ADSORPTION OF OLEIC ACID USING MCM-41 SYNTHESIZED FROM RICE HUSK SILICA

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Abstract

Adsorption is one of the methods used to reduce free fatty acid in feedstock oils with high acid content that are used for the production of biodiesel. This work investigated MCM-41 synthesized from rice husk silica for the adsorption of oleic acid in isooctane. The adsorption conformed to the Langmuir isotherm model and equilibrium adsorption capacities at 25.0°C were 277.8 mg/g for as-synthesized MCM-41 and 270.3 mg/g for template-removed MCM-41. The determined free energy and enthalpy of adsorption showed that the adsorption was spontaneous and exothermic. Adsorption of oleic acid in soy bean oil was also demonstrated. Results showed that as-synthesized MCM-41 was a better adsorbent than template-removed MCM-41 for oleic acid removal from soybean oil.

Keywords: Free fatty acid, adsorption, MCM-41, oleic acid, rice husk silica

Introduction

Vegetable oils from many plants such as soybean, palm, and jatropha have been used as reactants for the production of biodiesel. An extracted crude oil from plants is a mixture of mono, di- and triglycerides, free fatty acids (FFA), water, sterols, phospholipids, phosphatides, tocopherols, odorants, and other impurities (Bhosle and Subramanian, 2005; Demirbaş, 2003). In transesterification using basic catalysts, the FFA content in the oil should not exceed 1 wt%, otherwise the FFA and water could react with a catalyst to form soap (Demirbaş, 2003). The reaction will reduce the amount of the active catalyst and the formation of soap will cause a difficulty in the separation of biodiesel from the reaction mixture (Ma and Hanna, 1999). These processes lead to a lower biodiesel yield

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(Ramadhas *et al*., 2005). Therefore, it is important to remove or reduce the FFA in the feedstock oils.

There are reports of the methods used for the removal of FFA from vegetable oils. These are esterification with acid catalyst (Ramadhas *et al*., 2005), distillation (Martins *et al*., 2006), and adsorption (Proctor *et al*., 1995; Jamal and Boulanger, 2010; Yoon *et al*., 2011). Adsorption is one of the methods that have advantages such as a simple operating process and low operating cost. Many adsorbents, for example, mixed bed ion-exchange resins (Jamal and Boulanger, 2010), rice husk ash (RHA) (Saleh and Adam, 1994), silica gel (Atia *et al*., 2006), RHA and rice husk silica (Kim *et al*., 2008), acid-treated RHA (Farook and Ravendran, 2000; Yoon *et al*., 2011), aluminum- incorporated RHA (Adam and Chua, 2004), and silicate films produced from RHA (Kalapathy and Proctor, 2000) have been used for adsorption of FFA.

Rice husk is an agricultural waste largely generated in rice-producing countries. It contains 22 wt% silica (Yalçin and Sevinç, 2001). Silica extracted from rice husk can be used as a silica source for the production of a number of silica-based materials (Khemthong *et al*., 2007). This work reports the use of Mobil Composition of Matter No. 41 (MCM-41) synthesized from rice husk silica as the adsorbent for the adsorption of oleic acid. MCM-41 possesses a hexagonal array of cylindrical pores the diameter of which can be varied from 1.5 to 10 nm, a high surface area, high pore volume (Beck *et al*., 1992; Serrano *et al*., 2004), and high thermal stability (Grün *et al*., 1999). MCM-41 is used in many applications such as a support for catalysts and an adsorbent for various gases (Grün *et al*., 1999) and volatile organic compounds (Hu *et al*., 2001). In addition, the surfactant containing MCM-41 has been used for removal of nonionic organic compounds such as benzene, toluene, and phenol from contaminated wastewater (Ghiaci *et al*., 2004).

The present work evaluated the feasibility of using MCM-41 synthesized from rice husk silica for the adsorption of oleic acid. The adsorption was carried out in isooctane at various temperatures. The obtained adsorption data were modeled with the Langmuir and Freundlich isotherms. Adsorption of oleic acid in soybean oil was also studied.

Materials and Method

Materials

Ethyl alcohol, hydrochloric acid, isooctane, isopropyl alcohol, sodium hydroxide, and toluene were all purchased from Carlo ERBA. Phenolphthalein and potassium hydroxide were purchased from QRëc. Hexadecyltrimethyl ammonium bromide (CTAB) was purchased from Acros. Oleic acid and potassium hydrogen phthalate were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Preparation of Adsorbents

Silica was extracted from rice husk obtained from a local rice mill in Nakhon Ratchasima, Thailand using a method reported in the literature (Khemthong *et al*., 2007). The rice husk was washed thoroughly with water to remove adhering soil and dust. After that, the rice husk was dried at 100ºC overnight. Dried rice husk, 85 g, was refluxed with 700 mL of 3 M HCl in a round-bottomed glass flask at 85ºC for 3 h. After the acid reflux, the color of the rice husk changed from brown to black. The treated rice husk was separated from the solution and washed with water several times until the pH of the filtrate was ~7. The rice husk was dried at 100ºC overnight and calcined in a muffle furnace at 550ºC for 6 h. The white powder product obtained is denoted as rice husk silica (RHS).

