

Synthesis of Rice Husk Mesoporous Silica as pH Responsive Release Material

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ABSTRACT

The synthesis of mesoporous silica as a delivery agent for the ethyl para-methoxycinnamate has been carried out. The study aims to determine the process of mesoporous silica synthesis from sodium silicate from the smelting of rice husk ash, determine the adsorption capacity of mesoporous silica in the ethyl para-methoxycinnamate and the pH responsive release of ethyl para-methoxycinnamate with mesoporous silica as a delivery agent in simulated intestinal and gastric fluids. It was found that mesoporous silica can be synthesized from rice husk ash with a 30% tartaric acid template. Characterization of mesoporous silica using FTIR spectroscopy showed the presence of silanol (Si-OH) and siloxane (Si-O-Si) functional groups. Mesoporous silica from rice husk ash is able as adsorbent for the ethyl para-methoxycinnamate with the adsorption capacity of 8.26 mg/g. The release test of gastric simulation fluid (pH 1.2) showed that the ethyl-para-methoxycinnamate was released from silica for a period of 12 hours. In the intestinal simulation fluid (pH 7.4), the release of the ethyl para-methoxycinnamate occurred slowly at the first hour, then gradually increased at 5 hour up to 12 hour.

Keywords: mesoporous silica, rice husk ash, adsorption, ethyl para-methoxycinnamate, release test

INTRODUCTION

Free radicals have a bad influence on the body. The effects of free radical reactivity include cell and tissue damage, autoimmune diseases, degenerative diseases, to cancer. Consuming antioxidants is a solution to overcome the negative effects of free radicals in the body [1-4]. The ethyl para-methoxycinnamate from the kencur plant is a good antioxidant [5-6]. These antioxidants are expected to be delivered efficiently to the body. The adsorption method using mesoporous silica filled with ethyl methoxy cinnamon can be used. The capacity of mesoporous silica adsorption can increase the interaction between the adsorbent and ethyl para-methoxycinnamic so that it can be used as an agent for delivering antioxidant compounds.

In this study, silica gel was made from rice husk ash as a delivery agent. Waste from rice husk ash is usually not utilized maximally so that it can cause environmental pollution. The most dominant chemical compound in rice husk ash is silica which is 72.28% [7-8]. Therefore, silica from rice husk ash are utilized and modified into mesoporous silica for use as an adsorbent [9-10]. Thus, the purpose of this research is to find out the process of mesoporous silica synthesis from sodium silicate from the smelting of rice husk ash with tartaric acid template, to determine the adsorption capacity of mesoporous silica in the

ethyl para-methoxycinnamic compound, and to determine the release of ethyl para-methoxycinnamic with mesoporous silica as a material of mesoporous silica adsorption on the ethyl para-methoxycinnamic compound, and to determine the release of ethyl para-methoxycinnamic with mesoporous silica as the material carrier on simulating intestinal and gastric fluids.

METHODOLOGY

Tools and chemical

The characterization instruments in this study were infrared spectrophotometers (Shimadzu FTIR-8201 PC), UV-Vis spectrophotometers (Shimadzu) with additional devices in the form of magnetic stirrers, ovens (Fischer Scientific), analytical scales (Vibra AJ-1200E), heating furnaces, cups porcelain, grinding tools (lumping 40 and mortar), vacuum pumps.

The research materials include rice husk as a source of silica; tartaric acid (Merck), distilled water, 4M NaOH, 3M HCl, 0.1M NaOH, 0.1M HCl, pH 7,4 buffer solution, pH 1.2 buffer solution, universal pH indicator paper, filter paper and Whatman filter paper no . 42

Research procedure

Rice husk being used was originating from central Lombok, Indonesia. It was cleaned from other mixes such as twigs and leaves and burned

evenly until ash was formed. The husk ash that has been formed was then crushed and sieved. The making of Na_2SiO_3 from rice husk ash in this study followed the procedure carried out by our previous study [11-12]. A total of 20 g of rice husk ash sample was added with 200 mL of 4 M NaOH, then heated to boiling while stirring with a magnetic stirrer. After thickening and the solution is black, the solution is poured into a porcelain cup and melted at a temperature of 500 oC for 30 minutes. After cooling, the solution was added with 200 mL of distilled water, left overnight and filtered with Whatman filter paper no. 42. The resulting filtrate is a solution of sodium silicate (Na_2SiO_3) which is ready to be used as a material for making silica adsorbents.

The sol-gel process of making mesoporous silica with the tartaric acid.

A total of 20 mL of sodium silicate compound resulting from the smelting of rice husk ash was put into a plastic container, then added the tartaric acid template. Furthermore, 0.1 M HCl and 0.1 M NaOH were added dropwise while stirring with a magnetic stirrer to form a gel and continued until a neutral solution (pH 7). The gel formed is allowed to stand overnight, washed with distilled water until it is neutral against the universal indicator, and dried in an oven at 70oC. After drying, crushed and sieved with 200 mesh sieve. The silica obtained was characterized by FTIR.

