SYNTHESIS AND CHARACTERIZATION OF BAGASSE (*Saccharumofficinarum* L.) SILICA GEL MODIFIED DIPHENYLCARBAZONE

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Abstract: Bagasse is a solid waste from the sugar cane milling process in the sugar industry. The waste can be used as an ingredient in making silica gel which functions as an adsorbent. This can be done by changing its chemical structure composition to increase its role and function. This study aims to determine the characteristics of silica gel synthesized from bagasse (*Saccharumofficinarum L.*) and modified using diphenylcarbazone as much as 0.24 g with sol-gel technique. The characterization results obtained from Fourier transform infrared (FTIR) analysis of diphenylcarbazone modified silica gel, namely the absorption of Si-OH, Si-O-Si groups supported by the appearance of C=O, C=N, NH, and N=N groups. Characterization using x-ray diffraction (XRD) showed a change in amorphous silica to crystals, with the results obtained showing a crystal size of 41.468 nm.
Keywords: Bagasse, Silica Gel, Diphenylcarbazone

Abstrak: Ampas tebu merupakan limbah padat yang berasal dari proses penggilingan tebu pada produksi gula. Limbah tersebut dapat dimanfaatkan sebagai bahan pembuatan silika gel yang berfungsi sebagai adsorben. Hal tersebut dapat dilakukan dengan mengubah komposisi struktur kimianya agar dapat meningkatkan peran dan fungsinya. Penelitian ini bertujuan untuk mengetahui karakteristik silika gel yang disintesis dari ampas tebu (*Saccharumofficinarum L.)* dan dimodifikasi menggunakan difenilkarbazon sebanyak 0,24 gr dengan teknik sol-gel. Diperoleh hasil karakterisasi dari analisis *fourier transform infrared* (FTIR) terhadap silika gel termodifikasi difenilkarbazon menunjukkan adanya serapan gugus Si-OH, Si-O-Si yang didukung dengan pembentukan gugus C=O, C=N, N-H, dan N=N. Karakterisasi menggunakan difraksi sinar-x (XRD) menunjukkan perubahan silika *amorf* menjadi kristal dengan hasil yang diperoleh memperlihatkan ukuran kristal sebesar 41,468 nm.
Kata Kunci: Ampas Tebu, Silika Gel, Difenilkarbazon

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Introduction

Indonesia is one of the largest sugarcane producers globally (Sheth, 2017). Sugarcane is the easiest crop to grow in the lowlands and tropical climates, which only takes about a year to be harvested. One of the uses of sugarcane is as a sugar producer (Apriawan et al., 2015), which is a basic requirement, especially in Indonesia. In sugarcane processing, there are side products that will be released after the sugarcane is pressed. It is called bagasse (Sholeh et al., 2020).

One of the uses of bagasse containing a lot of silica can be used for making silica or biosilica (Mupa et al., 2015), (Sjamsiah et al., 2017), (Norsuraya et al., 2016) (Alves et al., 2017). Iqbal et al. (2016) reported that characterization of silica gel from bagasse waste was successfully made with the –OH and silanol functional groups. The resulted characteristics were almost the same as commercial silica gel. Channoy et al. (2018) also reported silica gel from bagasse ash which contained silica amorphous.

Synthesis of silica gel can be modified with organic compounds such as trimethylchlorosilane (Huang et al., 2018), 3-amino propyl triethoxysilane (Purwanto et al., 2017), 2,2′-(hexane-1,6-diylbis(oxy))dibenzaldehyde (SiO_2-NH_2-BH) (Banaei et al., 2017) and diphenylcarbazone to change the chemical composition or structure on the surface of the silica gel which affects the absorption process significantly. Sudiarta et al. (2013), Nopianingsih et al. (2015) produced a modification of silica gel with diphenylcarbazone from rice husk ash that was successfully made, as shown by the presence of a silanol group, a siloxane group, an N-H group, an Ar-H aromatic group and a C=O group with the characterization of the infrared spectrophotometer.

The modification process can be carried out by two chemical methods. They are homogeneous reactions (sol-gel technique) and heterogeneous reactions. The sol-gel technique is one of the simpler techniques that can be performed in the laboratory with a simple device whose binding reaction occurs simultaneously with the formation of solids. The sol-gel technique's advantages are it has high purity and it can be worked at room temperature. Furthermore, the particle properties can be controlled, and the adsorbent is obtained with mechanical stability (Buhani & Suharso, 2010) (Serena, 2019) (Carrera-Figueiras et al., 2019). The synthesis of bagasse-based silica gel with diphenylcarbazone modification has never been carried out. Therefore, this study will be carried out with the synthesis of bagasse silica gel modified diphenylcarbazone. So, this study aims to determine the characteristics of silica gel from bagasse (*Saccharumofficinarum* L.) modified diphenylcarbazone with the sol-gel technique.