The MCM-41 was synthesized according to the literature (Rintramee *et al*., 2012). Three g of RHS was mixed with 30 mL of 5 M NaOH under stirring in a polypropylene bottle. When the RHS had dissolved completely, the solution was poured into 90 mL of 0.14 M CTAB and stirred at room temperature. The solution pH was adjusted by slowly adding 2.5 M H_2SO_4 until the pH was within the range of 11-12. The mixture was transferred to a Teflon-lined, stainless- steel autoclave with a 250-mL capacity and heated at 100ºC for 3 days in the muffle furnace. A solid product was separated by centrifugation, washed thoroughly with deionized water until the pH of the filtrate was ~7, and dried at 100ºC. The as-synthesized MCM-41 is denoted as MCM-41 (A). To remove the CTAB, MCM-41 (A) was calcined in the muffle furnace at 540ºC for 6 h. The template-removed MCM-41 is denoted as MCM-41 (C). The adsorbents were ground in a grinder, sieved to the particle size of 63-75 μm, and kept at room temperature in a desiccator.

Characterization of Adsorbents

XRD powder patterns of samples were obtained using a Bruker AXS D5005 diffractometer with Cu K_α radiation at 40 kV and 40 mA within a range 2θ of 1.5 to 10º with the increment of 0.02º. A scan speed of 0.5º per min was used.

Textural characteristics of the samples were determined by nitrogen adsorption-desorption analysis at -196ºC from a relative adsorption pressure range of 0.01-0.99 using a Micromeritics ASAP 2010 analyzer. Before the measurement, MCM-41 (C) was degassed at 300ºC for 4 h (Rintramee *et al.*, 2012) and MCM-41 (A) was degassed at 250ºC for 2 h (Jabariyan and Zanjanchi, 2012). The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method from the adsorption data in the relative pressure range (P/P_0) of 0.02-0.2. The pore size was calculated by the Barrett-Joyner-Halenda method.

The Fourier transform infrared spectroscopy (FTIR) spectra of adsorbents were recorded on a Bruker IR TENSOR 27 spectrometer. FTIR transmittance measurements in the range 400-4000 cm^{-1} were performed using the standard KBr pellet technique.

^{29}Si MAS NMR spectra of MCM-41 samples were obtained with a Bruker nuclear magnetic resonance spectrometer (AscendTM 500, 500 MHz) equipped with a 4 mm probe (MAS BB/1HF19/F19) and zirconia rotors. Measurements were performed at an operation field of 11.7 Tesla, a frequency at 99.39 MHz, a pulse duration of 4 μs, a recycle delay of 5.0 s, and 12000 scans. The spectra were referenced to kaolin (δ = -93.1 ppm).

Adsorption of Oleic Acid on MCM-41 (A) and MCM-41 (C)

Solutions of oleic acid in isooctane with the concentrations in the range of 0.10-3.00 %w/v were used in the adsorption study. To 25 mL of an oleic acid solution, an adsorbent (predried at 110ºC and cooled) weight of 0.25 g was added. The mixture, contained in a 125 mL Erlenmeyer flask, was placed into a flask clamp mounted on a platform inside a stainless-steel water bath. The water in the water bath was circulated using a temperature-controlled bath (Heto Lab Equipment, AT110) to maintain a constant temperature during the adsorption study. Stirring was provided to the adsorption mixture using a multiposition stirrer (DiLigent). At a given time of adsorption, the adsorbent was separated from the oleic acid solution by gravitation. The clear solution was used for determination of oleic acid by titration with 0.01 M potassium hydroxide (KOH).

The effect of the adsorption time on the adsorption capacity was investigated in the time range of 10-180 min. The temperature for the adsorption study was fixed at 25ºC. A solution of oleic acid in isooctane with the concentration of 0.50 %w/v and the adsorbent weight of 0.50 g was used in the adsorption study.

The influence of the temperature on the adsorption was investigated in the temperature range of 25-50ºC. A concentration of oleic acid in isooctane of 0.50 %w/v and the weight of the adsorbent of 0.25 g were used in the study. The amount of adsorption at equilibrium, q_e (mg/g), was calculated according to Equation 1:

$$q_e = \frac{(X_0 - X_e)V}{W} \tag{1}$$

where X_0 and X_e (mg/L) are the initial and equilibrium concentration of oleic acid, respectively. V is the volume of the solution (L) and W is the mass of the adsorbent (g) (Tan *et al.*, 2007).

Determination of Oleic Acid

The oleic acid concentration in isooctane solutions was determined using the American Oil Chemists' Society method for the determination of free fatty acids (AOCS Ca 5a 40) based on a titration with a KOH solution (American Oil Chemists' Society, 2009). Oleic solutions were titrated against 0.01 M KOH using phenolphthalein as the indicator.

