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Adsorption of β-carotene onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solution: equilibrium and thermodynamic study

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ABSTRACT

Mesoporous carbon coated monolith prepared from furfuryl alcohol by the dip-coating method was utilized as an adsorbent for adsorption of β-carotene from crude palm oil. The effect of temperature on the adsorption was investigated by batch adsorption experiments. The adsorption quantity increased with increasing temperature. The adsorption was performed using two different solvents, isopropyl alcohol and *n*-hexane. The maximum adsorption capacity of β-carotene was 62.118 mg/g for isopropyl alcohol at 50 °C. The experimental results were fitted using the Langmuir and Freundlich isotherms. The Langmuir described the adsorption process better. The negative values of Gibbs free energy change suggested that the adsorption was a spontaneous process. The positive values of heat of enthalpy and entropy change confirmed the endothermic nature of the adsorption.

1. Introduction

Crude palm oil usually contains 500–700 ppm of carotenoids, mainly in the form of β-carotene. The majority of the carotenoids in the palm oil are destroyed in the conventional refining process for producing clear oil. This represents a loss of the natural source of carotenoids. In an effort to reduce or to prevent these losses, methods of extraction and recovery of carotene have been developed, *e.g.* nanofiltration membrane technology [1], adsorption using polymeric adsorbents [2], and supercritical carbon dioxide [3].

Porous carbons are commonly used as adsorbent. The use of carbon in the form of fixed bed is associated with high pressure drops, potential channelling, and other disadvantages. These problems can be overcome by the use of carbon monoliths. Compared to the conventional fixed bed column, monolithic columns provide the advantages of low pressure drop, large external surface area, and shorter diffusion lengths [4]. They can also be placed in vertical or horizontal position and in mobile system without losing shape and is easier to be scaled up due to its simple design and uniform flow distribution [5,6].

In this study, mesoporous carbon coated monolith (MCCM), prepared using the dip-coating method, was used for the adsorption of carotene. The objective of this study was to investigate the ability of β-carotene adsorption onto carbon coated monolith. The effect of temperature and type of solvent on the adsorption was studied. The thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy were also evaluated. The adsorption equilibrium was fitted by two different isotherms, namely the Langmuir and Freundlich model.

2. Materials and methods

2.1. Adsorbent

Cordierite monoliths with channel width 1.02 ± 0.02 mm or 400 channels per square inch (400 cpsi) and wall thickness 0.25 ± 0.02 mm were obtained from Beihai Huihuang Chemical Packing Co. Ltd, China. Its chemical composition of monolithic substrate used in this investigation are SiO_2 50.9 ± 1%, Al_2O_3 35.2 ± 1%, MgO 13.9 ± 0.5%, and others <1%. The starting chemicals for the preparation of carbon coated monolithic supports were furfuryl alcohol (FA) (Fluka), pyrrole (Fluka), poly(ethylene glycol) (PEG) (Mw 8000, Fluka), and nitric acid (HNO_3) 65% (Fisher).The polymerized samples were prepared with a starting mix of 40:60 of FA and PEG by percentage volume. The PEG with molecular weight 8000 was waxy solids at room temperature and was ground to powder before dispersion in the FA. The polymerization catalyst, HNO_3, was added stepwise, at every 5 min. After addition of the acid, the mixture was stirred for 1 h while maintaining temperature at approximately 21–23 °C [7]. The monolith substrate was immersed in a reactor with sufficient polymer solution to com-

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pletely cover the monolith substrate. The dried coated monolith substrate precursor was carbonized in flowing pure nitrogen at 650 °C for 3 h with a heating rate of 10 °C /min. Activation process was performed at 350 °C for 4 h by flowing argon gas with 5% oxygen.

2.1.1. Surface area and pore size

Specific surface area and pore volume of the samples were determined by the nitrogen adsorption/desorption isotherms measured at 77 K by gas sorption analyzer (Sorptomatic Series 1990). Prior to each measurement, carbon samples were outgassed at 150 °C. Adsorption isotherms were used to analyze the surface area and pores structure. Total pore volume was obtained from the single point adsorption at the relative pressure of 0.995. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The mesopore surface area was determined by subtracting the micropore surface area from the BET specific surface area.

