Calcium alginate-TiO$_2$/SiO$_2$ nanocomposite for glucose conversion to 5-hydroxymethylfurfural

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Abstract. The sodium alginate biopolymer used to form calcium alginate-TiO$_2$/SiO$_2$ nanocomposite has been successfully synthesized. The first stage is synthesis of TiO$_2$/SiO$_2$ composites by the sol-gel method using tetraethyl orthosilicate (TEOS) and titanium isopropoxide (TTIP) precursors. Calcium alginate nanocomposite is formed from the crosslinking process between Ca$^2+$ ions from CaCl$_2$ and sodium alginate combined with TiO$_2$/SiO$_2$ composites, characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Tunneling Electron Microscopy (TEM). The average particle size of TiO$_2$/SiO$_2$ composite on the surface of calcium alginate obtained by TEM is about 50 nm. The application of calcium alginate-TiO$_2$/SiO$_2$ nanocomposite as catalyst is used for conversion of glucose into 5-hydroxymethylfurfural (HMF) using dimethyl sulfoxide (DMSO) solvents. The best glucose conversion obtained at 140 °C for 4 hours is 97 % and optimum HMF yield obtained at 140 °C and 5 hours is 40 %. Nanocomposites based on sodium alginate biopolymers combined with TiO$_2$/SiO$_2$ composites can be developed as new superior materials and promising catalysts because it is easily obtained and biodegradable.

Keywords: biodegradable, glucose, HMF, nanocomposite, sodium alginate

1. Introduction

The most widely used biopolymer in several industrial sectors is alginate based on brown algae in the form of sodium alginate. Indonesia is the second largest country to produce 50 % of seaweed, which is widely found in the waters. A species of seaweed is Sargassum sp, so that Indonesia has great potential in producing and using the alginate compound [1]. Calcium alginate nanoparticles can be formed from sodium alginate by ionic gelation method with the addition of calcium chloride to form a calcium alginate gel, which is crosslinked with Ca$^2+$ ion. Nano calcium alginate has a large surface area, mechanical strength and high stability [2].

Recently, heterogeneous catalysts are used as substitute for homogeneous catalysts, due to the use of heterogeneous catalysts have advantages, such as the properties of acids or bases can be controlled, have stability to heat and environmentally friendly. The heterogeneous catalysts mostly used are metal oxides namely, SiO$_2$, TiO$_2$, ZrO$_2$, and so on, because it has the acid and base properties [3]. The formation of metal oxide nanocomposite with biopolymers is one alternative to increase the catalyst activity. The incorporation of alginate with metal oxides such as TiO$_2$ and SiO$_2$ will produce a porous catalyst, thermal stability, mechanical strength and better catalytic activity [4].

Glucose and fructose can be converted into furan derivatives, namely 5-hydroxymethylfurfural (HMF) and 5-ethoxymethylfurfural (EMF). The source of glucose in nature is easier to obtain than fructose [5], so the synthesis of 5-hydroxymethylfurfural is more economical using glucose as raw material [6]. 5-hydroxymethylfurfural (HMF) is a compound that is widely used for the production of chemicals and fuels. HMF compounds are taken from petroleum sources, with limited availability [7]. The synthesis process of 5-hydroxymethylfurfural uses solvents; high boiling point of organic solvents.
is preferable than water, such as dimethyl sulfoxide (DMSO) [8]. Some researchers have conducted studies of HMF synthesis from cellulose, glucose and fructose. Glucose conversion to 5-hydroxymethylfurfural using TiO₂ catalyst in water, the glucose conversion obtained 30 % HMF [9]. The catalysts of SO₄/TiO₂/SiO₂, which have a large number of Bronsted acid sites, produce 77 % HMF from fructose in DMSO solvents [10].

In this study, calcium alginate-TiO₂/SiO₂ nanocomposite was synthesized in several stages; the first stage was the synthesis of TiO₂/SiO₂ composites, which referred to the previously reported study [10]. The second stage is the formation of TiO₂/SiO₂ calcium alginate nanocomposite which referred to the study reported [11,12] in which composite TiO₂/SiO₂ is combined into sodium alginate solution with crosslinked Ca²⁺ ion. The success of nanocomposite synthesis is supported by characterization with Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Tunneling Electron Microscopy (TEM). The nanocomposite is used as a catalyst for conversion of glucose to HMF by referring to the previously reported study [3,8].

2. Materials and methods

2.1. Materials
Sodium alginate from brown algae according to our previous study [13,14]; CaCl₂·2H₂O (Merck Co) as calcium alginate forming material; tetraethyl orthosilicate, TEOS (Merck Co); titanium isopropoxide, TTIP (Sigma Aldrich) as a precursor of TiO₂ and SiO₂; glucose anhydrous (Merck Co) as reactants to form 5-hydroxymethylfurfural, HMF and dimethyl sulfoxide, DMSO (Merck Co) as glucose solvents.