A solution of toluene and isopropyl alcohol with a volume ratio of 1:1 was used as a solvent for the titration of oleic acid in isooctane and in vegetable oil. Before using the solvent, it was neutralized with the standardized 0.1 M KOH.

Results and Discussion

Characterization of MCM-41 (A) and MCM-41 (C)

The X-ray patterns of the as-synthesized MCM-41 [MCM-41 (A)] and the calcined MCM-41 [MCM-41 (C)] are shown in Figure 1 at low angles between 2.5° and 7°. For MCM-41 (A), characteristic peaks at 2.07° and weak peaks at 3.50°, 4.10°, and 5.4° are reflections of (100), (110), (200), and (210), respectively. The pattern demonstrated the hexagonal arranged channels (Bhagiyalakshmi *et al.*, 2010). A similar pattern was also observed for MCM-41 (C); however, there is a small shift of the diffraction peaks toward higher 2θ. This is due to the lattice shrinkage as a result of the template removal by calcination (Kleitz *et al.*, 2003). It is noted that lower intensity was obtained with MCM-41 (A). This is caused by the template filled in the mesopore structure (Kleitz *et al.*, 2001; Goworek *et al.*, 2007).

The nitrogen adsorption-desorption isotherms of MCM-41 (A) and MCM-41 (C), as shown in Figure 2, are the typical type IV according to the IUPAC classification. The values of the specific surface area and pore volumes are summarized in Table 1. The results show that the surface area and pore volume of MCM-41 (C) were increased after calcination because of the removal of the template molecules.

Adsorption Study

The adsorption of oleic acid proceeds via hydrogen bonding between the oxygen of the carboxyl group of the acid with hydrogen of the silanol group of the adsorbents. The hydrogen of the carboxyl group of the acid can also form a hydrogen bond with the oxygen of the silanol group (Atia *et al.*, 2006).

The adsorption of oleic acid on the adsorbent surface can be verified through the IR spectroscopy. An IR spectrum of MCM-41 (A) before the adsorption of oleic acid in Figure 3 shows bands related to asymmetric Si-O-Si stretching at 1240 cm^{-1} and 1090 cm^{-1}, Si-O-Si bending vibration at 457 cm^{-1}, and free silica at 804 cm^{-1}. C-H stretching modes at 2925 and 2858 cm^{-1} and C-H bending vibrations at 1480-1590 cm^{-1} are associated with the carbon long-chain template molecules (Braga *et al.*, 2011). After the adsorption of oleic acid, a new band occurred at 1722 cm^{-1}

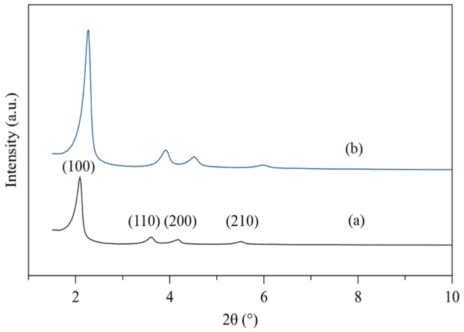


Figure 1. XRD patterns of (a) MCM-41 (A)and (b) MCM-41 (C)

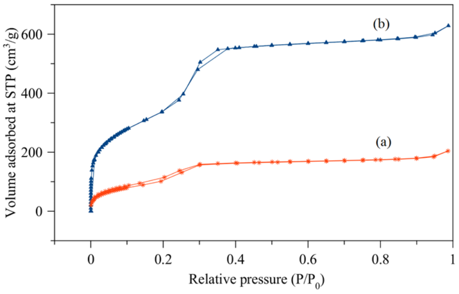


Figure 2. Nitrogen adsorption-desorption isotherms for (a) MCM-41 (A) and (b) MCM-41 (C)

which is assigned to C = O (Morais *et al*., 2005) suggesting the presence of oleic acid on the adsorbent.

An IR spectrum of MCM-41 (C) before the adsorption of oleic acid is shown in Figure 4; the spectrum is relatively similar to that of MCM-41 (A) except that the bands related to the template molecules clearly have disappeared. After the adsorption, there are 2 bands at 2862 and 2933 cm^{-1} which could be assigned to asymmetric and symmetric vibration of CH_2, respectively. In addition, a peak at 1710 cm^{-1} was from C = O stretching (Lenẓa and Vasconcelos, 2001; Kumar *et al.*, 2002) indicating the presence of oleic acid. It is noted that on the spectra of MCM-41 (C) the intensity of the band around 3500 cm^{-1} decreased after oleic acid adsorption. This could be attributed to the hydrophobic nature of oleic acid on the surface of MCM-41 (C) that reduced the adsorption of water (Choi *et al*., 2014).