A ethyl para-methoxycinnamate release test on the simulation of gastric and intestinal fluids in this study followed the procedure carried out [13-14]. Drug release was carried out by immersing a number of mesoporous silica samples with the para-methoxycinnamic ethyl compound with the highest amount of mesoporous silica in 50 mL buffer solution at pH 1.2 (simulated gastric fluid) and at pH 7.4 (simulated intestinal fluid). A buffer of pH 1.2 was prepared by mixing 250 mL of HCl 0.2 M and 147 mL KCl 0.2 M, while a buffer solution of pH 7.4 was made by mixing 250 mL KH_2PO_4 0.1 M and 195.5 mL NaOH 0.1 M. The mixture is stirred at 300 rpm using magnetic stirrer at 37oC. Every 1 hour interval, 5 mL samples are taken and replaced with the same buffer volume. The samples taken were then filtered, and their concentration measured using a UV-Vis spectrophotometer at a wavelength of 350 nm. This drug release test is carried out over a 12 hour period.

RESULTS AND DISCUSSION

Characterization of mesoporous silica carried out in this study is chemical

characterization by identifying functional groups contained in mesoporous silica using FTIR instruments. The results of the characterization of mesoporous silica powder using FTIR are shown in Table1. The absorption of Si-O functional groups in silica gel is shown in the dominant wave number at wavelengths 1091.84 cm^{-1} , 958.36 cm^{-1} , 796.07 cm^{-1} and 466.86 cm^{-1} . There is a bending vibration of siloxane at the wave number 466.86 cm^{-1} . Vibration of stretching Si-O from siloxane was shown by absorption band at wave number 796.07 cm^{-1} . The stretching vibration of Si-O silanol is shown by the absorption at the wave number 958.36 cm^{-1} . The strong absorption band at wave number 1091.84 cm^{-1} is the symmetric stretching vibration of Si-O from siloxane (Si-O-Si). At the wave number 1638.41 cm^{-1} there was absorption from the vibration vibrations of O-H silanol, and at wave number 3467.1 cm^{-1} there was absorption from the stretching vibrations of O-H silanol. In general, the absorption bands that appear in silica gel spectra indicate that the functional groups found in silica gel produced from rice husk ash are silanol (Si-OH) and siloxan (Si-O-Si) groups.

In silica gel with the addition of tartaric acid, the sharp band at 3400.81 cm^{-1} is caused by not forming hydrogen bonds in the interaction between mesoporous silica and tartaric acid. The strong and characteristic band at 1735.2 cm^{-1} indicates the presence of the C=O carbonyl group of tartaric acid. The addition of tartaric acid also increased the intensity of the asymmetric stretching of Si-O from the siloxan group which is 1083.11 cm^{-1} compared to silica gel. This is probably caused by the transfer of electron O atoms from the carboxyl group or silanol group, can attack Si atoms from mesoporous silica to form Si-O-Si. This also shows that there has been an increase in the intensity of silanol groups and the formation of siloxane bonds (Si-O-Si). For mesoporous silica with the tartaric acid template that has been removed by the solvent extraction method, there is a shift in the wave number for the siloxane (Si-O-Si) bond to 1055.31 cm^{-1} . This shows the siloxane binding energy decreases, so that the bond between the antaratomes weakens and results in the breaking of the Si-O-Si bond between the surfaces of the mesoporous silica with the surface of the tartaric acid. In addition, the characteristic absorption of C = O carbonyl group from tartaric acid at 1735.2 cm^{-1} and sharp bands in the area of about 1132.81 cm^{-1} which is the wave number for the C-O bond has no longer appeared. This shows that the tartaric acid template has been successfully removed from mesoporous silica.

Table 1 FTIR absorption bands and wave numbers (a) Silica Gel, (b) Silica Gel with Addition of Tartaric Acid and (c) Mesoporous Silica

	Silica Gel		Silica Gel with Tartaric acid			Mesoporic silica		
	current study (cm ⁻¹)	Reference [14] (cm ⁻¹)		current study (cm ⁻¹)	Reference [15] (cm ⁻¹)		current study (cm ⁻¹)	Reference [15] (cm ⁻¹)
O-H	3467.1	3425.58	Si-OH	3400.81	3409.9	Si-OH	3400.81	3409.9
O-H	1638.41	1627.9	C=O	1735.20	1739.7	-	-	-
Si-O	1091.84	1095.57	Si-O	1083.11	1087.8	Si-O	1055.31	1058.8
Si-O	958.36	956.69	C-O	1132.81	1134.1	-	-	-
Si-O	796.07	802.39	-	-	-	-	-	-
Si-O	466.86	470.63	-	-	-	-	-	-

Table 2 shows that there was a shift in mesoporous silica wave numbers before and after adsorption. The wave number shift occurs in the Si-OH functional group and the Si-O group where the percent transmittance increases after the adsorption process. This is in accordance with the Lambert-Beer law which states that transmittance is inversely proportional to absorbance and concentration [16]. The shift of the wave number

after adsorption indicates that the para-methoxycinnamic ethyl compound has been adsorbed by the adsorbent. The formation of a bond between the adsorbent and the para-methoxycinnamic ethyl compound will cause the vibrational motion of the adsorbent structure to become stiffer so that the resulting frequency is lower.