Materials and Methods

Preparation of bagasse ash

The materials used in this study were bagasse (*Saccharum officinarum* L.) obtained from a sugar factory in Takalar, South Sulawesi. The bagasse was dried by aerating at room temperature. The sample was burned before it was ignited in the furnace. Then, it was treated in a furnace at 800 ºC for 4 hours. After that, it was put into a desiccator and then sieved using a sieve shaker with 100 mesh.

Synthesis of sodium silicate

100 g of as-prepared bagasse ashes were washed using 750 mL of 4 M of hydrochloric acid (HCl) solution, stirred, and soaked for 24 hours. After 24 hours, the sample was filtered and rinsed with distilled water until the washed water pH showed 7 (neutral). The clean bagasse ash was dried in the oven at 100 ºC for 2 hours and cooled to room temperature (Nopianingsih et al., 2015). Approximately 20 g of bagasse ash were added 60 mL of sodium hydroxide (NaOH) 4 M and heated until the sample was thickened. The obtained gel was put in an oven at 200 ºC for 2 hours and dissolved in 250 mL of distilled water. The obtained solution was left for 24 hours and filtered using a Whatman 42 filter paper. The obtained filtered solution was then known as the sodium silicate solution (silica gel) (Astuti et al., 2012).

Modification and Characterization of Silica Gel

The modification began by solving the diphenylcarbazone using a mixture of 10 ml toluene and 5 mL ethanol. 20 mL of sodium silicate solution was mixed with 10 mL of diphenylcarbazone solution and stirred well. The obtained mixture was dropped using HCl 3 mol L^{-1} until the gel formed. The obtained gel was rinsed with distilled water a couple of times and dried in the oven at 200 ºC for 2 hours. The obtained material was crushed until it became powder (Nopianingsih et al., 2015). To see the effect of diphenylcarbazone concentration, the concentration of diphenylcarbazone was changed to 1; 1.5; and 2 mmol using a similar procedure. The prepared silica gel was characterized using Fourier Transform Infra-Red (FTIR) and X-Ray Diffraction (XRD) instruments. The FTIR function determines the functional groups present in the silica gel, and XRD determines the crystallinity of as-prepared silica gels.

Result and Discussion

Bagasse silica gel modified diphenylcarbazone

In this study, the resulting bagasse ash has the brownish-gray color, where the sodium silicate has the clear brownish yellow color shown in Figure 1. The resulting sodium silicate solution is clear brownish-yellow. The reaction mechanism in the formation of sodium silicate is shown in Figure 2 (Nopianingsih et al., 2015).

(a) (b)

Figure 1. Bagasse ash (a) and sodium silicate solution (b)

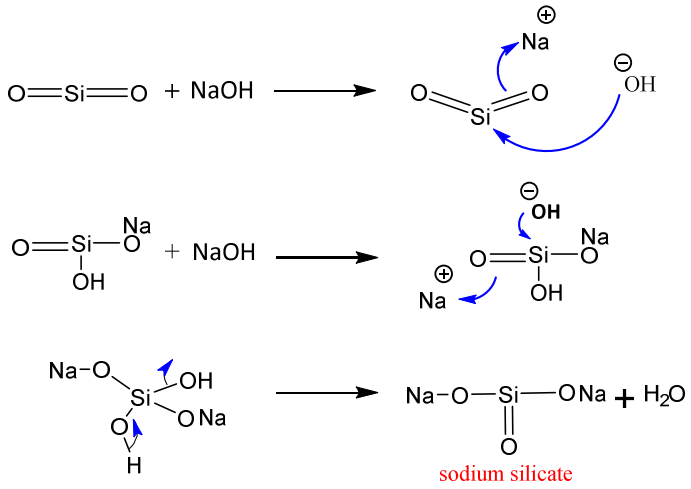

Figure 2. The reaction mechanism of sodium silicate formation

In the process, the high temperature caused NaOH to form sodium ions and hydroxide ions. The O-atom, which has a high electronegativity, formed an unstable intermediate because it made Si electropositive. The reaction that occurred was dehydrogenation and form H_2O because the hydroxyl ion bind to hydrogen. To balance an unstable compound, two Na^+ ions, which react with SiO_3^{2-} were needed to form sodium silicate (Mujiyanti et al., 2010)(Chindaprasirt & Rattanasak, 2020). Furthermore, the modification of sodium silicate using diphenylcarbazone formed a different pathway shown in Figure 3. Immobilized silica gel diphenyl carbazone was obtained by reacting sodium silicate with diphenylcarbazone in toluene with a pyridine catalyst. The dark red mixture stirred while adding HCl dropwise. The gel formation process occurs at the moment of neutralization with acids to produce immobilized silica gel diphenylcarbazone.