2.2. Synthesis of TiO₂/SiO₂ composites
The synthesis of TiO₂/SiO₂ refers to previous studies [10]. The precursors of tetraethyl orthosilicate and titanium isopropoxide were dissolved with ethanol separately. Then, the tetraethyl orthosilicate solution was added with HCl solution until pH 3 is reached. The solution of titanium isopropoxide was mixed into a tetraethyl orthosilicate solution and stirred for 2 hours at 80 °C. The mixture was calcined at temperature 550 °C for 6 hours.

2.3. Synthesis of TiO₂/SiO₂ calcium alginate nanocomposite
The synthesis of calcium alginate-TiO₂/SiO₂ nanocomposite referred to previous studies [11,12]. TiO₂/SiO₂ composites were added to sodium alginate solution which has been mixed with calcium chloride and stirred until the suspension was formed and stirred for 1 hour, furthermore dried by freeze drying, to obtain calcium alginate-TiO₂/SiO₂ nanocomposite and characterized by FTIR, SÉM and TEM.

2.4. Nanocomposite application as catalyst of glucose to HMF
The conversion of glucose to HMF referred to previous studies [3,8]. Anhydrous glucose was dissolved in DMSO, and then calcium alginate-TiO₂/SiO₂ nanocomposite catalyst was added to the glucose solution. The unreacted glucose and HMF concentrations formed were analyzed by High Performance Liquid Chromatography (HPLC). Glucose analysis was used EC-C18 columns, refractive index detectors, and water mobile phases. HMF analysis was used C18 reversed phase column with a UV-Vis detector at a wavelength of 285 nm. A mixture of methanol and water was used as the mobile phase. Glucose and HMF concentrations were obtained using a standard curve.

3. Results and discussion

3.1. Calcium alginate - TiO₂ / SiO₂ nanocomposite
The first stage of TiO₂/SiO₂ composites synthesis was using sol-gel method with tetraethyl orthosilicate precursors dissolved in ethanol Si(OEt)₄ and titanium isopropoxide dissolved with ethanol Ti(OPr). The hydrolysis process occurs when adding water to tetraethyl orthosilicate solution produces Si(OH)(OEt)₄, silica colloid as can be seen in equation (1). The addition of Ti(OPr)₄ produces Ti(OSi(OEt)₃), titanium-silica colloidal in equation (2). Furthermore, it was heated to form TiO₂/SiO₂ composite, where the remaining water and ethanol will evaporate; the estimated reaction can be seen in equation (3) by referring to Kibombo et al. [15] with modification.

\[
\text{Si(OEt)}_4 + H_2O \rightarrow Si(OH)(OEt)_3 + EtOH
\]

\[
4Si(OH)(OEt)_3 + Ti(OPr)_4 \rightarrow Ti(OSi(OEt)_3)_4 + 4PrOH
\]

\[
\text{Si(OEt)}_4 + H_2O \rightarrow Si(OH)(OEt)_3 + EtOH
\]
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Figure 1. FTIR spectrum of (a) sodium alginate (b) TiO/\(\text{SiO}_2\), and (c) nanocomposite of calcium alginate-TiO/\(\text{SiO}_2\),

\[
\text{Ti}[\text{OSi(}\text{OEt}_3\text{]}_4 + n \text{H}_2\text{O} \rightarrow O - Si - O - Ti - O - Si - O + n \text{EtOH}
\]

The second stage was done for the synthesis of calcium alginate-\(\text{TiO}/\text{SiO}_2\) nanocomposite, by combining sodium alginate, which has been mixed with calcium chloride, then added to \(\text{TiO}/\text{SiO}_2\) composites. The nanocomposite formed will provide pore properties, thermal stability and mechanical strength so that catalytic activity will be better [16].

3.2. Characterization

3.2.1. Analysis of FTIR. Figure 1a shows the sodium alginate FTIR spectrum around 2900–3300 cm\(^{-1}\), is stretching O-H vibration with high intensity; it causes sodium alginate to have many hydroxyl groups. The asymmetric and symmetric stretching vibrations of COO\(^-\) at 1604.1 cm\(^{-1}\) and 1407.1 cm\(^{-1}\), respectively. The C-O stretching vibration of the pyranose ring at 1135.19 cm\(^{-1}\) and 1025.02 cm\(^{-1}\). The alginate typical vibrations of C-O uronic acid at 946.8 and 885.2 cm\(^{-1}\) and vibrations of C-H mannuronic acid at 805.6 cm\(^{-1}\). Figure 1b shows spectrum of \(\text{TiO}/\text{SiO}_2\) composite, the peak Si-O-Si at 1075.9 cm\(^{-1}\) derived from SiO\(_2\) compound and the peak of Si-O-Ti at 942.7 cm\(^{-1}\), this indicates that Si-O-Ti bonds was formed. The peak of Ti-O-Ti appears at 641.00 cm\(^{-1}\) derived from TiO\(_2\) compound. Figure 1c showed calcium alginate-TiO/\(\text{SiO}_2\) spectrum consists of O-H vibration around 2925–3275 cm\(^{-1}\), its intensity decreases compared to sodium alginate in figure 1a; it is caused O-H group to bind with \(\text{TiO}/\text{SiO}_2\). The asymmetric of COO\(^-\) at 1691.5 cm\(^{-1}\) which overlaps to vibration of C = O and the symmetric of COO\(^-\) at 1499.6 cm\(^{-1}\). The Si-O-Si vibration at 1025.7 cm\(^{-1}\) overlaps with vibration of C-O and C-C. The Si-O-Ti vibration at 1075.4 cm\(^{-1}\), which overlaps with the vibration of C-O uronic acid at 995.4 cm\(^{-1}\). There is Si-OH vibration at 840.9 cm\(^{-1}\), which overlaps with the vibration of C-H mannuronic acid. The Ti-O-Ti vibration is shifted to 600 cm\(^{-1}\). The characterization with FTIR showed the successful formation of \(\text{TiO}/\text{SiO}_2\) calcium alginate nanocomposite.