Table 2 Comparison of FTIR waveform data before and after adsorption

	adsorption		after adsorption	
	Wave numbers (cm ⁻¹)	Transmittan (%)	Wave Numbers (cm ⁻¹)	Transmittan (%)
Si-OH	3400.81	0.59	3466.73	4.64
Si-O	1055.31	1.59	960.77	6.67

Adsorption

The para-methoxycinnamic ethyl adsorption level was based on the influence of pH, concentration and contact time. The optimum pH was obtained at pH 9 with an adsorption capacity value of 2.35 mg/g, the optimum concentration was obtained at a concentration of 9 ppm with an

adsorption capacity value of 8.265 mg/g and the optimum contact time was obtained at 30 minutes with an adsorption capacity value of 8.494 mg/g. The suitable isotherm model is the Freundlich isotherm model which means that the absorption of the para-methoxycinnamic ethyl occurs physically.

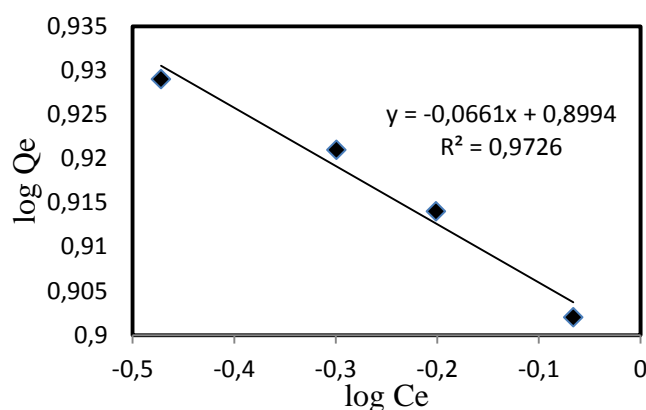


Figure 1 Freundlich isotherm curve

Figure 1 shows the comparison of the R2 values in the Freundlich isotherm. Values are calculated based on the results of the adsorption capacity and concentration on the effect of contact time. The isotherm model that fits the research data is tested using simple linear regression analysis by looking at the correlation coefficient (R2). If the value of R2 is getting closer to 1 then it can be said that there is a greater influence and the relationship between variables is getting stronger [17]. In this study, the value of R2 in the Freundlich isotherm is closer to 1 compared to R2 in the Langmuir isotherm. This shows that in this study the Freundlich isotherm is used, which means that the absorption of the ethyl para-methoxycinamic compound that occurs is physical. The Freundlich isotherm model assumes that the adsorbent has a heterogeneous surface

and each molecule has different application potentials and the assumption that the adsorption occurs multilayer on the surface of the adsorbent.

Adsorption kinetics

Determination of the mechanism and rate of adsorption can be determined by the kinetic model approach. One of the main objectives of adsorption kinetics research is to determine a suitable model for the adsorption kinetics of para-methoxycinamic ethyl compounds, and to obtain the values of the adsorption kinetics parameters. The kinetics of adsorption of para-methoxycinamic ethyl compounds by adsorbents can be determined by processing the adsorption results data on the influence of the contact time on the adsorption capacity value.

Table 3 Data from the determination of the adsorption kinetics model

Kinetics Model	Parameters	Parameter Values
Orde I	R ²	0.99112
	K (minute ⁻¹)	53,8 x 10 ⁻³
Orde II	R ²	0.9997
	K (minute ⁻¹)	82,9x10 ⁻³
Pseudo orde I	R ²	1
	K (minute ⁻¹)	115610,6 x 10 ⁻⁶
Pseudo orde II	R ²	1
	K (g.mg ⁻¹ minute ⁻¹)	0,06250

Therefore it can be concluded that mesoporous silica adsorbs para-methoxycinamic ethyl compounds both chemically and physically. Physical adsorption is proven by the isotherm

model to describe the adsorption that occurs, namely the Freundlich isotherm model. The Freundlich model which states the adsorption of para-methoxycinamic ethyl by mesoporous silica

occurs physically and forms a multilayer layer. The results of the calculation of the adsorption kinetics model with the results of the kinetics model occurred in pseudo order II and II which meant that the adsorption process occurred physically and chemically. Chemical adsorption is also evidenced by the shift in wave numbers and the increase in transmittance value in the FTIR mesoporous silica after adsorption [18-21].

