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KINETICS OF ISOTHERMAL ADSORPTION OF β-CAROTENE FROM CRUDE PALM OLEIN USING ATTAPULGITE

KINETIKA ADSORPSI ISOTERMAL β-KAROTEN OLEIN SAWIT KASAR DENGAN MENGGUNAKAN ATAPULGIT

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ABSTRAK

Tujuan dari penelitian ini adalah untuk menentukan kondisi steady state dan nilai konstanta kinetika reaksi seperti konstanta adsorpsi (k) dan energi aktivasi (Ea) dari proses adsorpsi β-karoten dari CPO menggunakan atapulgit sebagai pembanding dalam penelitian ini juga digunakan arang aktif. Pada kondisi steady statekonsentrasi β-karoten menggunakan atapulgitdipengaruhi oleh faktor suhu dalam proses reaksi. Kondisi steady state diperoleh ketika konsentrasi β-karoten menurun secara konstan dalam olein hingga konstan. Kinetika reaksi adsorpsi isothermal pada tiga tingkat suhu (40ºC, 50ºC, and 60ºC) menghasilkan nilai konstanta adsorpsi (k) mengikuti isothermal model Freundlic. Nilai konstanta adsorpsi pada suhu reaksi dengan adsorben atapulgit adalah 2,31×10^{-7}mL.g^{-1}, 4,94×10^{-5}mL.g^{-1}, dan 7,82×10^{-5}mL.g^{-1}, sedangkan menggunakan arang aktif sebesar 3,10×10^{-4}mL.g^{-1}, 1,29×10^{-4}mL.g^{-1}, dan 6,16×10^{-3} mL.g^{-1}. Suhu adsorpsi yang tinggi dapat digunakan sebagai faktor pemercepat reaksi. Nilai energi aktivasi pada kondisi tersebut sebesar 62,04 kkal mole^{-1} untuk atapulgit, dan 30,45 kkal mole^{-1} untuk arang aktif. Berdasarkan nilai energi aktivasi (Ea) dapat disimpulkan bahwa proses adsorpsi β-karoten dari CPO menggunakan atapulgit lebih efektif daripada menggunakan arang aktif.

Kata kunci: adsorsi, β-karoten, crude palm *olein*, atapulgit, arang aktif

ABSTRACT

The objectives of this research were to determine the steady state condition and the values of kinetics parameters, which were adsorption constantrate (k) and activation energy (Ea) of β-carotene adsorption process from crude palm olein using attapulgite. Another adsorbent used in this study was activated carbon. The steady state condition of β-carotene concentration using attapulgite was influenced by adsorption process temperature. The steady state condition was achieved when the declining of β-carotene concentration in crude palm olein in constant rate. Kinetics of isothermal adsorption at three temperatures (40ºC, 50ºC, and 60ºC) resulting the adsorption constants rate value (k) pursuant by Freundlic isotherm model. The adsorption constants rate values at those temperature reactions using attapulgite were 2.31×10^{-7}mL.g^{-1}, 4.94×10^{-5}mL.g^{-1}, and 7.82×10^{-5}mL.g^{-1}, while for activated carbon were 3.10X10^{-4}mL.g^{-1}, 1.29×10^{-4} mL.g^{-1}, and 6.16×10^{-3} mL.g^{-1}. Higher adsorption temperature could be used as a factor to accelerate the reaction. Values of activation energies at that condition were 62.04 kcal mole^{-1} for attapulgite, and 30.45 kcal mole^{-1} for activated carbon. According to the value of activation energy (Ea), it can be concluded that adsorption process of β-carotene from crude palm olein using attapulgite was more effective than using activated carbon.

Keywords: adsorption, β-carotene, crude palm olein, attapulgite, activated carbon

INTRODUCTION

Currently, Indonesia is the largest palm oil producer in the world, where the vast production and their area has surpased than Malaysia. Most of palm oil products handled in Indonesia is in the form of crude palm oil (CPO) which is extracted from the husk (mesocarp) oil palm. CPO production in 2010 reached 19.84 million tons with oil palm plantation area of 7.82 million hectares (Ditjenbun, 2011).The changing pattern of consumption from coconut oil to palm oil provides a good development for the palm oil industry. The world journal of vegetable oil (Oil World) predicts in 2015, share of palm oil in the total oil world production will reach 23%.

Palm oil processing industry used the chemical and physical technology processes to obtain derivative products of oil. Bleaching in the purifying industry of palm oil is needed to remove the red color of a carotenoid pigment from crude palm olein oil in addition to obtain a refined oil as the consumer desires. Nutritional value of the potential active components in the crude palm olein and the sensitivity of those components shoud be considered toward high temperature or oxidation toward separation and purification process of β-carotene in the palm oil refining industry.

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The usage of adsorbent was generally proposed to adsorb certain components in the olein. Attapulgite (magnesium aluminum silica) was a mineral compound that potentially used as an adsorbent of β-carotene from crude palm olein. Nowadays, attapulgite only be used as the active ingredient in the pharmaceuticalindustry. Non-polar adsorbent is required for the separation process of β-carotene. Attapulgite is a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral with exchange able cations and reactive OH groups on its surface, is less sensitive to salts compared to other clays (such as smectite) (Neaman and Singer, 2004).

Attapulgite was an adsorbent that not easy to saturated, and temperature resistant up to 500ºC. Furthermore this attapulgite has an ability to choose the spesific components in the adsorption process which easy for desorption (Lansbarkis, 2000). The type, combination and ratio of adsorbent with CPO affected the results of adsorption. β-carotene adsorption performed at a temperature of 50-55ºC (Latip *et al.*, 2001). Tocopherol adsorption process could be done until 80ºC of temperature (Sanagi *et al.*, 2005). Kinetics is needed in an adsorption process to show the relationship between the velocity parameters adsorption and pore adsorbent diameter (Kadirvelu *et al.*, 2000). Langmuir and Freundlich isotherm used to indicate a suitable model for the kinetics of an adsorption process (Ribeiro *et al.*, 2001).