This modification process was carried out at room temperature because the organic groups at high temperatures caused the compound to be irregular (Figure 3). The addition of HCl results the presence of protons in the siloxy group (Si-O-) to silanol group (Si-OH) with the help of a catalyst quickly and continuously to

form amorphous silica. It was reacted with diphenylcarbazone resulting in a change in the shape of the silica structure into crystals (Mujiyanti et al., 2010).

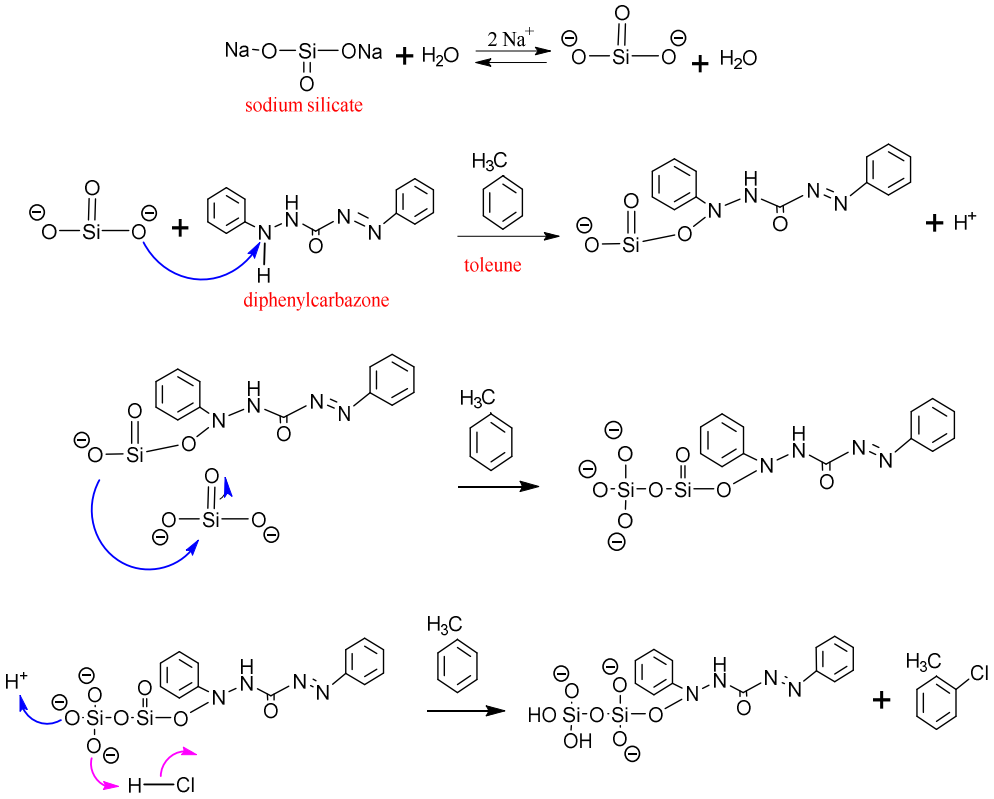

Figure 3. Reaction mechanism of formation silica gel modified diphenylcarbazone

Fourier Transform Infra Red (FTIR)

The components of the bagasse silica gel modified diphenylcarbazone were analyzed using the FTIR spectrophotometer. Table 1 showed the functional group that occurred in the as-prepared silica gel. The FTIR analysis was carried out to determine the success of making bagasse silica gel modified diphenylcarbazone. The typical absorption changes for functional groups on the adsorbent were known through Figure 4.