3.2.2. Morphology with SEM. The morphology using SEM is shown in figure 2. Figure 2a is the morphology of sodium alginate having fibril layer with uniform surface. Figure 2b is composite of \(\text{TiO}/\text{SiO}_2\) shows the small granular of TiO\(_2\) compounds and the SiO\(_2\) silica in larger granular and non-uniform. Figure 2c is calcium alginate-\(\text{TiO}/\text{SiO}_2\) nanocomposite shows the presence of evenly distributed \(\text{TiO}/\text{SiO}_2\) composites on the surface of sodium alginate. These results support the successful synthesis of \(\text{TiO}/\text{SiO}_2\) nanocomposites.
Figure 2. SEM Morphology of (a) sodium alginate (b) TiO$_2$/SiO$_2$ (c) nanocomposite of calcium alginate-TiO$_2$/SiO$_2$

Figure 3. TEM morphology of calcium alginate-TiO$_2$/SiO$_2$ nanocomposite

3.2.3. TEM morphology. The morphology of calcium alginate-TiO$_2$/SiO$_2$ nanocomposite analyzed by TEM is shown in figure 3. It can be seen the grey colored of calcium alginate, while the TiO$_2$/SiO$_2$ composite is black, it was caused by TiO$_2$/SiO$_2$ composite on the surface of calcium alginate, so that can be observed clearly. The average particle size of TiO$_2$/SiO$_2$ composite at calcium alginate surface obtained by TEM is about 50 nm.

3.2.4. Application nanocomposite as catalyst of HMF from glucose. The formation of HMF from glucose using catalyst of calcium alginate-TiO$_2$/SiO$_2$ nanocomposite was done with reaction temperature variations of 80º, 100º, 120º, 140º and 160 ºC and time variations of 1, 2, 3, 4 and 5 hours. The unreacted glucose and formed HMF were analyzed by HPLC. Figure 4 shows the effect of temperature of glucose conversion, it was observed the unreacted glucose or conversion of glucose to HMF. It was seen that glucose conversion increases as the temperature rises and optimal conversion was obtained at 140 ºC, and then constant up to 160 ºC. This is because at low temperatures the reaction rate is slow and at high temperature at 140 ºC the optimum reaction rate is obtained, so that glucose conversion is 97 %. Figure 5 shows the effect of time to glucose conversion. It can be seen that as the reaction time rises, the glucose reacted will increase and the obtained optimum time is 4 hours and constant up to 5 hours is 97 %.

After obtaining the optimum temperature and time for glucose conversion to HMF by measurement of unreacted glucose, it was obtained at 140 ºC and 4 hours. Furthermore, the concentration of HMF formed was determined against the reaction time as can be seen in figure 6. It shows that the formation of HMF can be observed at 4 hours and maximum at 5 hours is 40 %.

The reaction profile of glucose concentration consumption and HMF formation at temperature 140 ºC by time variation 1, 2, 3, 4, 5 and 6 hours are illustrated in figure 7. In figure 7 it can be
Figure 4. Effect of temperature to glucose conversion

Figure 5. Effect of reaction time to glucose conversion

Figure 6. Effect of reaction time to HMF yield

Figure 7. Profile of reaction to glucose conversion (red) and HMF yield (blue)

Figure 8. The reaction of HMF formation from glucose

observed that glucose concentration (red) decreases towards time and reaches equilibrium at 4 hours, whereas, HMF concentration (blue) can be observed after 4 hours and rises at 5 hours then the equilibrium is obtained, this is due to the formation of HMF needs a long time, which causes the first fructose to be formed then formed the HMF and fructose in reversible reaction with glucose as shown in figure 8. This supports the fact that the synthesized nanocomposite is capable to be applied as a catalyst for HMF formation from glucose.

4. Conclusions
The nanocomposite of calcium alginate-TiO$_2$/SiO$_2$ was successfully synthesized, supported by FTIR, SEM and TEM. The average particle size of TiO$_2$/SiO$_2$ composite on the surface of calcium alginate obtained by TEM was about 50 nm. The application of calcium alginate-TiO$_2$/SiO$_2$ nanocomposite as catalyst was used for conversion of glucose into 5-hydroxymethylfurfural (HMF) using dimethyl sulfoxide (DMSO) solvents. The best glucose conversion obtained at 140 °C and 4 hours is 97 % and optimum HMF yield obtained at 140 °C and 5 hours is 40 %.

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