Effect of Adsorption Time

Adsorption of oleic acid at various times was investigated using the adsorbents' weight of 0.25 g and the concentration of oleic acid solution of 0.5% w/v. The temperature was controlled at 25ºC. MCM-41 (A) adsorbed oleic acid rapidly and the adsorption capacity reached the equilibrium in about 15 min, as shown in Figure 5. However, adsorption by MCM-41 (C) was slower and the equilibrium was reached in 60 min. Faster adsorption for MCM-41 (A) could be from a hydrophobic character of CTAB (Ghiaci *et al*., 2004) that could enhance the interaction with oleic acid. For further study, the adsorption time of 60 min was used for both adsorbents to ensure the equilibrium adsorption.

It was noted that the adsorption capacities of MCM-41 (A) and MCM-41 (C) at equilibrium were about the same, ~160 mg/g, although the surfactant still remained in the pore of the MCM-41 (A). Therefore, further investigation dealing with OH groups on the adsorbents that were assumed to be the sites of adsorption was conducted using nuclear magnetic resonance spectrometry.

Hydroxyl groups associated with Si atoms on MCM-41 (A) and MCM-41 (C) were investigated using ^{29}Si MAS-NMR

Table 1. Surface area and pore volumes of the adsorbents

Samples	BET surface area (m^2/g)	Total pore volume(cm^3/g)
MCM-41 (A)	332	0.316
MCM-41 (C)	1229	0.972

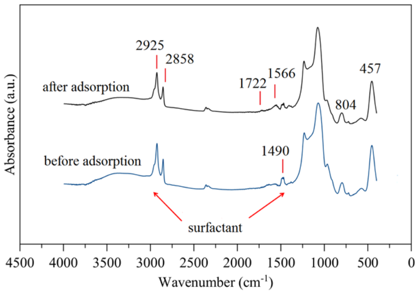


Figure 3. IR spectra of MCM-41 (A) before and after the adsorption of oleic acid

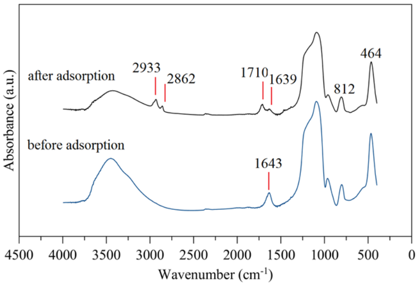


Figure 4. IR spectra of MCM-41 (C) before and after the adsorption of oleic acid

spectroscopy and the spectra are shown in Figures 6 and 7. After deconvolution of the NMR spectra, 3 peaks were obtained and can be used to calculate parameters such as the condensation degree (Shylesh and Singh, 2006), relative proportion of different silicon environments (Costa *et al.*, 2008), and molar percentage of silanol groups (Igarashi *et al.*, 2003).

Chemical shifts of the 3 peaks for both MCM-41 (A) and MCM-41 (C) are shown in Table 2. These chemical shifts are assigned to 3 silicon environments that are Q2, 2 OH groups attached to the same silicon atom, Q3, 1 free OH group attached to a silicon atom, and Q4, no OH groups associated to a Si atom (Hamdan *et al.*, 1997). Figure 8 shows the silicon environments of the aforementioned chemical shifts.

From the deconvolution of the NMR spectra of MCM-41 (A) and MCM-41 (C) percentages of Q2, Q3, and Q4 are obtained and shown in Table 3. When the template molecules were removed by calcination, the percent of Q4 increased and that of Q3 decreased. This is due to the condensation of silanol groups and the formation of siloxane bridges in the structure (Costa *et al.*, 2008). The percentage of total silanol groups of MCM-41 (C) is about a factor of 2 lower than that of MCM-41 (A). However, the adsorption capacities of the 2 adsorbents are about the same. From the results, it is assumed that besides hydrogen bonding, hydrophobic interaction between alkyl chains of CTAB in MCM-41 (A) and oleic acid could also be responsible for the adsorption.

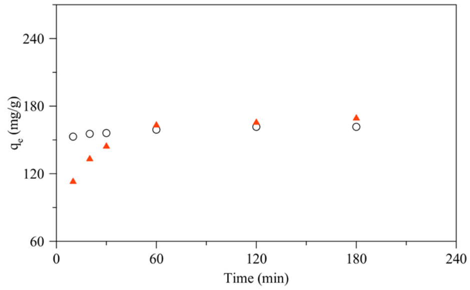


Figure 5. Time-dependent adsorption of oleic acid for (○) MCM-41 (A) and (▲) MCM-41 (C)

Adsorption Isotherms

Langmuir and Freundlich isotherm models were used to fit the obtained data. The Langmuir adsorption equation can be represented as Equation 2:

$$\frac{q}{q_m} = \frac{K_A X_e}{1 + K_A X_e} \tag{2}$$

where X_e (mg/L) is the amount of the adsorbate in a solution at equilibrium and q (mg/g) is the