This research was expected to obtain β-carotene which contained in the crude palm olein using an attapulgite as adsorbent. In addition, it was also expected to produce the profile of attapulgite activity in β-carotene adsorption and to obtain the adsorption kinetics models which were important for process engineering purposes.

MATERIALS AND METHOD

Materials

The main material used in this study was crude palm oil (CPO). Adsorbent used were attapulgite (150 mesh) and activated carbon (150 mesh). Chemicals used were β-carotene standard (Sigma-Aldrich), α-tocopherol standard (Sigma-Aldrich), hexane, phenolphthalein, aquadest, 95% alcohol, and 0.1 N KOH.

The main equipment used were reactors equipped with stirrer, spectrophotometer, refractometer, High Performance Liquid Chromatrography (HPLC), erlenmeyer, glass trophies, glass stirrer, spatula, scale, analytical balance, volumetric pipettes, mohr pipettes, burettes, squash drinks, threaded tubes, containers, water bath, and the vacuum pump.

Methods

This researchconsists of 5 stages: the characterization of crude palm olein, adsorption of β-carotene from crude palm olein using attapulgite and activated carbon, the determination of equilibrium adsorption process, the determination of kinetics β-carotene adsorption parameters which consist with rate constants (k) and energy activation (Ea), and the final stage was the determination of adsorption quality.

Adsorption Process

β-carotene adsorption process on crude palm olein performed with several stages, the first is mixing the adsorbent (300 g) with olein (900 ml) in a stirred reactor (stirring speed of 120 rpm; in temperature of 40°C, 50°C, 60°C; and adsorption for 171 minutes). The scheme of stirred reactor design can be seen in Figure 1.

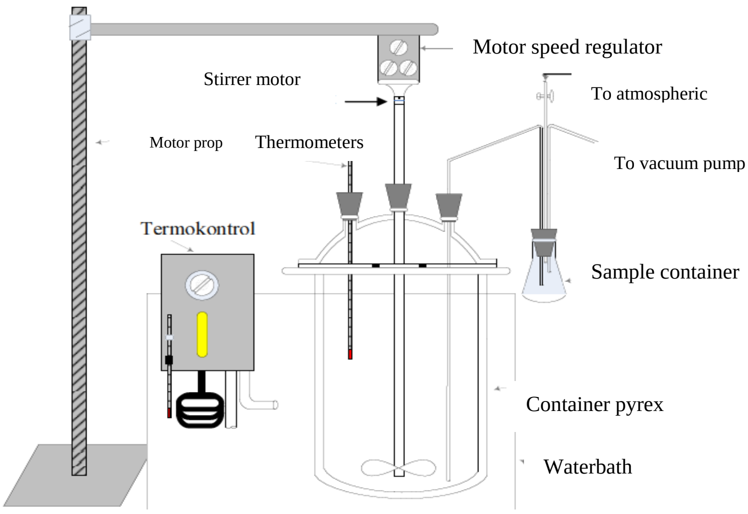

Figure 1. The scheme of stirred reactor design

Second Stage is mixing adsorbent samples and olein in reaction temperature and duration of specific adsorption. Third is separating the adsorbent from the crude palm olein, and the final stage is of analysing the performed olein, namely β-carotene and α-tocopherol concentrations, free fatty acid level, the refractive index and desorption capability

Determination of Adsorption Equilibrium Process

Equilibrium condition is obtained from the relationship between the length ofadsorption with the concentration of β-carotene in crude palm olein when an increase in the length of the adsorption no longer cause reduction in β-carotene content in crude palm olein. Condition of equilibrium is determined for each treatment type adsorbent used (attapulgite and activated charcoal) and temperature (40ºC, 50ºC, and 60ºC). Equilibrium parameters to be determined are old and value (the concentration of β-carotene in olein rude oil) to achieve equilibrium conditions. Furthermore, it is known relation between the concentration adsorption in the adsorbent (q) with a concentration in solution (C) using appropriate adsorption isotherm models of experimental data. The calculation of the value of q = (C_0 - C_t) V/m, where C_0 is concentration of crude palm olein, C_t is the concentration at time t, V is the volume of crude palm olein used (900 mL) and m is the mass of adsorbent used (300 g). Value Ca at certain concentration and a time t. Curve relationship between q and C can indicate the type of isotherm formed in attapulgite and activated charcoal.

Determination of The Adsorption Rate Constant (k)

The value of the adsorption rate constant (k) can be determined by plotting the concentration of β-carotene in the adsorbent (q) with β-carotene concentration value in olein (c) using the Langmuir equation and Freundlich. The plot of 1/q and 1/C resulted in a linear form Langmuir modele. Linear equations can be seen in equation 1:

$$\frac{1}{q} = \frac{k}{qmaks}\frac{1}{C} + \frac{1}{qmaks} \quad \text{.......................................(1)}$$

Slope of the linear regression results of equation, produce value k/qmaks where k is the rate constant of adsorption and intercepts showed 1/qmax value. While the plot of log q and log C resulted in a linear form of the Freundlich models is shown in equation 2:

$$\text{Log } q = \log kf + n \log C \quad \text{................................ (2)}$$

Slope of the linear regression results of equation 2 is the value of n and demonstrate the value of rate constant its intersept adsorption (kf).

