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Adsorption kinetics and thermodynamics of β -carotene on silica-based adsorbent

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ABSTRACT

The adsorption behaviour of β -carotene on synthetic adsorbent was studied by batch tests. This study was to develop the adsorption isotherm and thermodynamic aspects of β -carotene from crude palm oil on native silica. The experiments were studied by employing a spectrophotometer to measure the concentration of β -carotene before and after adsorption. The effects of various parameters such as contact time, temperature and initial β -carotene concentration were determined. The adsorption capacity increased with increasing contact time and temperature. Langmuir and Freundlich isotherms were applied to fit the equilibrium data to identify the best isotherm to describe the β -carotene adsorption. The data were best described by Langmuir isotherm, maximum monolayer adsorption capacity of β -carotene onto florisil was 86.207 mg/g. Three kinetic models were used to investigate the adsorption mechanism which included pseudo-first-order kinetic, pseudo-second-order kinetic and intraparticle diffusion models. The adsorption followed second-order kinetic model. The data obtained from adsorption isotherm models were used to determine the thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG). The positive value of ΔH indicated that the adsorption process was endothermic in nature. The negative value of ΔG indicated the spontaneity of the adsorption of β -carotene on the adsorptents.

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1. Introduction

Crude palm oil is the world's richest natural plant source of carotenes in terms of retinol. Crude palm oil possesses 1% minor components which amongst them are the carotenoids, vitamin E (tocopherols and tocotrienols) and sterols [1]. The orange-red colour of palm oil is due to the relatively high content of these carotenes. Its concentration normally ranges between 700 ppm to 800 ppm [2]. The major carotenes in palm oil are α - and β -carotenes, which account for 90% of the total carotenes [2,3].

Colour is an important quality parameter of edible oil and colour in oil is used as the basis for its acceptance or rejection in the trade. Dark coloured oil requires expensive processing for conversion to an acceptable light-coloured product since dark colour may be an indication of poor quality [4]. Lighter coloured oils are preferred by consumers because they believe that these oils have less effect on the organoleptic characteristics of the food which they are preparing [5]. The refining process involved the removal of colouring pigments originating from carotenoids, chlorophyll and related compounds. The removal is achieved by adsorption of oil pigments onto an adsorbent. In normal practice, activated clays, activated carbon and silica-based products are adsorbents commonly used in the edible oil refining process [6]. Synthetic silica is commonly used in edible oil bleaching process where small amounts of it are used in combination with bleaching clay and their synergic action reduce the amount of clay needed to optimize the bleaching process [7].

One of the important coloured compounds removed in the refining process is β -carotene. Some researchers have reported the adsorption of β -carotene from different types of oils such as soy oil [8], crude palm oil [4], rapeseed oil [6] and also acetone solution [9]. This study focused on adsorption of β -carotene on silica gel and florisil from *n*-hexane solution. The adsorption capacities of silica gel and florisil for the removal of β -carotene was being investigated. The applicability of common isotherm models to represent the adsorption process was determined. The experimental data were analyzed using pseudo-first-order, second-order kinetic and intraparticle diffusion models. Thermodynamics data of the adsorption were calculated to understand the adsorption process.

2. Materials and methods

2.1. Materials

 β -Carotene used in the adsorption experiments was purchased from Sigma–Aldrich (M) Pte. Ltd. The chemical structure of β carotene is shown in Fig. 1. The identification information of



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Fig. 1. Molecular structure of β-carotene.

Table 1 Properties of the β -carotene used in the study.

Chemical formula	Molecular weight (g/mol)	$\lambda_{max}\left(nm\right)$	Colour	CAS	C.I.
C ₄₀ H ₅₆	536.89	446	Dark red	7235-40-7	75130

 β -carotene is given in Table 1. Silica gel and florisil were used as adsorbents in this study. Their respective properties are listed in Table 2.