Table 1. Analysis of functional group with FTIR

Functional group	Wavenumber (cm^{-1})				
	Si-TMF	Si-DPZon 0.5 mmol	Si-DPZon 1.0 mmol	Si-DPZon 1.5 mmol	Si-DPZon 2.0 mmol
Silica gel					
Vibration of Si-OH	847.23	±950	±930	±950	±910
Stretching vibration of-OH and Si-OH	3445.39	3374.07	3373.88	3363.2	3382.87

Functional group	Wavenumber (cm^{-1})				
	Si-TMF	Si-DPZon 0.5 mmol	Si-DPZon 1.0 mmol	Si-DPZon 1.5 mmol	Si-DPZon 2.0 mmol
Vibration of Si-O-Si	1053.42	±1000	±1050	±1010	±1000
Diphenhylcarbazone					
Vibration of C ≡ N	-	2266.26	2251.38	-	2268.68
Vibration of C = O	1644.25	1636.06	1636.38	1636.16	1636.17
C-H Aromatic	675.58	677.34	668.54	668.52	667.32
Bending vibration N-H	-	1389.53	1394.50	1394.28	1395.38
Bending vibration N = N	-	±1550	±1570	±1560	1558.93

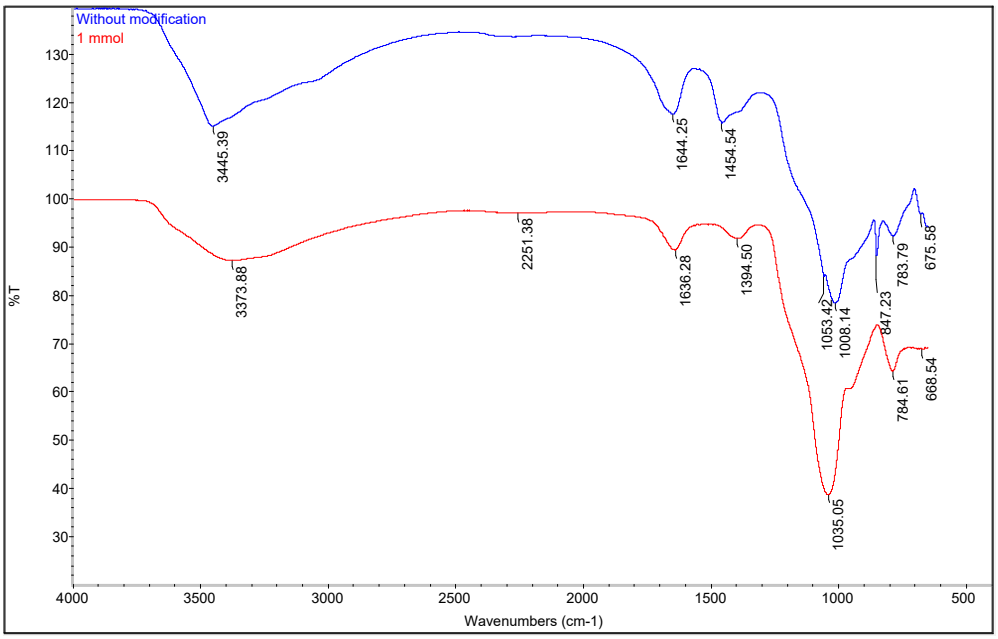

Figure 4. The FTIR analysis of bagasse silica gel without modification (blue) and with modified 1 mmol of diphenylcarbazone (red)

The FTIR spectrophotometer analysis of the silica gel spectrum without modification at a wavenumber of 1053.42 cm^{-1} indicated the presence of siloxane group absorption. The emergence of siloxane group absorption was supported by a wavenumber of ± 675.58 cm^{-1}, which indicated the vibrational presence of Si-O from Si-O-Si. The wavelength number of 847.23 cm^{-1} indicated the presence of silanol groups. It was supported by the appearance of the stretching vibration –OH at the wavenumber of 3445.39 cm^{-1}. This analysis shows that there siloxane functional groups (Si-O-Si) and silanol groups (Si-OH), which the main functional groups in silica gel (Kenneth, 2015) (Rahman, N.A Widiyastuti et al., 2017).

The interpretation of silica gel modified diphenylcarbazoneat 0.5 mmol, 1 mmol, 1.5 mmol, and 2 mmol indicated OH stretching vibrations from Si-OH. The results of spectrum analysis on Si-DPZon at the variation of concentrations yielded that the greater the concentration, the more completed groups. However, the result absorption less close to the silica gel without modification. Furthermore, silica gel can be successfully modified with diphenylcarbazone ligands (Silverstein et al., 2005). Si-DPZon of 1 mmol indicated the best absorption in the Si-O-Si group area. It has an absorption almost in accordance with Si-TMF, namely ±1050 cm^{-1}, compared to Si-DPZon 0.5 mmol, 1.5 mmol, and 2 mmol.