Determination of Activation Energy

The value of activation energy (Ea) was determined by linear regression results of the adsorption rate constant (k) and temperature (T). Determination of the activation energy using the Arrhenius equation can be seen in equation 3:

$$\ln k = -\left(\frac{1}{T}\right)\left(\frac{Ea}{R}\right) + \ln Ao \quad \text{..(3)}$$

RESULT AND DISCUSSION

Characterization of Crude Palm Olein

The characterization of palm oil olein fraction was done to know its physicochemical characteristics.

Table 1. Physicochemical of crude palm olein

Characteristic	Value	SNI 1998
FFA (%)	5.06	Max 5
Acid value (mg KOH g^{-1})	11.09	-
β-Carotene Concentration (ppm)	409.05	-
Refraction Index 26.9ºC	1.46	-

Based on Table 1, the FFA value of olein was 5.06% which was higher than the standard value of 5%. It might be caused by the hydrolysis reaction in olein. The acid value showed the total of free fatty acid in olein. These results showed that olein fatty acid in this research was 11.09 and the refraction index was 1.46. The refraction index showed that the double bound in olein was not too much and therefore the oil was classified as good.

Attapulgite Characteristic

Characterization of attapulgite and activated carbon were done to know the capability of adsorption process. To view the adsorbent characteristic, an adsorbent characterization need to be done which include visual colour and shape of material,and particlessize. The characterization of the adsorbent can be seen in the Table 2.

Table 2. Characterizations of atapulgite and activated carbon

Adsorbent	Characteristic		
	Colour	Shape	Particle size
Attapulgite	Greyish white	Powder	150 mesh
Activated carbon	Black	Powder	150 mesh

Table 2 show that attapulgite and activated carbon have particle size of 150 mesh and in the powder form. This characterization facilitates the adsorption process for materials separation of a small concentration compound from a mixture which contains others high concentration of other compound. The adsorption power toward colour would be more effective if adsorbent has a low specific gravity, high water content, small particle size and pH close to neutral (Zhang *et al*., 2010).

The Equilibrium Adsorption

Equilibrium condition is a condition when the process of separating certain components from a fluid phase move to the surface of adsorbent at the saturated condition until the separation process no more take place. According to the reaction rate theory which states that the rate of reaction followsto the rate of concentration reactants changes,sothe rate adsorptionreaction fromcrude palm oil was determined based on declining of β-carotene concentrationsduring the adsorption reaction. Declining of β-carotene concentration in olein side provoked increase the β-carotene concentration in the adsorbent side. In this study, we used activated carbon as an adsorbent for comparison (see Figure2).

Based on Figure 2, itcould be seen that the timeof reaction would decrease the β-carotene concentration in olein. This condition continue until equilibrium conditions were reached and there was no decreasing the β-carotene concentration in olein side. The declining of β-carotene concentration in olein side was caused by adsorption of β-carotene in the adsorbent. β-carotene concentration in olein side which declines with the length of time causes the concentration of β-carotene that absorbed in the adsorbent increasesuntil the condition of adsorbent could not adsorbanymore. Equilibrium condition was a condition where the adsorbent with saturation capacity adsorption experience. In this process, the higher temperature would make the colors of olein gotmore paleand color of adsorbent could be more intense due to Al^{3+} ions on the surface of adsorbent particles adsorbthe pigment particles.

Equilibrium conditions differ in each temperature reaction. Higher reaction temperature in β-carotene adsorption using attapulgite would leadto the increasing of equilibrium conditions.The durationwhich is achievedto give the same effect on reducing the concentration of β-carotene at high temperature reaction wasmore rapidly than at low temperatures reaction. Equilibrium condition with activated carbon as catalyst is better than attapulgite. It could be seen from the value of β-carotene concentration using activated carbon lower than in olein which lower than the concentration of β-carotene using attapulgite as adsorbent. On activated carbon, the higher temperatures, the lower of equilibrium conditions is and thedurationof process declines more slowly. The value of β-carotene concentration in olein at equilibrium conditions for each temperature and the type of adsorbent was shown in Table 3.