2.2. Method

Adsorption of β -carotene on silica gel and florisil was studied by batch experiments. β-Carotene solutions with initial concentrations of 50–300 mg/l were prepared with *n*-hexane of analytical grade. A fixed amount of each dry adsorbent (0.2 g silica gel and 0.1 g florisil, respectively) and 100 ml of β -carotene solution was placed in a capped Erlenmeyer flask (250 ml). The flasks were shaken in an isothermal shaker at 150 rpm, 30 °C for 45 h to reach equilibrium. The samples were pipetted from the flask at appropriate time intervals. The absorbency of the β -carotene was measured twice for each sample by using spectrophotometer (Model Genesys 20; Thermo Spectronic Co., USA) at 446 nm wavelength. Calibration was performed in a series of standard β -carotene solutions. The effect of temperature on the adsorption process was studied at 30, 40 and 50 °C. The amount of β -carotene adsorbed on adsorbents at any time, t, was calculated from the concentrations in solutions before and after adsorption. The amount of adsorption at time t, q_t (mg/g) was calculated from the mass balance equation as follows:

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

where C_0 and C_t (mg/l) are the liquid-phase concentrations of β carotene at initial and at time *t*, respectively. *V* is the volume of the solution (1) and *W* is the mass of dry adsorbent used (g).

3. Results and discussion

3.1. Adsorption capacities

Fig. 2(a) and (b) shows the adsorption capacity versus the adsorption time at various β -carotene initial concentrations on silica gel and florisil, respectively. The increase in adsorption capacity indicated the increase in amount of β -carotene adsorbed as a function of time until the adsorption process approached saturation, implying that adsorption equilibrium had been reached. The figures

Table 2

Properties of the adsorbents.

	Silica gel	Florisil
Purchased from Particle size (µm) Physical state Colour	Sigma–Aldrich (M) Sdn. Bhd. 63–200 Solid White	Merck Sdn. Bhd. 150–250 Solid Colourless to white
Chemical composition pH	SiO ₂ 6.5-7.5	SiO ₂ 84.0% MgO 15.5% Na ₂ SO ₄ 0.5% 9.4



Fig. 2. Adsorption capacities of β -carotene on (a) silica gel and (b) florisil versus adsorption time at various initial concentrations at 30 °C.

show that the initial adsorption was rapid, followed by a slower adsorption as the available adsorption sites gradually decreased. The values of equilibrium time were found to be about 10 h for silica gel and 32 h for florisil. Solutions of higher initial concentrations take relatively longer contact time to achieve equilibrium due to higher amount of adsorbate. This observation could be explained by the theory that in the process of adsorption, the adsorbates have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and finally diffuse into porous structure of the adsorbent [10].

The initial concentration provides an important driving force to overcome all mass transfer resistances of the adsorbate between the liquid and solid phases [11]. The adsorption increased with increasing initial β -carotene concentration. The amount of β -carotene adsorbed at equilibrium time reflected the maximum adsorption capacity of the adsorbent under those operating conditions. The adsorption capacity of β -carotene on silica gel at equilibrium (q_e) increased from 5.5 to 16 mg/g by increasing the initial concentration from 50 to 300 mg/l, while the q_e for florisil increased from 55 to 300 mg/l.

Fig. 3 shows the percentage removal of β -carotene by silica gel and florisil as a function of initial concentration. As the initial concentration increased from 50 to 300 mg/l, the percentage removal decreased from 22 to 11% for adsorption on silica gel and 72 to 21% for adsorption on florisil. The increase in initial concentration decreased the percentage removal due to the faster saturation of adsorption sites in the adsorbent. This is because the amount of adsorbate increased but the amount of adsorbent remained the same. Therefore, adding more adsorbate could not increase the adsorption because all sites had been occupied. The adsorption removals of β -carotene on silica gel which was ~22% were much lower than that of florisil which was ~72%. This means that there were greater amount of adsorption sites in florisil than in silica gel.



Fig. 3. Percentage removal of β -carotene by adsorption on (a) silica gel and (b) florisil versus adsorption time at various initial concentrations at 30 °C.

3.2. Effect of temperature

Fig. 4 shows the effect of temperature on the adsorption equilibrium of β -carotene on silica gel and florisil. It can be seen that the adsorption equilibrium increased with the increase in temperature for initial concentrations of 100-300 mg/l which indicated the endothermic nature of the process. However, at low initial concentration of β -carotene (50 mg/l), the effect of temperature on the adsorption equilibrium was not significant. The adsorption equilibrium increased when temperature was increased due to the increase in mobility of β-carotene in the solution. Physical adsorption was normally considered to be important for temperature lower than 100 °C and chemisorption for temperature higher than 100 °C [8]. The adsorption temperatures studied here were lower than 100 °C and the most probable mechanism was physisorption. Although high temperature may increase the adsorption equilibrium, the temperature should not be raised without limitation because destruction of β -carotene will occur at higher temperature.



Fig. 4. Effect of temperature on adsorption equilibrium of β -carotene on silica gel and florisil at various initial concentrations.