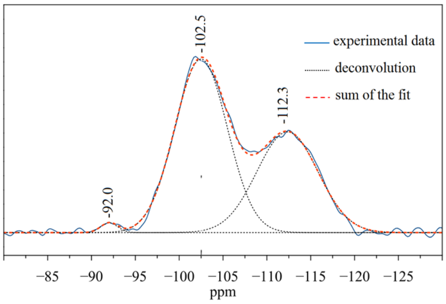


Figure 6. ^{29}Si MAS NMR spectrum of MCM-41 (A) and the deconvolution. The correlation coefficient of the fit is 0.9964

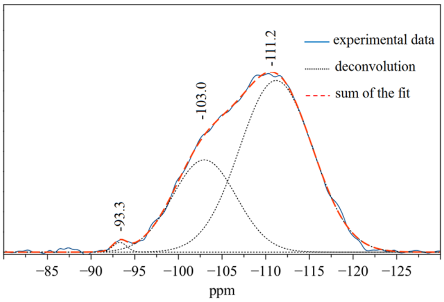


Figure 7. ^{29}Si MAS NMR spectrum of MCM-41 (C) and the deconvolution. The correlation coefficient of the fit is 0.9990

amount of the adsorbate adsorbed per gram of the adsorbent at equilibrium. q_m (mg/g) is the amount of the adsorbate adsorbed to form a monolayer coverage on the solid. K_A (L/mg) is the Langmuir adsorption equilibrium constant. The adsorption data can be fitted in a linear form of the Langmuir model as Equation 3:

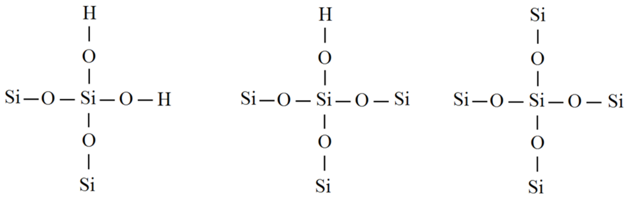
$$\frac{X_e}{q} = \frac{X_e}{q_m} + \frac{1}{K_A q_m} \qquad (3)$$

The Freundlich isotherm is expressed by Equation 4:

$$q = K_F X_e^{1/n} \qquad (4)$$

where q and X_e are the same as described in Equation 2, K_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent, and 1/n is an empirical constant. Adsorption data are commonly fitted into a linear form of the Freundlich isotherm as Equation 5:

$$\ln q = \ln K_F + \frac{1}{n} \ln X_e \qquad (5)$$



(Geminal silanol or silanediols) (Isolated silanols or single silanol) (Siloxanes)

Figure 8. Chemical environments of silicon on silica surfaces (Costa *et al.*, 2008; Shylesh and Singh, 2006)

Table 2. ^{29}Si chemical shifts of MCM-41 (A) and MCM-41 (C)

Adsorbent	Q_2 (ppm) $Si(OSi)_2(OH)_2$	Q_3 (ppm) $Si(OSi)_3(OH)$	Q_4 (ppm) $Si(OSi)_4$
MCM-41 (A)	-92.3	-102.3	-113.2
MCM-41 (C)	-93.1	-104.0	-111.5

Table 3. Relative proportions of the different silicon chemical environments determined by ^{29}Si MAS-NMR

Adsorbent	Relative proportion of the chemical environment (%)			SiOH (mol %-Si)[a]
	Q_2	Q_3	Q_4	
MCM-41 (A)	1.1	59.0	39.9	61.2
MCM-41 (C)	0.7	31.7	67.6	33.1

[a] *Relative amount of silanol groups = $[(2Q_2 + Q_3)/(Q_2 + Q_3 + Q_4)] \times 100$ % (Igarashi et al., 2003).*

Figures 9 and 10 show the obtained data from MCM-41 (A) and MCM-41 (C) fitted with the Langmuir model, respectively. Table 4 to Table 7 show equations obtained from fitting the experimental data with the Langmuir and Freundlich models, for both adsorbents. The adsorption data for both adsorbents were fitted better with the Langmuir model with correlation coefficient values in the range of 0.98-0.99. In general, the Langmuir adsorption isotherm assumes monolayer adsorption onto homogeneous sites in the adsorbent.

Thermodynamic Parameters

Thermodynamic parameters including the Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o) of adsorption are useful in providing information about the adsorption process. The relationship among a distribution coefficient (K_D), ΔH^o, and ΔS^o can be described by Equation 6:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

where R is the gas constant, 8.314 J/mol.K, and T is the absolute temperature (Kelvin). K_D is the distribution coefficient (mL/g) and defined as Equation 7:

$$K_D = \frac{q}{X_0} \tag{7}$$

The Gibbs free energy change can be determined using Equation 8:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8}$$