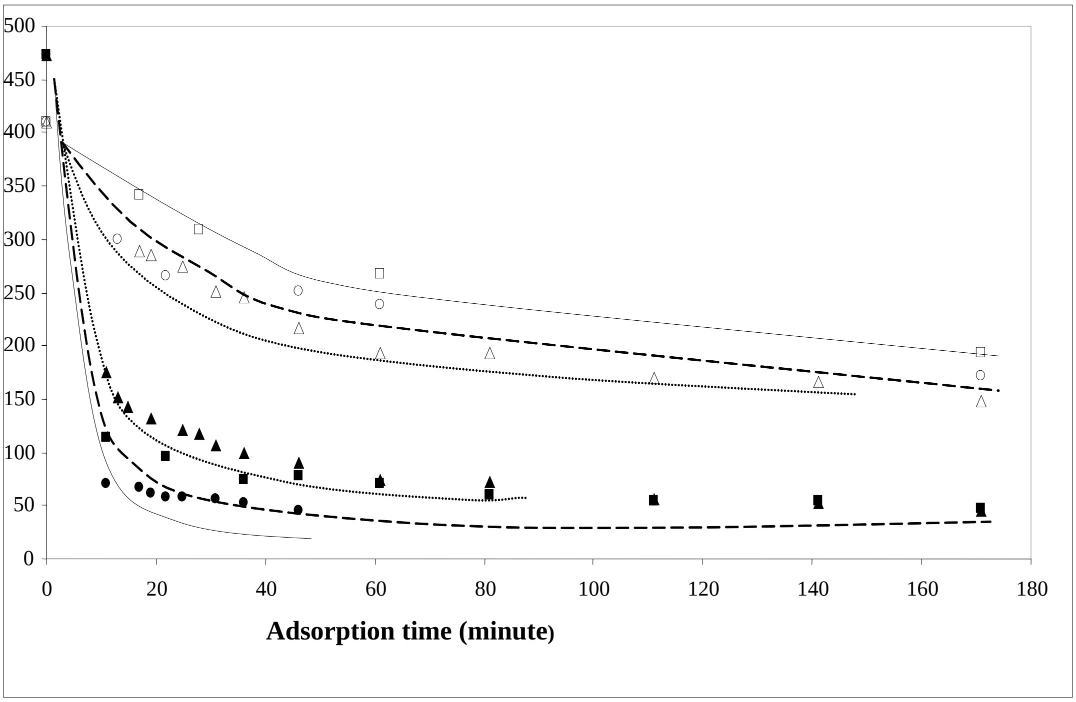

Figure2. The relation between the decline in the value of β-carotene concentration in crude palm olein with adsorption time (○, atapulgit 40º C; □, atapulgit 50º C; Δ, atapulgit 60º C; ●, activated carbon 40º C; ■, activated carbon 50º C; ▲, activated carbon 60º C)

Table 3. Valueof β-caroteneconsentrationin oleinat equilibriumconditions for each temperature

Type of adsorbent	Temperature reaction (°C)	Reaction time (minute)	B-carotene concentration in olein (μg ml^{-1})
Attapulgite	40	33	249
	50	31	264
	60	25	210
Activated Carbon	40	22	45
	50	22	60
	60	19	85

Based on Figure 2, tell that timeof reaction would decrease the β-carotene concentration in crude palm olein. This condition continue until equilibrium condition reached and there was no decreasing the β-carotene concentration in crude palm olein side. The declining caused by adsorption of β-carotene by adsorbent. β-carotene concentration in crude palm olein side which declines with the length of time causes the concentration of β-carotene that absorbed in the adsorbent increasesuntil the condition of adsorbent could not adsorbanymore. Equilibrium condition was a condition where the adsorbent with saturation capacity adsorption experience. In this process, the higher temperature would make the colors of crude palm olein gotmore paleand color of adsorbent could be more intense due to Al^{3+} ions on the adsorbent surface particles adsorbthe pigment particles (β-carotene).

Equilibrium condition which is obtained differently in each temperature reaction. On adsorption β-carotene using atapulgit reaction, the higher temperature reaction, the equilibrium is increasing. The time reached to give the same effect to the reduction in the concentration of β-carotene at high temperature reaction was more rapidly than at low temperatures reaction. Equilibrium condition in the activated carbon was better than attapulgite. It could be seen from β-carotene concentration values in crude palm olein that was lower than the concentration of β-carotene in crude palm olein by using attapulgite as the adsorbent. On active carbon, the higher the temperatures used, the equilibrium conditions declined and the time achieved was slower. The value of the concentration of β-carotene in crude palm olein at equilibrium conditions for each type of adsorbent and adsorbent temperature was shown in Table 3.

Based on Table 3, it could be seen that the condition of equilibrium at each temperature were based on the type of adsorbent. In the β-carotene adsorption using attapulgite, the equilibrium increases as temperature increases. This proves that the temperature affects the rate of adsorption and the adsorption equilibrium conditions.

The increase of adsorption rate was caused by the adsorption physically of β-carotene from crude palm olein to adsorbent. Gibon *et al*. (2007), stated the bleach theory of adsorption that is an adsorption process at low temperature such as bleaching caused more by intermolekular bond formation than by new chemical bonds. Absorbed molecules retain its identity and do not result in termination of the bond.

The simplest adsorption process occurs when the Gibbs free energy at the lowest conditions where the adsorbent and adsorbat had the same polarity, so adsorbat tend to adsorb because its Gibbs free energy was low. In addition, adsorption of β-carotene by adsorbent caused by hydrophobic interactions between the adsorbent and β-carotene (Srivastava *et al.*, 2006).

Attapulgite structure consists of double silica chains which bonded with oxygen in configuration of tetrahedral which was a non-polar cluster, aluminum and magnesium then bonded to oxygen, hydroxyl cluster, and OH clusterin configuration of octahedral which was a polar cluster (Zhang *et al*., 2006). The existence of polar and non-polar clusterin this attapulgite causes the adsorbent classified to the semi-polar adsorbent.

According to Chu *et al*. (2004), the less polar bond was a bond between the silica and oxygen (Si-O-Si) that called silocsan. β-carotene was a non-polar molecules whichwas adsorbed on siloksan cluster. The interaction of siloksan cluster with electron clouds were scattered on the double bond which conjugated with β-carotene molecule through dipoles bond. β-carotene was an aseptor properties of protonswhich tends to attract cations from the outside.The probability of van der walls bond between β-carotene and attapulgite shown in Figure 3.

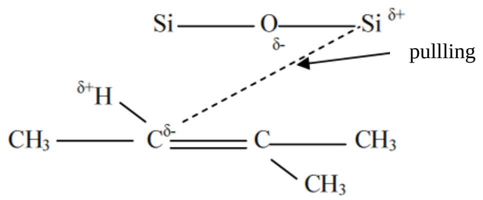

Figure 3. Van der walls bond between β-carotene and attapulgite

In β-carotene adsorption using attapulgite, the concentration of β-carotene in olein at equilibrium conditions increase withincreasing the adsorption temperature from 40ºC to 50ºC and then decresase with increasingadsorption temperature from 50ºC to 60ºC. This is dueto the adsorption of componen in olein,such as α-tocopherol, which had a lower molecular weight than β-carotene, but the rate of adsorption in this process was elevated remained. At 60ºC,it reachedequilibrium condition and showedincreasing in its adsorption rate. This was caused by the oxidation of unsaturated fatty acids in olein toward the double bond. On the activated carbon, physical adsorption process occurs by the attractiveness or polarity differences of activated carbon surface that was greater than the attraction to holding β-carotene in olein. This polarity difference causes the adsorbentinherent in such a strong on activated carbon. Both pore and adsorbent surface area affected onadsorption rate.The greater of pores and its surface area would accelerate the adsorption reaction. This situation causes the adsorption of activated carbon greater than the attapulgiteadsorption.