In vitro pH release test

Figure 2 and 3 show the pattern of para-methoxycinnamic ethyl release in a simulated

gastric fluid made with a pH of 1.2. It can be seen that there is no release of para-methoxycinnamic ethyl at that pH for a period of 12 hours. This indicates the strong interaction of ethyl para-methoxycinnamic with mesoporous silica at this pH. At acidic pH, mesoporous silica active sites are protonated and cause these active sites to be positively charged. This causes the drug to remain trapped in the silica framework. These results can give an idea, that the para-methoxycinnamic ethyl is not absorbed in the stomach, as a result the bioavailability of ethyl para-methoxycinnamic in the blood can be high.

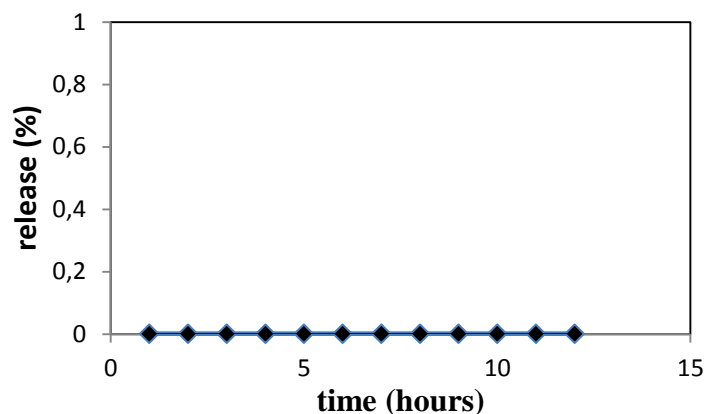


Figure 2. Pattern of para-methoxycinnamic ethyl release in a simulated gastric fluid

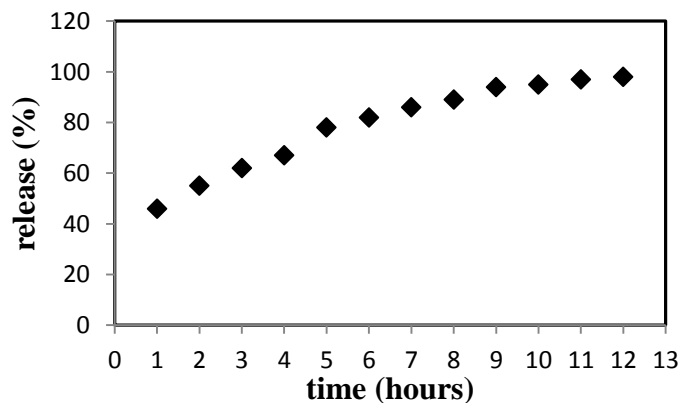


Figure 3. Pattern of para-methoxycinnamic ethyl release in a simulated intestinal fluid

In the intestinal simulation fluid (pH 7.4), the release of para-methoxycinnamic ethyl occurs slowly in the first 4 hours (Figure 3). The release of para-methoxycinnamic ethyl occurs because the total surface charge of mesoporous silica becomes neutral. At neutral surfaces no bonding occur between mesoporous silica and ethyl para-methoxycinnamic so that there is release of intestinal simulation fluid. Drug release occurs and then slowly decreases until the 12th hour. This is because the amount of para-methoxycinnamic

ethyl bound to mesoporous silica decreases. The function of using a buffer solution in the stomach and intestine simulation is to maintain the pH. The buffer system is in the form of a weak acid with a conjugate base or vice versa a weak base with a conjugate acid. To simulate the pH in the stomach and intestine, the buffer solution is used.

CONCLUSION

Based on the data and discussion of test results in this study, some conclusions can be drawn as follows:

(1) Mesoporous silica can be synthesized from sodium silica from the smelting of rice husk ash through the sol gel process by the addition of a tartaric acid template.

(2) The para-methoxycinnamic ethyl compound has an adsorption level based on the influence of pH, concentration and contact time. The optimum pH was obtained at pH 9 with an adsorption capacity value of 2.35 mg / g, the optimum concentration was obtained at a concentration of 9 ppm with an adsorption capacity value of 8.265 mg / g and the optimum contact time was obtained at 30 minutes with an adsorption capacity value of 8.494 mg / g. The suitable isotherm model is the Freundlich isotherm model which means that the adsorption of the para-methoxycinnamic ethyl compound occurs physically.

(3) The release of para-methoxycinnamic ethyl compound in gastric simulation fluid (pH 1.2) shows that the para-methoxycinnamic ethyl compound is not separated from silica for a period of 12 hours, whereas in intestinal simulation fluid (pH 7.4), release The para-methoxycinnamic ethyl compound occurs slowly every hour until the 12th hour.

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