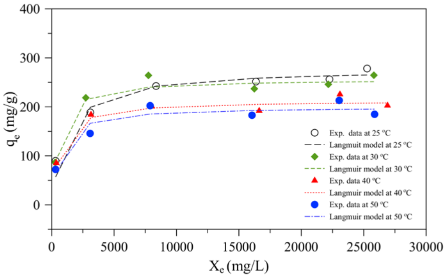


Figure 9. **Adsorption of oleic acid on MCM-41 (A) at different temperatures**

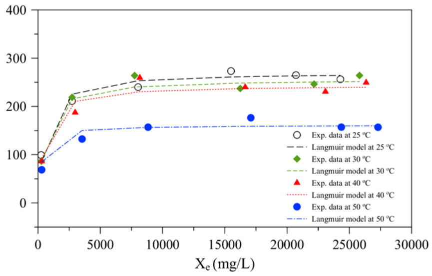


Figure 10. **Adsorption of oleic acid on MCM-41 (C) at different temperatures**

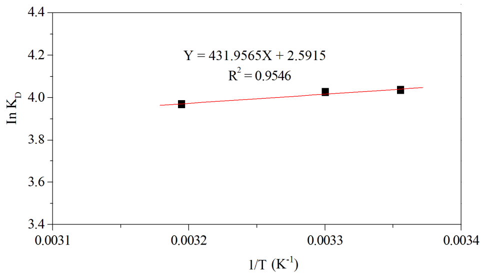


Figure 11. **The plot of lnKD vs 1/T for MCM-41 (A)**

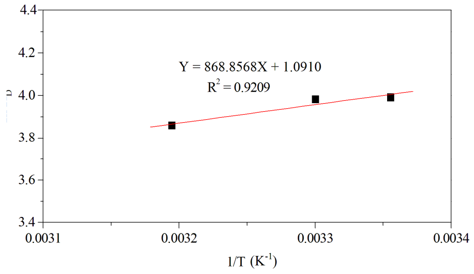


Figure 12. **The plot of lnKD vs 1/T for MCM-41 (C)**

Table 4. Langmuir isotherm equations and other derived parameters for the adsorption of oleic acid onto MCM-41 (A)

Temperature (°C)	Langmuir equation	R^2	q_m (mg/g)	K_A (L/mg)
25.0	$X_e/q = 0.0036X_e + 4.4041$	0.9951	277.8	8.17×10^{-4}
30.0	$X_e/q = 0.0039X_e + 2.0501$	0.9946	256.7	1.90×10^{-3}
40.0	$X_e/q = 0.0047X_e + 2.8752$	0.9904	212.8	1.64×10^{-3}
50.0	$X_e/q = 0.0050X_e + 3.1015$	0.9860	200.0	1.61×10^{-3}

Table 5. Langmuir isotherm equations and other derived parameters for the adsorption of oleic acid onto MCM-41 (C)

Temperature (°C)	Langmuir equation	R^2	q_m (mg/g)	K_A (L/mg)
25.0	$X_e/q = 0.0037X_e + 2.0100$	0.9972	270.3	1.84×10^{-3}
30.0	$X_e/q = 0.0039X_e + 2.0286$	0.9949	256.4	1.92×10^{-3}
40.0	$X_e/q = 0.0041X_e + 1.9384$	0.9951	243.9	2.12×10^{-3}
50.0	$X_e/q = 0.0062X_e + 1.6319$	0.9940	161.3	3.80×10^{-3}

Table 6. Freundlich isotherm equations and other derived parameters for the adsorption of oleic acid onto MCM-41 (A)

Temperature (°C)	Freundlich equation	R^2	1/n	K_F (mg/g)
25.0	$\ln q = 0.2488\ln X_e + 3.1381$	0.9611	0.2488	23.06
30.0	$\ln q = 0.2279\ln X_e + 3.3409$	0.8406	0.2279	28.24
40.0	$\ln q = 0.2009\ln X_e + 3.3864$	0.8486	0.2009	29.56
50.0	$\ln q = 0.2280\ln X_e + 3.0595$	0.8933	0.2280	21.32

Table 7. Freundlich equations and other derived parameters for the adsorption of oleic acid onto MCM-41 (C)

Temperature (°C)	Freundlich equation	R^2	1/n	K_F (mg/g)
25.0	$\ln q = 0.2127\ln X_e + 3.5142$	0.9289	0.2127	33.59
30.0	$\ln q = 0.2278\ln X_e + 3.3423$	0.8402	0.2278	28.28
40.0	$\ln q = 0.2285\ln X_e + 3.2776$	0.8822	0.2285	26.51
50.0	$\ln q = 0.1911\ln X_e + 3.2213$	0.9036	0.1911	25.06

From the adsorption data obtained from different temperatures, ΔH° and ΔS° were calculated from a slope and intercept of a graph plotting between $\ln K_D$ versus 1/T, as shown in Figures 11 and 12. The results are given in Table 8. The negative values of ΔH° suggest that the adsorption is an exothermic process, that is, the adsorption decreases when the temperature of the system increases. ΔS° is related to variations of the order-disorder in a system. The positive values of ΔS° suggest that the adsorption system was in a higher state of randomness at equilibrium (Adam and Chua, 2004). The negative values of ΔG° indicate that the adsorption of the acid on both adsorbents is a spontaneous process.