2.2. Chemicals

All the chemicals used were of analytical grade. The reagents used in this study, *i.e.* β-carotene, isopropyl alcohol and *n*-hexane were purchased from Sigma–Aldrich, Malaysia. The stock solution of β-carotene (500 mg/L) was prepared by dissolving a required amount of commercial β-carotene in solvent for adsorption experiments. The β-carotene solution with initial concentration 50, 100 up to 450 mL/g were prepared by dilution from stock solution (500 mL/g).

2.3. Adsorption equilibrium

In batch experiment, β-carotene in *n*-hexane and isopropyl alcohol miscellas with different concentrations (50, 100 up to 500 mg/L) were put into 250 mL conical flasks. The adsorption process was performed under a nitrogen atmosphere. Each flask was plugged with a silicone rubber stopper and was also wrapped with aluminium foil to minimize carotene degradation by light. The flasks were shaken in a water bath shaker (Stuart SBS40) at the desired temperature and 150 rpm. Approximately 0.8 g of adsorbent was put into the conical flask. The effect of temperature on the adsorption process at 30, 40 and 50 °C was studied. After equilibrium was reached, a few milliliters samples were withdrawn and diluted to the appropriate concentration if it was required and then analyzed by using UV/Vis Spectrophotometer (Thermo Electron Corporation) at wavelength 446 nm [8].

The concentration of solute adsorbed on the adsorbent (solid phase) at equilibrium can be calculated from:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where q_e is the solid phase concentration at the equilibrium phase (mg/g), C_0 is the initial concentration of the liquid phase (mg/L), C_e is the liquid phase concentration at the equilibrium (mg/L), V is the volume of liquid (L) and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Characteristics of the adsorbent

Nitrogen adsorption–desorption at 77 K is a standard method used in characterization of adsorbents. Fig. 1 shows a N_2 adsorption–desorption isotherm onto carbon coated monolith, where a progressive increase in adsorbed nitrogen is observed at all relative pressure (p/p_0) ranges. These isotherms can show hysteresis from the shape of N_2 adsorption–desorption isotherms shown. The N_2 adsorption isotherms can be considered as type IV isotherm.

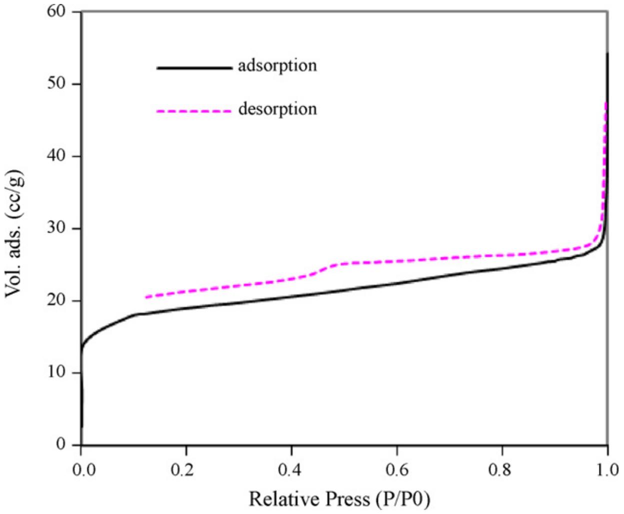

Fig. 1. Nitrogen adsorption–desorption isotherms of carbon coated monolith at 77 K.

The Brunauer–Emmett–Teller (BET) specific surface area (BET area) obtained from N_2 adsorption isotherm data and other parameters of the carbon coated monolith are given in Table 1.

The adsorbent pores are classified into three groups: micropore (diameter < 2 nm), mesopore (2–50 nm), and macropores (>50 nm) [9]. Fig. 2 shows that the pore size distribution of the carbon coated monolith exhibit two main peaks. One peak is located at 2.0 nm and the other at 3.6 nm. Furthermore, the pore size distributions after 6.2 nm are broadened. The pore size distribution curve indicates that the porous carbon is bimodally distributed.