3.3. Adsorption isotherm

The partition of β -carotene molecules between liquid phase and adsorbent is a measurement of the position of equilibrium in the adsorption process [6]. Therefore, it is important to find the most appropriate correlations for the equilibrium data in the design of adsorption systems. Equilibrium data for this present study were analyzed with two common isotherm models: Langmuir and Freundlich models. The applicability of the isotherm models was compared based on the correlation coefficient, R^2 . The mathematical forms of the Langmuir and Fre-undlich isotherms are represented by Eqs. (2) and (3).

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{K_{\rm L}b} + \frac{1}{b}C_{\rm e} \tag{2}$$

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), b is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption equilibrium constant (l/mg) related to direct measure of the intensity of the adsorption process in Eq. (2). A plot of C_e/q_e versus C_e yields the values of b and K_L from the slope and intercept, respectively, as shown in Fig. 5(a).

In Eq. (3), K_F (mg/(g(mg/l)^{1/n})) and *n* are Freundlich adsorption isotherm constants, affecting the adsorption capacity and intensity of adsorption. K_F is a constant related to bonding energy and can be defined as the adsorption or distribution coefficient which describes the quantity of β -carotene adsorbed onto adsorbent for a unit equilibrium concentration. The slope 1/n is an irrational fraction varies between 0 and 1 which is a measurement of adsorption intensity or surface heterogeneity. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption [12]. When $\log q_e$ was plotted against $\log C_e$, a straight line with slope of 1/n and intercept of $\log K_F$ was obtained, as shown in Fig. 5(b).

Table 3 lists the values of adsorption constants for Langmuir and Freundlich isotherm model for adsorption of β -carotene on sil-



Fig. 5. (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm for β -carotene on silica gel at 303, 313 and 323 K.

A.L. Ahmad et al. / Chemical Engineering Journal 148 (2009) 378-384

Isotherms	Temperature (K)	Constants ^a		R^2	Constants ^b	R^2	
		K _L (l/mg)	<i>b</i> (mg/g)		K _L (l/mg)	<i>b</i> (mg/g)	
Langmuir	303	0.0089	22.422	0.9813	0.0562	67.568	0.9919
C	313	0.0151	20.833	0.9831	0.0476	78.740	0.9795
	323	0.0131	25.316	0.9379	0.0538	86.207	0.9868
		$K_{\rm F}({\rm mg}/({\rm g}({\rm mg}/{\rm l})^{1/n}))$	1/ <i>n</i>		$K_{\rm F}({\rm mg}/({\rm g}({\rm l/mg})^{1/n}))$	1/n	
Freundlich	303	0.8204	0.5408	0.9568	20.319	0.2147	0.9404
	313	1.5736	0.4356	0.9307	23.480	0.2105	0.9484
	323	1.2442	0.5152	0.8290	23.950	0.2305	0.9692

Table 3	
Langmuir and Freundlich isotherm model constants and correlation coefficients for β -carotene adsorption on silica gel and florisil	

^a Constants for adsorption on silica gel.

^b Constants for adsorption on florisil.

ica gel and florisil at different temperatures. The Langmuir model yields a better fit than the Freundlich model as reflected by the correlation coefficient, R^2 of above 0.938 and 0.980 for silica gel and florisil, respectively. The monolayer adsorption capacity of β -carotene on silica gel (25.316 mg/g) was significantly lower than that of adsorption on florisil (86.207 mg/g). However, the adsorption capacities of silica and florisil were higher than the values reported in others literature such as adsorption capacity of β -carotene by acid-activated sepiolite was reported to be 6.22 mg/kg [6] and adsorption capacity of β -carotene from acetone solution on acid treated bentonite was 10.80×10^{-8} mol/g [9]. From Table 3, the adsorption capacities increased with the increasing temperature due to the increasing kinetic energy of the sorbent particles. This increased the frequency of collisions between the adsorbent and adsorbate thus enhanced the adsorption process [13].

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which is defined by Eq. (4).

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_0} \tag{4}$$

where K_L is the Langmuir constant and C_0 is the highest β -carotene concentration (mg/l). The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [14,15]. The value of R_L was found to be 0.2 and 0.06 at 323 K for silica gel and florisil, respectively. This indicated that the Langmuir isotherm model was favorable for adsorption of β -carotene on both the adsorbents under the conditions used in this study.