Adsorption of Oleic Acid in Soybean Oil

Both MCM-41 (A) and MCM-41 (C) were used for the adsorption of 1.0% oleic acid in soybean oil. The mixture of the adsorbent and the acid solution was stirred for 60 min at 25°C. After that the adsorbent was removed by centrifugation and the amount of the acid in the solution was determined. The results are shown in Table 9. The adsorption capacity of MCM-41 (A) was 178.7 mg/g which was lower than that of the adsorption conducted in isooctane, q_e = 242.5 mg/g, with the same concentration of oleic acid and adsorption temperature. The lower adsorption capacity for oleic acid in soybean oil could be explained from triacylglycerol also being adsorbed on MCM-41 (A) via the hydrophobic interaction between alkyl chains of CTAB and triacylglycerol. For MCM-41 (C), the adsorption of the acid was not observed. This could be due to triacylglycerol being adsorbed on the adsorbent via the hydrogen bonding of the carbonyl group to the silanol group (Yates *et al.*, 1997). Triacylglycerol is a major component in the soybean oil. With its bulky structure when it was adsorbed on the adsorbent, it could hinder the adsorption of oleic acid.

Conclusions

In this work, MCM-41 synthesized from rice husk silica was used for the adsorption of oleic acid. The as-synthesized MCM-41 and the template-removed MCM-41 could adsorb oleic acid in isooctane with about the same adsorption capacity. The adsorption followed the Langmuir isotherm model. The adsorption process has been found to be spontaneous and exothermic. The as-synthesized MCM-41 could be potentially applied for the adsorption of oleic acid in soybean oil.

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Table 8. Thermodynamic parameters calculated for the adsorption of oleic acid onto the MCM-41 (A) and the MCM-41 (C)

Adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol)		
			25.0°C	30.0°C	40.0°C
MCM-41 (A)	-3.59	21.5	-10.01	-10.12	-10.34
MCM-41 (C)	-7.22	9.07	-9.93	-9.97	-10.06

Table 9. The adsorption capacities of MCM-41 (A) and MCM-41 (C) in soybean oil

Adsorbent	q_e (mg/g)	% removal
MCM-41 (A)	178.7	16.2
MCM-41 (C)	no adsorption	-

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References

American Oil Chemists' Society. (2009). Official Methods and Recommended Practices of the AOCS. 6th ed. American Oil Chemists' Society, Urbana, IL, USA, 1200p.

Adam, F. and Chua, J-H. (2004). The adsorption of palmytic acid on rice husk ash chemically modified Al (III) ion using the sol-gel technique. J. Colloid Interf. Sci., 280:55-61.

Atia, A.A., El-Nahas, A.M., Marie, A.M., and Al Mahdy, L.D. (2006). Adsorption of oleic acid on silica gel derived from rice ash hulls: Experimental and theoretical studies. Adsorpt. Sci. Technol., 24(9):797-814.

Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., and Schlenker, J.L. (1992). A new family of mesoporous molecular sieves prepared with liquid crystal templates. J. Am. Chem. Soc., 114:10834-10843.

Bhagiyalakshmi, M., Yun, L.J., Anuradha, R., and Jang, H.T. (2010). Synthesis of chloropropylamine grafted mesoporous MCM-41, MCM-48 and SBA-15 from rice husk ash: their application to CO_2 chemisorption. J. Porous Mat., 17:475-484.

Bhosle, B.M. and Subramanian, R. (2005). New approaches in deacidification of edible oils - a review. J. Food Eng., 69:481-494.

Braga, P.R.S., Costa, A.A., de Macedo, J.L., Ghesti, G.F., de Douza, M.P., Dias, A.J., and Dias, S.C.L. (2011). Liquid phase calorimetric-adsorption analysis of Si-MCM-41: Evidence of strong hydrogen-bonding sites. Micropor. Mesopor. Mat. 139:74-80.

Choi, J., Han, Y., Park, S., Park, J., and Kim, H. (2014). Pore characteristics and hydrothermal stability of mesoporous silica: role of oleic acid. J. Nanomater., 2014:1-8.

Costa, A.A., Ghesti, F.G., de Macedo, J.L., Braga, V.S., Santos, M.M., Dias, J.A., and Dias, S.C.L. (2008). Immobilization of Fe, Mn and Co tetraphenylporphyrin complexes in MCM-41 and their catalytic activity in cyclohexene oxidation reaction by hydrogen peroxide. J. Mol. Catal. A-Chem., 282:149-157.

Demirbaş, A. (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. Energ. Convers. Manage., 44:2093-2109.

Farook, A. and Ravendran, S. (2000). Saturated fatty acid adsorption by acidified rice hull ash. J. Am. Oil Chem. Soc., 77:437-440.