Equilibrium conditions on activated carbon decreas ealong when the temperature was increased. This was caused by the activated carbon tends to adsorb straight-chain molecules.In addition, activated carbon could adsorbpigmentsat95-97 percent of the total pigments which contained in the oil and it can used in a very small amount. Thedifferencesof equilibrium conditions proves that the temperature and the type of material adsorbent affected the rate of adsorption and theequilibrium adsorption conditions fromthese processes(Li *et al.*, 2004).

The usage of activated carbon in β-carotene adsorption process from crude palm olein was better than attapulgite. On attapulgite, the higher temperature will increased the concentration of β-carotene in the solid phase. Increasing of temperature caused not only β-carotene in the solid phase but also activated carbon was decreased. Despite, the increase of temperature might increase the number of micro pores on activated carbon, the rate of β-carotene adsorbedby activated carbon was diminished. This result wascaused by anadsorption activity that occurs not only to adsorb β-carotene but also the others pigmentthat was produced by oxidation in olein,so the saturation of activated carbon was going faster and less to adsorb of β-carotene.In morethis activated carbon adsorbed the pigment with great molecular weights fasterly. Activated carbon was not classified to the selective adsorbent, so the other pigments would beabsorbed by activated carbon.Activated carbon mightbe saturated fasterlyby another substance and did not adsorbof β-carotene component. When the two types of molecular structureswerethe same,the larger molecular weight would be more absorbed by activated carbon. But, if the molecular structureswere not the same,the adsorption was more influenced by molecular composition (Amir, 2003). The amount of adsorption capacity on activated carbon and attapulgite was shown in Figure 4.

Based on Figure 4,it showed that the concentration of β-carotene in olein declined with the length of time. It caused the concentration of β-carotene that adsorbed in adsorbent had increased, so that, in this condition,the adsorbent could not be able to adsorb anymore. The condition of equilibrium was a condition where the adsorbent has a saturated adsorption capacity.

The move of adsorbate to the surface of the adsorbent was directly affected by the viscosity and velocity.Indirectly, itwas affected by adsorbat particle size. The mechanism of this diffusion consisted the diffusion phase to adsorbent surface and the diffusion into the poreof adsorbent.

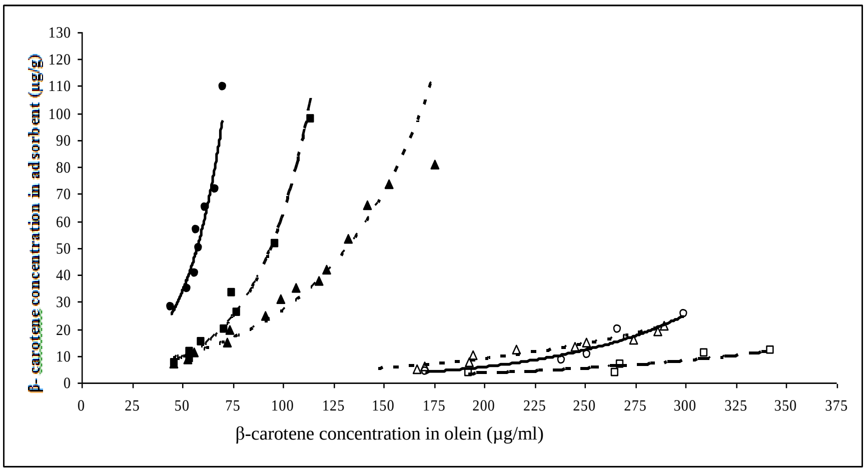

Figure 4 .The relation between the values of β-carotene concentration in olein with β-carotene concentration in the adsorbent (○, atapulgite 40ºC; □, atapulgite 50ºC; Δ, atapulgite 60ºC; ●, activated carbon 40ºC; ■, activated carbon 50ºC; ▲, activated carbon 60ºC)

Figure 4 showed the illustration of the molecules surface which was adsorped and the number of quantity thatadsorptedat higher temperatures. The curve had a value of n ≥ 1 which describes the adsorption process that had no inclination or its shape concave to upward, so the mass transfer zone in the process had a longer time and desorption would require a lower temperature.

Adsorption efficiency index (n) affects the adsorption process. Isotherm form related with the value of efficiency adsorption. The higher ofn value would make the adsorption process slower. On the attapulgite and activated carbon, increasing of temperature would increase the efficiency of adsorption process. The value of would discuss in further adsorption kinetics.

Kinetic Adsorptionof β-carotene

Adsorption kinetics results were used for setting up the operating conditions, controllingthe methods,instrument and the technology requirement process that used to design the appropriate process. This section would discuss the adsorption rate constant (k) and activation energy (Ea). Both of these parameters show the performance of the two types adsorbent in the adsorption β-carotene.