In general, as K_F value increases, the adsorption capacity of the adsorbent also increases. As presented in Table 3, the value 1/n is in the range of 0.21–0.54 and appears to be in agreement with the usual range of 0–1 which indicates a favorable Langmuir isotherm.

3.4. Adsorption kinetics

Three kinetic models were used to examine the controlling mechanisms of adsorption process based on the experimental data. The pseudo-first-order equation given by Lagergren [16] as shown in the following equation was used to analyze the adsorption kinetic of the process.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t are the amounts of β -carotene adsorbed (mg/g) at equilibrium and at time t(h), respectively, and k_1 is the rate constant of adsorption (h^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t for different initial concentrations at 30 °C as shown in Fig. 6.

The pseudo-second-order model based on equilibrium adsorption is expressed by the following equation [17].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(6)

where k_2 is the second-order constant (g/(mg h)) and can be determined from the slope and intercept of plot t/q_t versus t, as shown in Fig. 7.

Intraparticle diffusion model by Weber and Morris [18] which is a common diffusion model that described the uptake varies almost proportionally with $t^{1/2}$, rather than with the contact time *t*, is expressed by Eq. (7).

$$q_t = k_{\rm int} t^{1/2} + C \tag{7}$$

where k_{int} is the intraparticle diffusion rate constant (mg/(g h^{1/2})) calculated from the slope of the straight line of q_t versus $t^{1/2}$ (Fig. 8).

The fit of these models was checked by each linear plot of $\ln(q_e - q_t)$ versus $t, (t/q_t)$ versus t and q_t versus $t^{1/2}$, respectively, as well as the regression coefficients for each expression. The kinetic



Fig. 6. Pseudo-first-order kinetics for β -carotene adsorption on (a) silica gel and (b) florisil at 30 °C.



Fig. 7. Pseudo-second-order kinetics for β -carotene adsorption on (a) silica gel and (b) florisil at 30 °C.

parameters for adsorption of β -carotene at 30 °C with different initial concentrations were calculated from Eqs. (5) to (7) and are shown in Table 4. It was seen from Figs. 6–8 that the adsorption on silica gel and florisil fitted in the second-order kinetic model better than first-order kinetic model or intraparticle diffusion model. For the first-order kinetic model and intraparticle diffusion model, the experimental q_e values did not agree well with the calculated values obtained form the linear plots. Based on the results listed in Table 4, the kinetics of the β -carotene adsorption onto silica gel and florisil followed the pseudo-second-order with the correlation coefficient (R^2) higher than 0.993 for all the conditions in the study of adsorption on silica gel. However, there was exceptional case for initial concentration of 50 mg/l where the correlation coefficient was 0.958. While the correlation coefficient for adsorption on florisil was more than 0.984. The calculated q_e values for second-

Table 4

Values of adsorption rate constants for different adsorbents with different initial concentrations at 30 $^\circ$ C.



Fig. 8. Intraparticle diffusion model for β -carotene adsorption on (a) silica gel and (b) florisil at 30 °C.

order kinetic model also agreed well with the experimental data at this initial concentration (Table 4).

For intraparticle diffusion model, Weber–Morris plots have three general features which are initial curved portion, linear portion and plateau portion. The first, sharper portion is the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion is the gradual adsorption stage where intraparticle diffusion is the rate limiting. The third portion is the final equilibrium stage

Initial concentration (mg/l)	$q_{\rm e,exp}~({\rm mg/g})$	First-order kinetic model		Second-order kinetic model			Intraparticle diffusion model			
		k_1 (h ⁻¹)	$q_{\rm e,cal}~({\rm mg/g})$	R^2	k_2 (g/(mg h))	$q_{\rm e,cal}~({\rm mg/g})$	R^2	$k_{\rm int} ({\rm mg}/({\rm g}{\rm h}^{1/2}))$	$q_{\rm e,cal}~({\rm mg/g})$	R^2
Silica gel										
50	5.5066	0.0795	5.0956	0.9799	0.0141	5.4399	0.9582	0.9162	5.9739	0.9666
100	9.2371	0.0868	6.0195	0.8604	0.0257	9.1571	0.9968	1.4000	10.6353	0.8089
150	12.6094	0.1635	11.3674	0.9889	0.0189	12.8231	0.9935	1.9569	14.8587	0.8447
200	13.9027	0.1494	11.9568	0.9771	0.0188	14.0114	0.9937	1.8569	15.6795	0.9182
250	14.0960	0.3498	29.5091	0.7624	0.0189	14.3393	0.9954	2.1164	16.6391	0.7977
300	15.9635	0.0767	9.1786	0.8099	0.0193	15.6211	0.9966	2.2810	18.1867	0.7626
Florisil										
50	35.8552	0.0888	35.9722	0.9921	0.00125	35.3392	0.9836	6.6079	36.8081	0.9956
100	46.3751	0.1022	45.0933	0.9942	0.00185	46.8657	0.9850	8.3110	49.2485	0.9765
150	53.6274	0.1035	47.1162	0.9881	0.00227	53.0270	0.9906	9.0974	57.6572	0.9444
200	64.9978	0.1172	53.6714	0.9787	0.00196	65.5260	0.9846	11.0310	72.3683	0.8751
250	61.2834	0.0787	48.7047	0.9822	0.00206	58.6415	0.9810	9.4105	61.4307	0.9623
300	62.7614	0.1095	59.5907	0.9854	0.00158	62.6196	0.9980	10.7790	66.4053	0.9560