As part of good absorption, the water content of Si-DPZon 1 mmol also lower than the other concentration of Si-DPZon. A study also supported this study that stated that the lower the water content, the better the silica gel. It was caused closer to the general water content of silica-gel (Iqbal et al., 2016), which in this study, the result of commercial silica gel is 2%. Furthermore, Si-DPZon of 1 mmol was chosen for the XRD characterization.

X-Ray Diffraction (XRD)

Characterization of the crystalline structure of bagasse silica gel modified diphenylcarbazone was analyzed by XRD. The results of the characterization presented in Figure 5 (without modification) and figure 6 (modification).

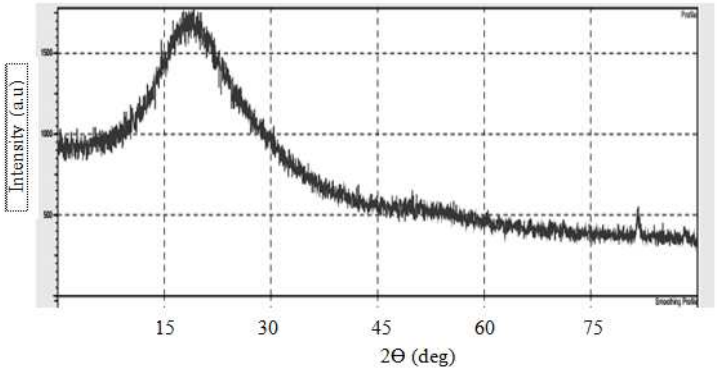

Figure 5. The XRD analysis of silica gel without modification

Based on the results obtained from the XRD diffractogram (Figure 5), the silica gel from the bagasse without modification showed a typical peak with the highest intensity at an angle of 2θ, namely 22.4800; 23.3000˚; and 21.3400˚ with a distance of *d*, respectively 2.95190; 3.81464; and 4.16036. In previous research, Nopianingsih et al. (2015) stated that the diffraction at the peak of the angle widened at an angle of 2θ=21-23˚. Based on the typical peak at the angle, it showed an amorphous structure. This is according to the theory because the results obtained on unmodified silica gel were also widened at the peak of the 2θ angle, between 21-23˚.

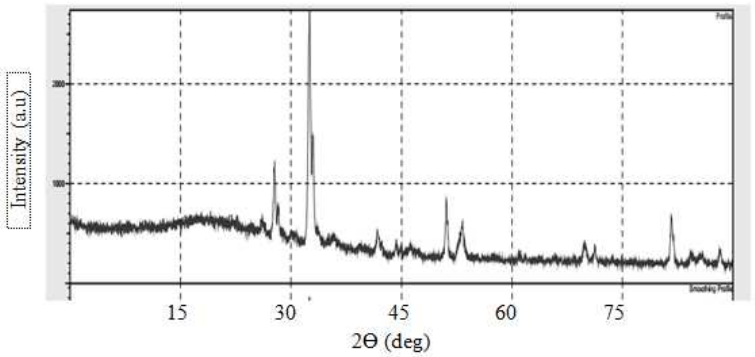

Figure 6. The XRD analysis of silica gel (1 mmol) with diphenylcarbazone

Meanwhile, the results obtained from the XRD diffractogram of bagasse silica gel modified diphenylcarbazone (Figure 6) indicated a typical peak with the highest intensity at 2θ angle was 31.6439˚; 31.9600˚; and 28.4915˚ with a distance of *d*, respectively 2.82525; 2.79802; and 3.13027. The crystal size can be calculated using the Scherrer equation to obtain the bagasse silica gel modified diphenylcarbazone. The crystal size is 41.469 nm.

These results were in accordance with the theory that the calculation of the crystal size with a crystal structure is at 10-200 nm (Amri et al., 2017). (Astuti et al., 2012) reported the change in the silica gel structure, which was originally amorphous. It can turn into crystals if the addition of organic compounds, so the more crystalline structure of the adsorbent were obtained (Iqbal et al., 2016). Therefore, according to the theory, the silica gel-modified diphenylcarbazone obtained a crystal form with an average crystal size of 41.469 nm.

Conclusion

The term of modified silica gel using FTIR indicated Si-OH, Si-O-Si group absorption, which could also be realized by the factors of CO, C=N, NH, and N=N. What as using of XRD showed the form of silica gel modified diphenylcarbazone. It was shaped crystalline with an angle of 2θ. There were 31.6439; 31.9.600˚; and 28.4915˚ with a crystal size of 41.468 nm.

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