Adsorption Rate Constant (k)

Relation curve of concentration β-carotene values with adsorption capacity was an experiment data that used for determining the rate of β-carotene from crude palm olein adsorption reaction. Possiblity reaction order of the crude palm olein adsorption reaction was the first semi-order reaction because the β-carotene crude palm olein adsorption reaction involves only a single reactant which was a crude palm olein. The form of reaction rate equation was transformed into a straight line form equation (linear). Regression was a mathematical equation that assumed the relation of equation of olein fraction adsorption reaction rate of experimental data which show the relation between a free variable that was the value of β-carotene concentration (in this case was called C) and the decrease of value of β-carotene concentration in the adsorbent (in this case called q) be used with a fit regression method. A relation of regression between q in C was transformed to follow a straight line equation (linear) form. The adsorption rate used two adsorption equations, that were Freundlich isotherm and Langmuir isotherm. The size to see the compliance level of experimental data was determined based on the largest of the coefficient determination (R^2). The calculation showed that the rate of physical adsorption of activated carbon and attapulgite was more suitable using Freundlich isotherm. Isothermal adsorption parameter values using the model of Langmuir and Freundlich β-carotene from crude palm olein adsorption with attapulgite and activated carbon were presented in Table 4.

In Table 4 could be known that the equation of adsorption reaction rate of olein fraction in crude palm oil had the best suitability with an experiment data for three temperatures that was using Freundlich isothermal model. It was showed by its determination coefficient. The value of isothermal Freundlich coefficient determination was bigger than the value of isothermal Langmuir in three reaction temperature. The bigger determination coefficient showed in the variation of β-carotene concentration was better explained by Freundlich isothermal. It showed that the non-linear adsorption and sorbent layer formed heterogenic because the layer of all adsorbent had the adsorption multilayer form. The regression curve between β-carotene concentrations in adsorbent (log q) with β-carotene concentration in olein (log C) for Freundlich equation could be seen in Figure 5 and 6.

Based on regression in Figure 5 and *6*, it resulted the slope of each reaction rate equation for three reaction temperature. The slope was a reaction rate constant (kf) and their intercept which showed the adsorption efficiency index (n). The value of reaction rate constant (k) was the slope of isothermal reaction rate equation which was chosen. The value of β-carotene reaction rate constant were at 40ºC, 50ºC and 60ºC based on Freundlich isothermal model could be seen in Table 5.

Table 4. Isothermaladsorption parameter of β-Carotene using Langmuir and Freundlich Model

Adsorbent	Temperature (ºC)	Isothermal model					
		Langmuir			Freundlich		
		k	qm	R^2	k	n	R^2
Attapulgite	40	-346.09	-4.24	0.975	2.31×10^{-7}	3.23	0.9019
	50	-585.78	-7.21	0.6664	4.94×10^{-5}	2.11	0.7247
	60	-376.15	-7.46	0.9293	7.82×10^{-5}	2.02	0.9575
Activated carbon	40	-89.12	-26.81	0.9398	3.10×10^{-4}	2.97	0.9071
	50	-113.25	-11.52	0.9391	1.29×10^{-4}	2.8	0.974
	60	-192.91	-25.58	0.9771	6.16×10^{-3}	3.42	0.9899

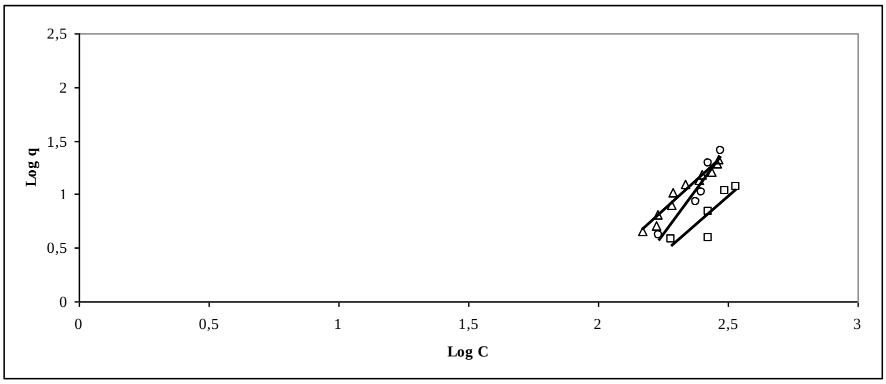

Figure 5. The reaction rate of palm oil olein adsorbtion for attapulgite (○, attapulgite 40ºC, r^2 = 0.8573; □, attapulgite 50ºC, r^2 = 0.9872; Δ, attapulgite 60ºC, r^2 = 0.9407)

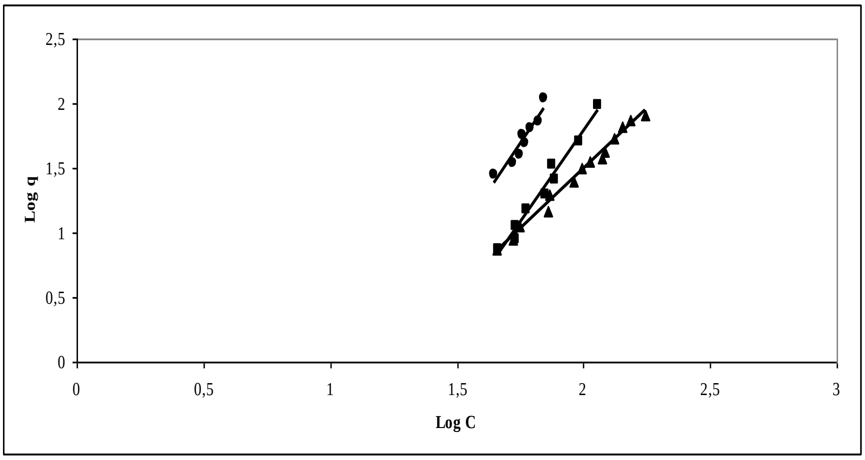

Figure 6. The adsorption reaction rate of crudepalm oil oleinfor activated carbon (●, activated carbon in 40ºC, r^2 = 0.9131; ■, activated carbon 50ºC, r^2 = 0.974; ▲, activated carbon 60ºC, r^2 = 0.9899)