3.2. Equilibrium isotherms

Adsorption isotherms display qualitative information about the nature of the solid/liquid interaction as well as the specific relationship between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at constant temperature. The adsorption capacity can be evaluated by determining the concentrations of carotene adsorbed at equilibrium.

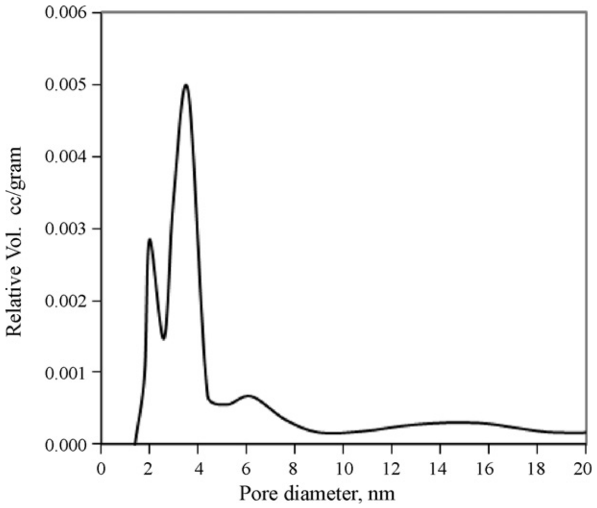

Fig. 2. Pore size distribution from N_2 adsorption of carbon coated monolith.

Table 1
Characteristics of the mesopores carbon coated monolith used in this work.

BET area (m^2/g)	Total pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)	Mesopore area (m^2/g)	Micropore area (m^2/g)
61.13	0.041	0.028	0.013	49.39	11.741

Table 2
Isotherm parameters for β-carotene adsorption onto carbon coated monolith at different temperatures by using IPA as solvent.

Isotherms	Parameters	30 °C	40 °C	50 °C
Langmuir	b (mg/g)	51.5464	57.1429	62.118
	K_L (L/mg)	0.0061	0.0058	0.0075
	R_L	0.2456	0.2555	0.2102
	R^2	0.9890	0.9878	0.9938
Freundlich	K_F (L/mg)	1.6155	1.6129	2.8003
	$1/n$	0.5275	0.5429	0.4750
	R^2	0.9411	0.9382	0.9418

The Langmuir isotherm implies formation of monolayer coverage of adsorbate on the surface of the adsorbent. A linearised form of the Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{1}{b} C_e \tag{2}$$

where K_L is Langmuir adsorption equilibrium constant (L/mg), and b is the monolayer capacity of the adsorbent (mg/g). The constants b and K_L in Eq. (2) can be calculated from the slope and intercept of the straight line by plotting C_e/q_e versus C_e.

Freundlich isotherm describes equilibrium on heterogeneous surfaces where adsorption energies are not equal to all adsorption sites. The heterogeneity was caused by difference in pore size, pore shape, and adsorbate–adsorbent. The linear form of Freundlich equation is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F is the Freundlich constant for a heterogeneous adsorbent (L/mg), and n is the heterogeneity factor. Value $1/n$ is in the range of 0.1–1.0 [10]. The Freundlich isotherm constants for $1/n$ and K_F in Eq. (3) were obtained from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$.

The Langmuir linearised adsorption and the Freundlich linearised adsorption isotherms are shown in Figs. 3 and 4. The applicability of the isotherms was determined by judging the coefficient of determination (R^2). The R^2 for the Langmuir isotherms for temperature 30, 40 and 50 °C were 0.9890, 0.9878 and 0.9938 in IPA, and 0.9985, 0.993 and 0.9988 in n-hexane, respectively. The monolayer adsorption capacity b and K_L generally increased with increasing temperature (see Tables 2 and 3). Due to lower values of R^2 in comparison to Langmuir, namely 0.9411, 0.9382, 0.9418 for IPA and 0.9588, 0.9523, 0.9728 for n-hexane, respectively, the Freundlich isotherm does not describe the experimental data as accurate as the Langmuir model. The maximum adsorption capacity of β-carotene was 62.118 mg/g at 50 °C using IPA as solvent. Sarier and Güler [11] studied the adsorption of β-carotene from solution in benzene on acid-activated Canakkale montmorillonite of Turkey. The isotherm was described well by the Langmuir model for concentration of about 600 ppm. Ahmad et al. [12] also reported that the Langmuir model described well the adsorption of β-carotene on silica-based adsorbent. However, in the adsorption of β-carotene from crude maize and sunflower oil using an acid-activated bentonite, adsorption isotherms followed the Freundlich equation [13].

