Diffractogram Cellulose and cellulose ester](image)

By comparison, the commercial cellulose ester intensity was higher than others, indicating the higher degree of crystallinity. Degree of crystallinity was calculated based on peak area, measured by approach methods using gravimetric. As result degree of crystallinity of cellulose, cellulose citrate and commercial cellulose ester were 57.31%, 64.59% and 78.34%, respectively.

The presence of carbonyl functional groups cause molecules was more regular of structure, since it was hydrogen bonding obtained from carbonyl oxygen atomic and hydroxyl hydrogen atomic. This was produced since condensation was performed at material heating stage, both intra and inter molecular.

Consequently, changing in regularity and hydrophobicity will cause the role of material in application (Halib, 2012). Cellulose was hydrophilic; hence it was not suitable used as an adsorbent for adsorption in water system. Otherwise, cellulose citrate has potency. Thus, in order to predict, the determination of surface area has been done.

3.5. Potency Cellulose Citrate as an Adsorbent

In order to confirm the possibility of using cellulose citrate as an adsorbent, the surface area through stearic acid adsorption has been conducted. It has been done using benzene...
as a solvent and various stearic acid concentration.

![Figure 9. Adsorption of stearic acid on cellulose citrate](image)

It was shown at figure 9, the point of x/m of 0.44 g/g cellulose citrate was an important number. It was calculated that cellulose citrate has a surfaces area of 460.3 m²/g. In brief, it was showed that cellulose citrate has potency used as adsorbent.

4. CONCLUSION

1. The optimal esterification composition was at mass ratio of nata cellulose : citric acid was 1 : 3, obtained 0.314 in degree of substitution
2. Esterification of nata cellulose using citric acid cause the increasing in hydrophobicity and degree of crystallinity.
3. Cellulose citrate could be used as an adsorbent

5. Acknowledge

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