Table 5. The β-carotene adsorption rate constants value

Adsorbent	Temperature (ºC)	N	The adsorption rate constants [mL g^{-1}]
Attapulgite	40	3.23	2.31×10^{-7}
	50	2.11	4.94×10^{-5}
	60	2.02	7.82×10^{-5}
Activated carbon	40	2.97	3.10×10^{-4}
	50	2.8	1.29×10^{-4}
	60	3.42	6.163×10^{-3}

Increasing values of k was in line with the increasing of total adsorbent capacity that bond the adsorbed molecule. The increasing of temperature would influence the constant of reaction rate. From the reaction rate constant, it could be known the highest k value on theuseful of attapulgite and activated carbon happened at 60ºC. The usage of activated carbon in 50ºC was not increasing the reaction rate. It caused there was no β-carotene adsorption. It was proven that temperature influenced the equilibrium condition. Increasing of temperature would increase the frequency of intermolecular collisions in form of activated complex. Therefore, the increase in temperature can be used as a factor to accelerate a reaction.

Change the value ofn would be proportional to the change in the value of k. The smaller of the n value would increase the efficiency of adsorption process. Value of n in both types of adsorbent was more than one and the isotherm was not tend to its form. This result effected in mass transfer zone in the expansewas more be long. If the value of n reach in the high steady condition, adsorbent work effectively in the bleaching process of olein but less efficient as an absorbent material at high color concentration. This efficiency index had a value in the range of 0.1-1. Index value of n was less than 1 relatedtoisotherm adsorption in linear curve.

Activation Energy

Activation energy is calculated from a single curve of a derivative of mass loss perturbed by a sinusoidal modulation of a temperature-time relationship.

Energy that possessed by the molecules and then they can be reacted, the energy stored in intermediate species as an activated complex formed during the collision of molecules. The species held in a short time then decomposesat the first of reactants (in this case there was no reaction) or become moleculesof reaction results. In this activated complex, there were an old bond that close to break condition and a new bond that formed only in part. Only molecules with have greater kinetic energy than its activation energy be able to react or to shape anactivated component which was decomposes into molecules of the reaction result. The molecules were referred to the activated molecules fraction (Nur *et al.*, 2002).

To get the activation energy value of the reaction rate constant was used Arrhenius equation values at those three reaction temperatures. Arrhenius equation was an equation that formulated by Svante Arrhenius which quantify the relation between reaction temperature and activation energy (Ea) with the reaction rate constant (k). Arrhenius equation then modified to a straight line equation form (linear regression). Straight-line relation of Arrhenius equation for the β-carotene adsorption process can be seen in Figure 7 and 8.

Based on the slope of the linear regression equation in Figure7 and 8, it resulted an activation energy was multiplied by the slope of the gas constants (R). Based on the role of adsorbent with the acquisition of an activation energy of adsorption process with adsorbent,it would beshow the effectiveness of an adsorbent than the other adsorbent. Activation energy values show the characteristics of the bond between the adsorbent and adsorbat. The low activation energy value indicates the bond with a weak physical adsorption. The specific chemical adsorption would make the bond was stronger than physical adsorption. Activation energy of β-carotene adsorption process could be seen in Table 6.

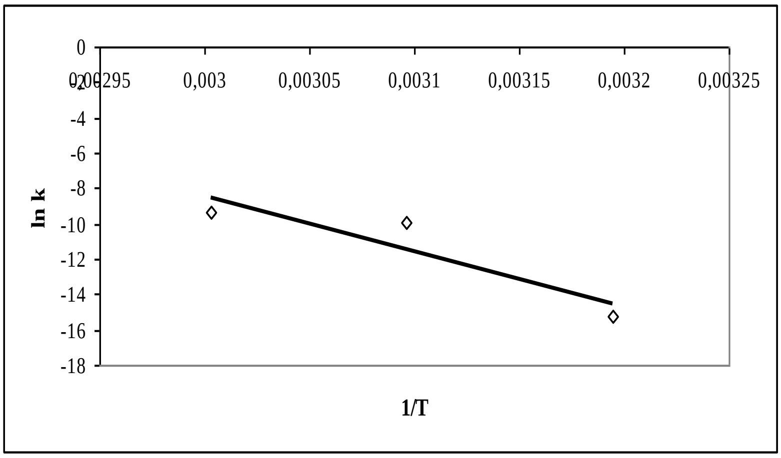

Figure 7. Relation oflinear regression between 1 / T with ln k in the adsorption using attapulgite ($r^2 = 0.8356$)

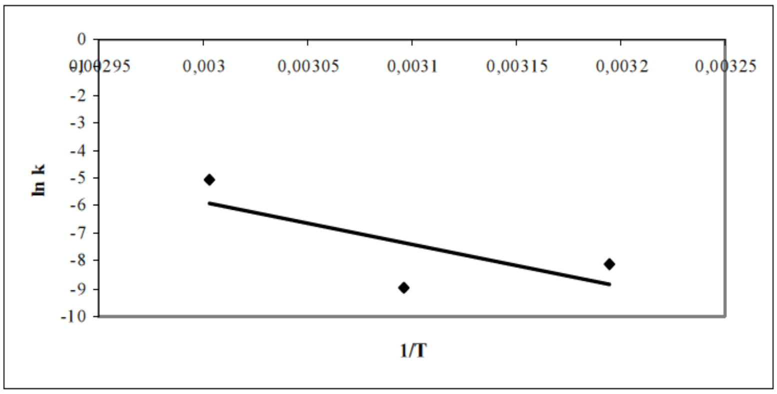

Figure 8. Relation oflinear regression between 1/T with ln k in the adsorption using attapulgite ($r^2 = 0.5255$)

Table 6. Activation energy of β-Carotene adsorption using attapulgite and activated carbon

Adsorbent	Ea [kcal mol^{-1}]
Attapulgite	62.04
Activated carbon	30.45

The lower of activation energy value was in line with the greater of the activated molecules fraction and would accelerate the reaction. Activation energy was obtained by using lower attapulgite amount. This was show that the activated carbon was more effective toward the β-carotene adsorption process from crude palm olein thanattapulgite. Activation energy values also show the characteristics of the bond between the adsorbent and adsorbat. The low of activation energy value indicates the bond that occure in physical adsorption was a weak.