Ghiaci, M., Abbaspur, A., Kai, R., and Seyedeyn-Azad, F. (2004). Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. Sep. Purif. Technol., 40:217-229.

Goworek, J., Kierys, A., and Kusak, R. (2007). Isothermal template removal from MCM-41 in hydrogen flow. Micropor. Mesopor. Mat., 98:242-248.

Grün, M., Unger, K.K., Matsumoto, A., and Tsutsumi, K. (1999). Novel pathways for the preparation of mesoporous MCM-41 materials: Control of porosity and morphology. Micropor. Mesopor. Mat., 27:207-216.

Hu, X., Qiao, S., Zhao, X.S., and Lu, G.Q. (2001). Adsorption study of benzene in ink-bottle-like MCM-41. Ind. Eng. Chem. Res., 40:862-867.

Igarashi, N., Koyano, K.A., Tanaka, Y., Nakata, S., Hashimoto, K., and Tatsumi, T. (2003). Investigation of the factors influencing the structural stability of mesoporous silica molecular sieves. Micropor. Mesopor. Mat., 59:43-52.

Jabariyan, S. and Zanjanchi, M.A. (2012). A simple and fast sonication procedure to remove surfactant templates from mesoporous MCM-41. Ultrason. Sonochem., 19:1087-1093.

Jamal, Y. and Boulanger, B.O. (2010). Separation of oleic acid from soybean oil using mixed-bed resins. J. Chem. Eng. Data, 55:2405-2409.

Kalapathy, U. and Proctor, A. (2000). A new method for free fatty acid reduction in frying oil using silicate films produced from rice hull ash. J. Am. Oil Chem. Soc., 77(6):593-598.

Khemthong, P., Prayoonpokarach, S., and Wittayakun, J. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. Suranaree J. Sci. Technol., 14(4):367-379.

Kim, M., Yoon, S.H., Choi, E., and Gil, B. (2008). Comparison of the adsorbent performance between rice hull ash and rice hull silica gel according to their structural differences. Food Sci. Technol-Leb, 41:701-706.

Kleitz, F., Schmidt, W., and Schüth, F. (2001). Evolution of mesoporous materials during the calcinations process: structural and chemical behavior. Micropor. Mesopor. Mat., 44-45:95-109.

Kleitz, F., Schmidt, W., and Schüth, F. (2003). Calcination behavior of different surfactant- templated mesostructured silica materials. Micropor. Mesopor. Mat., 65:1-29.

Kumar, T.V.V., Prabhakar, S., and Raju, G.B. (2002). Adsorption of oleic acid at sillimanite/ water interface. J. Colloid Interf. Sci., 247:275-281.

Lenza, R.F.S. and Vasconcelos, W.L. (2001). Preparation of silica by sol-gel method using formamide. Mat. Res., 4(3):189-194.

Ma, F. and Hanna, A.M. (1999). Biodiesel production: a review. Bioresource Technol., 70:1-15.

Martins, P.F., Ito, V.M., Batistella, C.B., and Maciel, M.R.W. (2006). Free fatty acid separation from vegetable oil deodorizer distillate using molecular distillation process. Sep. Purif. Technol., 48:78-84.

Proctor, A., Adhikari, C., and Blyholder, G.D. (1995). Mode of oleic acid adsorption on rice hull ash cristobalite. J. Am. Oil Chem. Soc., 72(3):331-335.

Ramadhas, A. S., Jayaraj, S., and Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. Fuel, 84:335-340.

Rintramee, K., Föttinger, K., Rupprechter, G., and Wittayakun, J. (2012). Ethanol adsorption and oxidation on bimetallic catalysts containing platinum and base metal oxide supported on MCM-41. Appl. Catal. B., 115-116:225-235.

Saleh, M.I. and Adam, F. (1994). Adsorption isotherms of fatty acids on rice hull ash in a model system. J. Am. Oil Chem. Soc., 71(12):1363-1366.

Serrano, D.P., Calleja, G., Botas, J.A., and Gutierrez, F.J. (2004). Adsorption and hydrophobic properties of mesostructured MCM-41 and SBA-15 material for volatile organic compound removal. Ind. Eng. Chem. Res., 43:7010-7018.

Shylesh, S. and Singh, A.P. (2006). Heterogenized vanadyl cations over modified silica surfaces. J. Catal., 244:52-64.

Yalçin, N. and Sevinç, V. (2001). Studies on silica obtained from rice husk. Ceram. Int., 27:219-224.

Yates, R.A., Caldwell, J.D., and Perkins, E.G. (1997). Diffuse reflectance Fourier transform infrared spectroscopy of triacylglycerol and oleic acid adsorption on synthetic magnesium silicate. J. Am. Oil Chem. Soc., 74:289-292.

Yoon, S.H., Kim, M., and Gil, B. (2011). Deacidification effects of rice hull-based adsorbents as affected by thermal and acid treatment. Food Sci. Technol-Leb, 44:1572-1576.