Table 5Thermodynamics parameters for the adsorption of β -carotene on silica gel and florisil at various temperatures.

T (K)	Silica gel			Florisil		
	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/(mol K))	ΔG (J/mol)	ΔH (J/mol)	$\Delta S (J/(mol K))$
303	-7834.59			-10613.5		
313 323	-7901.97 -8677.82	4822.45	41.41	-11362.0 -11968.3	9935.23	67.89

where intraparticle diffusion starts to slow down due to extremely low-adsorbate concentrations left in the solutions [11,14]. Fig. 8(a) and (b) shows that the intraparticle diffusion plots for adsorption of β -carotene on silica gel and florisil include sharper portion, linear portion and plateau portion for higher initial concentrations whereas lower initial concentrations (50 and 100 mg/l) only showed sharper portion and linear portion. The third region existed when the initial β -carotene concentrations were high, which was the final equilibrium stage where intraparticle diffusion started to slow down due to the low solute concentrations left in the solutions [19].

Intraparticle diffusion model was utilized to determine the ratelimiting step of the adsorption process. If intraparticle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion [20]. Otherwise, some other mechanism along with intraparticle diffusion is also involved. In this study, the intraparticle diffusion plot did not pass through the origin, suggesting that intraparticle diffusion is applicable to this system but was not the only rate-limiting step in the adsorption.

3.5. Adsorption thermodynamics

The data obtained from adsorption isotherm models can be conveniently used to determine thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The free energy change was calculated using the following equation.

$$\Delta G = -RT \ln b \tag{8}$$

where *R* (8.314 J/(mol K)) is the ideal gas constant and *T*(K) is the temperature. The values of ΔH and ΔS were computed using following equation.

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(9)

The enthalpy change and the entropy change were calculated from the slope and intercept of plot of $\ln b$ (from the Langmuir isotherm) versus 1/T (Fig. 9). The results of these thermodynamics are listed in Table 5.



Fig. 9. Plot of $\ln b$ versus 1/T for β -carotene adsorption on silica gel and florisil.

The free energy indicates the degree of spontaneity of the process and higher negative value reflects a more energetically favorable sorption [6]. The negative value of Gibbs free energy for β-carotene adsorption on silica gel and florisil indicated the feasibility of the process and spontaneous nature of the adsorption. The degree of spontaneity of the process also increased with increasing temperature. The positive value of ΔH showed that the adsorption process was endothermic. This result was also in line with the increased adsorption capacity from 67.568 to 86.207 mg/g with the increase of temperature from 303 to 323 K for adsorption of βcarotene on florisil. The positive value of ΔS suggested the increase in randomness at the solid/solution interface during the adsorption process. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent [13]. Thus, adsorption was likely to occur spontaneously at normal and high temperatures because $\Delta H > 0$ and $\Delta S > 0$.

4. Conclusions

This paper presented a detailed study of the β -carotene adsorption using silica-based adsorbents. The adsorption capacities increased with the increasing contact time and initial concentration. Increase in temperature also increased the adsorption capacity. The adsorption capacity of β -carotene from hexane solution on florisil was higher than the adsorption capacity of β -carotene on silica gel. Equilibrium data were best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 25.316 and 86.207 mg/g for silica gel and florisil, respectively. This showed that florisil was a good adsorbent to remove the β -carotene. The adsorption kinetics were well described by the pseudo-second-order kinetic model. The process was endothermic and spontaneous under the conditions studied.

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