Adsorption Selectivity

The selectivity of an adsorbent needed to observe to know the best adsorbent that used for adsorption of component. Besides, the oil stability influenced by some factors, such as the saturation degree of fatty acid, diffuse of double bonds which could block or accelerate the damage process. The analysis of free fatty acid, acid number and refracted index was being the parameter of oil damage which influences the β-carotene that contained in the oil. The quality parameter was shown in Table 7.

Based on Table 7, α-tocopherol was adsorbed by attapulgite and activated carbon. This was because attapulgite able to adsorb other molecules with low molecular weight and hydrophobic, whereas activated carbon tends to adsorb other molecules that straight-chain more than β-carotene. From the quality parameters Table 7showed activated carbon was 100% visible to adsorb α-tocopherol which higher than attapulgite. Tocopherol was more resistant to heat than β-carotene. Loss of α-tocopherol during the adsorption process was caused mostly by oxidation. This was because α-tocopherol was an antioxidant that easily to oxidized, mainly with the oxygen at high temperatures. From the quality parameters table was show that activated carbon had the adsorption power better than attapulgite.

Value of free fatty acids content and the high amino numbers could be cause by the time of oil storage from the adsorption. So, the hydrolyze and oxidation process make rancidity in the oil, so that, the activity of lipase in the system upset and the enzyme that produced was by microbial contamination. In olein, the higher of temperature reaction would decrease the carotenoids concentration value. So, the value of free fatty acids and acid number were declining. This was caused the fatty acids adsorption in the adsorbent that maked the fatty acid levels declined in olein.

Refractive index value was influenced by factors such as free fatty acid levels, the process of oxidation and temperature. The higher of refractive index value indicates the number of double bonds and the length of carbon chain. From the Table 7 seen with the usage of both adsorbent. The increase in temperature reaction was not increase the refractive index value.

The β-Carotene Desorption of Adsorbent Ability

Desorption process was needed to release the component that adsorbed in adsorbent to the solvent. The ability as solvent such as hexane, isopropanol and ethanol in releasing β-carotene could be seen in Table 8.

The Van der Waals bond isa weak bond, so it was easily irrespective at the desorptionprocess. Non-polar solvents such as hexane was a good solvent for β-carotene.

Non-polar componentswould be easy toelute with non-polar solvents. This was according to the principle that a particular component would be easily dissolved in solvent with the polarity that almost the same (like dissolved like principal).

Isoprophanol was a semi-polar solvent so it tend toelute α-tocopherol and still possible toelute β-carotene besides the elution of other pigments with the same polarity. Percentages of ethanol solvent desorption gave a high value. Ethanol was a polar solvent so the possibility of components that dissolved by ethanol was not a β-carotene component which is include in a nonpolar cluster.Hovewer, it was the other pigments with the same polarityof ethanol. The activated carbon was harder to desorped than attapulgite. This was because the solvent that adsorbedwas very strong.The adsorptioncauses the colors of solvent being more intense.

Table 7. The quality parameter

Adsorbent	60ºC, 171 minutes			
	Total adsorbed [%]		Free fatty acid [%]	Refract index
	β-carotene	α- tocopherol		
Attapulgite	52.97	84.17	3.67	1.4603
Activated carbon	90.24	100.00	2.97	1.4622

Table 8. Desorption process

Adsorbent	60ºC, 171 minutes		
	Total adsorbed [%]		
	Hexane	**Isoprophanol**	**Ethanol**
Attapulgite	3.29	6.17	21.71
Activated carbon	0.34	0.52	2.28

CONCLUSIONS AND RECOMENDATION

Conclusions

The equilibrium condition was obtained based on declining β-carotene concentration value during the palm oil olein adsorption process at three reaction temperature. The higher temperature reaction would cause the lower of β-carotene concentration and the increase of equilibrium condition.

The equilibrium concentration of β-carotene in olein using attapulgite for each reaction temperature of 40ºC, 50ºC, and 6ºC were 249 ppm, 264 ppm, and 210 ppm; while activated carbon in each temperature reaction of 40ºC, 50ºC, and 60ºC were 45ppm, 60 ppm, and 85 ppm. The β-carotene concentration in olein was increased using attapulgite for each reaction time of 40ºC, 50ºC, and 60ºC were 33, 31, and 25 minutes, while for activated carbon were 22, 22, and 19 minutes.

The constant rate reaction value at all of three temperatures reaction using attapulgitewere 2.31×10^{-7} mL.g^{-1}, 4.94×10^{-5} mL.g^{-1}, 7.82×10^{-5} mL.g^{-1}, whereas for activated carbon $3.10\text{x}10^{-4}$ ml.g^{-1}, 1.29×10^{-4}mL.g^{-1}and 6.16×10^{-3}mL.g^{-1}. Energy activation value (Ea) in these conditions was 62.04 kcal mol^{-1} for attapulgite, and 30.45 kcalmol^{-1} for activated carbon.

Recomendation

Suggestion for further research is necessary to activation of the adsorbent, for example, by acid. In addition, the desorption process should be carried out immediately after the adsorption process in order to avoid oxidation process.

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