Table 3
Isotherm parameters for β-carotene adsorption onto carbon coated monolith at different temperatures by using n-hexane as solvent.

Isotherms	Parameters	30 °C	40 °C	50 °C
Langmuir	b (mg/g)	39.8406	45.2489	48.7805
	K_L (L/mg)	0.0062	0.0066	0.0092
	R_L	0.2426	0.2328	0.1778
	R^2	0.9985	0.9930	0.9988
Freundlich	K_F (L/mg)	1.4391	1.6842	3.7914
	$1/n$	0.5031	0.5011	0.3891
	R^2	0.9588	0.9523	0.9728

The separation factor (R_L) is a dimensionless parameter which represents the characteristics of the Langmuir isotherm. The separation factor is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where C_0 is the initial concentration of carotene (mg/L).

In general, the value of R_L is in the range of 0.2102–0.2456 for isopropyl alcohol and 0.1778–0.2426 for n-hexane as presented in Tables 2 and 3, suggesting that the adsorption process was favourable.

3.3. *Effect of solvent*

Fig. 5 shows that the carotene adsorption using IPA is higher than using n-hexane as a solvent. This is because of the low polarity index of n-hexane (0.0, lowest polarity), compared to IPA (3.9, higher polarity). Therefore, β-carotene bonds stronger with n-hexane than IPA, inhibiting the transfer of carotene to the adsorbent. The same phenomenon had been reported by Baharin et al. [14] using synthetic polymer as an adsorbent. The adsorption capacity of adsorbent depends on the differences in the degree of affinity between the adsorbent and the adsorbed molecule in the solvent used. Chan et al. [2] used synthetic polymer adsorbents to adsorb the carotenoids, and they reported that when the HP 20 resin was used the amount of carotene adsorbed after treatment at IPA was about 4.5 times greater compared to that adsorbed after the treatment with n-hexane.

3.4. *Effect of temperature*

Adsorption of carotene increases with temperature (Fig. 6). This result suggested that the intra-particle diffusion rate of the adsorbate molecules into the pores increased with increasing temperature since diffusion is an endothermic process [15].

Physical adsorption is normally considered to be the dominant adsorption mechanism for temperature lower than 100 °C and chemisorption for temperature higher than 100 °C [16]. The pigment is adsorbed only on the outer surface of the adsorbent at lower temperatures, and both on the outer surface and pore surface at higher temperatures [17]. However, at higher temperature destruction of β-carotene will occur [12]. Therefore, the adsorption experiments were carried out up to 50 °C.

3.5. *Estimation of thermodynamic parameters*

The data obtained from the Langmuir isotherm can be used to determine thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The

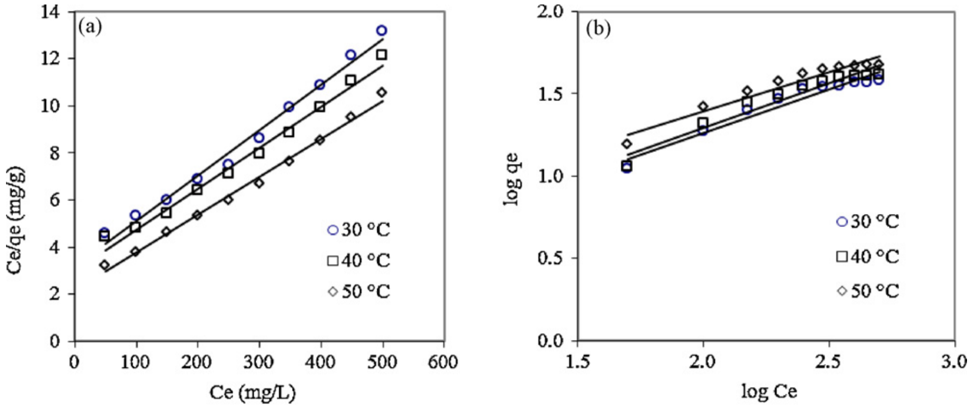

Fig. 3. Comparison of adsorption equilibrium of β-carotene at different temperature onto carbon coated monolith using IPA as solvent by (a) Langmuir and (b) Freundlich model.

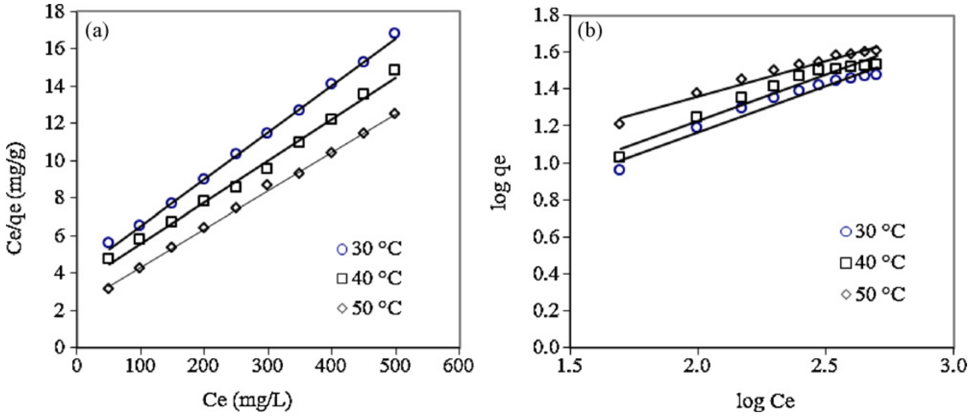

Fig. 4. Comparison of adsorption equilibrium of β-carotene at different temperature onto carbon coated monolith using *n*-hexane as solvent by (a) Langmuir and (b) Freundlich model.

Gibbs free energy change was calculated using the following equation:

$$\Delta G = -RT \ \ln b \tag{5}$$

where T is the absolute temperature (K) and R is the universal gas constant (8.314 J/(mol K)). The enthalpy change (ΔH) and entropy change (ΔS) were determined from the following equation [10]:

$$\ln \ b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

The values of parameters (ΔH) and (ΔS) were estimated from the slope and intercept of the plot of ln b versus $1/T$ (Fig. 7) and are listed in Table 4. The ΔG values are in the range of −9931.67 to −11087.9 J/mol and −9282.75 to −10439.12 J/mol for IPA and *n*-hexane solvent, respectively. The decrease of ΔG values with temperature suggests that more β-carotene is adsorbed with increasing temperature [10]. This implies that the adsorption is favoured at higher temperature. The positive value of enthalpy change (ΔH) indicates that the adsorption is endothermic, which is in agreement with observation above, namely the amount of carotene adsorbed increases with increasing temperature. The ΔH value of IPA (7591.68 J/mol) is lower than that of *n*-hexane (8255.97 J/mol), indicating a weaker bonding between the carotene molecules and the adsorbent surface. The positive value of ΔS sug-

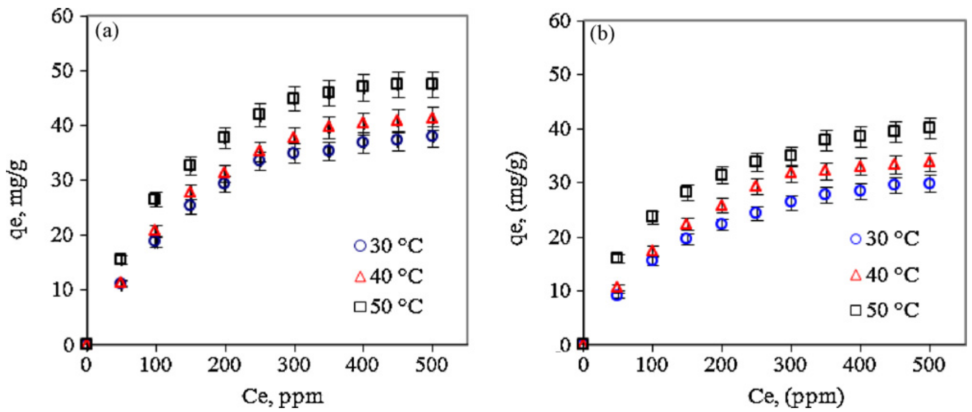

Fig. 5. Comparison of adsorption of carotene using different solvent (a) isopropyl alcohol (IPA) and (b) *n*-hexane.

Table 4
Thermodynamic parameters for adsorption of β-carotene.

T (K)	IPA			n-hexane		
	ΔG (J/mol)	ΔS (J/(mol K))	ΔH (J/mol)	ΔG (J/mol)	ΔS (J/(mol K))	ΔH (J/mol)
303	−9931.67	57.85	7591.68	−9282.75	57.95	8255.97
313	−10527.67			−9920.36		
323	−11087.9			−10439.12		

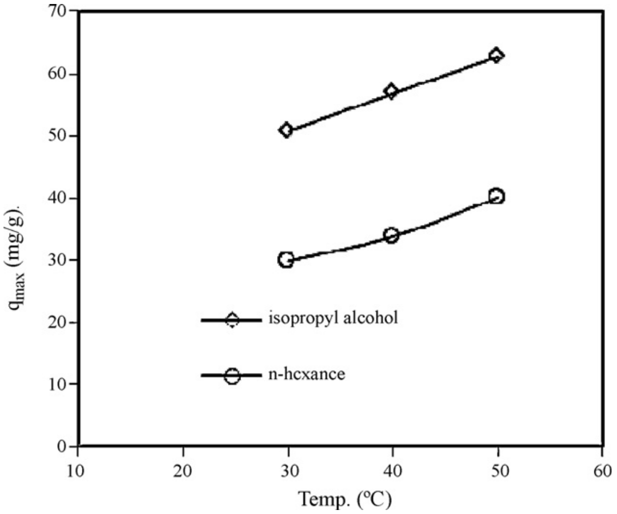

Fig. 6. Effect of temperature on adsorption β-carotene onto carbon coated monolith using isopropyl alcohol and n-hexane as solvent.

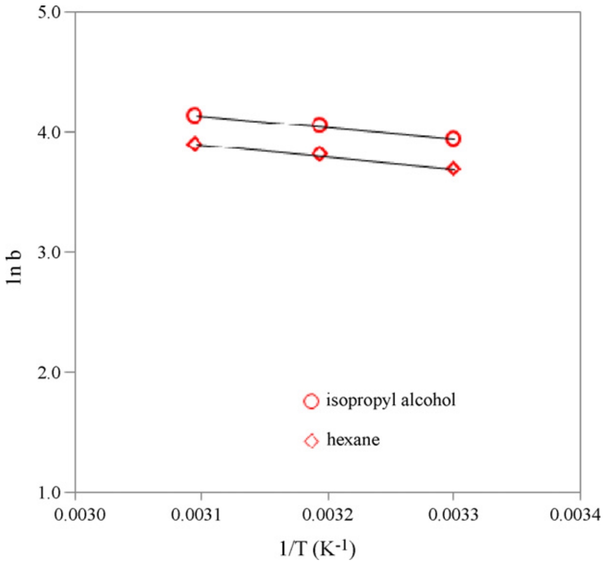

Fig. 7. Plot of ln b versus 1/T for the estimation of thermodynamic parameters of β-carotene adsorption by using isopropyl alcohol and n-hexane as solvent.

gests increasing randomness at the solid/liquid interface during the sorption of carotene on the carbon coated monolith.

4. Conclusions

Adsorption of β-carotene onto carbon coated monolith was conducted at three different temperatures. The adsorption capacity of β-carotene from IPA solution on carbon coated monolith was higher than the adsorption capacity of β-carotene using n-hexane as solvent. Equilibrium data were best fitted by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 62.12 and 48.78 mg/g for isopropyl alcohol and n-hexane, respectively. The adsorption capacities increased with increasing temperature. Based on the thermodynamic parameters obtained, the β-carotene adsorption follows the physisorption mechanism and is an endothermic process.

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