Research Article

Adsorptive Separation Studies of β -Carotene from Methyl Ester Using Mesoporous Carbon Coated Monolith

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Adsorption of β -carotene on mesoporous carbon coated monolith (MCCM) from methyl ester as a solvent was investigated. Kinetics and thermodynamics parameters have been evaluated. Maximum β -carotene adsorption capacity was 22.37 mg/g at 50 °C. Process followed Langmuir isotherm. The adsorption was endothermic and spontaneous. Contact time studies showed increase in adsorption capacity with increase in β -carotene initial concentration and temperature. Pseudo-second-order model was applicable to the experimental data. The value of activation energy confirmed physical adsorption process.

1. Introduction

The characteristic orange color of crude palm oil is due to the presence of carotenoids (α - and β -carotenes). These carotenoids are of commercial importance as they are utilized as natural coloring agents in edible and pharmaceutical products. Transesterification of palm oil produces an ecofriendly diesel (or biodiesel) containing methyl ester as a major constituent. The biodiesel (or methyl ester) contains a rather high concentration of carotenoids. Therefore, it is essential to develop a method to recover this valuable product. Separation of carotenoids from methyl ester by nanofiltration was reported by Darnoko and Cheryan [1].

The utility of carbonaceous (powder and granular) materials in the form of fixed bed for separation is associated with high pressure drops, potential channeling, and many other demerits. Compared to carbonaceous material, mesoporous carbon coated monolith (MCCM) has large external surface area and a very less pressure drop across fixed bed MCCM column. High mechanical stability and thermal expansion coefficient are some of the other properties of MCCM. The MCCM columns can also be placed in vertical or horizontal position and in mobile system without deforming shape and

is easier to be scaled up due to its simple design and uniform flow distribution.

In our previous studies, we had reported the adsorption and desorption of β -carotene on MCCM using isopropyl alcohol and *n*-hexane as solvents [2, 3]. In this study we had utilized MCCM for adsorptive separation of β -carotene from methyl ester in synthetic solution system. Various thermodynamics and kinetics parameters were studied.

2. Materials and Methods

2.1. Materials. Cordierite monoliths (channel width 1.02 $\pm$ 0.02 mm and wall thickness 0.25 $\pm$ 0.02 mm) were obtained from Beihai Huihuang Chemical Packing Co., Ltd, China. Others materials like β -carotene was purchased from Sigma-Aldrich, Malaysia. The stock solution of β -carotene (500 mg/L) was prepared by dissolving required amount in solvent.

2.2. Chemical and Reagents. Methyl ester, a solvent for β -carotene was purchased from Sigma-Aldrich, Malaysia. Furfuryl alcohol (FA), pyrrole, and poly(ethylene glycol) (PEG,

MW-8000) were purchased from Fluka, Malaysia. Nitric acid (HNO_3) 65% was purchased from Fisher, Malaysia. All the chemicals used were of analytical grade.

2.3. Preparation of MCCM. The polymerization of samples was carried out by mixing FA and PEG in percentage volume ratio of 40 : 60. The polymerization catalyst, HNO_3 , was added stepwise, at every 5 min. After addition of the acid, the mixture was stirred for an hour while maintaining temperature at approximately 21–23°C. Detailed method of MCCM preparation was reported elsewhere [2].

2.4. Adsorption Equilibrium and Kinetics. Batch adsorption experiments were carried out under nitrogen atmosphere. β -carotene of concentrations 50 to 500 mg/L were taken in 250 mL conical stopper cork flasks. Methyl ester was used as a solvent. The MCCM, 0.8 g, was added to each flask. The flasks were wrapped with aluminium foil to minimize β -carotene photo degradation. The flasks were shaken at 150 rpm in a water bath shaker (Stuart SBS40) at desired temperatures (30, 40 and 50°C). At equilibrium, the samples were collected and were analyzed.

Kinetics studies were carried out under similar experimental conditions. The MCCM, 3 g, was taken in 250 mL conical flasks for reaction with β -carotene. Samples were collected at desired time intervals using a digital micropipette (Rainin Instrument, USA). The samples were analyzed using a double beam UV/VIS spectrophotometer (Thermo Electron Corporation) at wavelength 446 nm.

The concentration of solute adsorbed on the MCCM at equilibrium was calculated as

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

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

3. Results and Discussion

3.1. Equilibrium Isotherms. Langmuir isotherm implies formation of monolayer coverage of adsorbate on the surface of the adsorbent. A linearized form is given as

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{1}{b} C_e, \quad (2)$$

where K_L is Langmuir adsorption equilibrium constant (L/mg), and b is the monolayer capacity of the adsorbent (mg/g).

Freundlich isotherm describes equilibrium on heterogeneous surfaces where adsorption energies are not equal to all adsorption sites. Linear form is given as

$$\log q_e = \log K_F + 1/n \log C_e, \quad (3)$$

where K_F is the Freundlich constant for a heterogeneous adsorbent (mg/g)(L/mg) $^{1/n}$, and n is the heterogeneity factor.

TABLE 1: Isotherm parameters for β -carotene adsorption on MCCM at different temperatures.

Isotherms	Parameters	30°C	40°C	50°C
Langmuir	b	20	21.23	22.37
	K_L	0.0053	0.0064	0.0079
	R_L	0.28	0.24	0.20
	R^2	0.9803	0.9944	0.9919
Freundlich	K_F	0.61	0.96	1.43
	$1/n$	0.52	0.46	0.42
	R^2	0.9597	0.9842	0.9658

TABLE 2: Comparative monolayer adsorption capacities (b) for β -carotene at 50°C.

Adsorbent	b (mg/g)	Solvent	Reference
MCCM	62.12	Isopropyl alcohol	[2]
Silica gel	25.32	n -hexane	[5]
Florasil	86.21	n -hexane	[5]
MCCM	22.37	Methyl ester	This study

The coefficient of determination (R^2) values for Langmuir model at 30, 40, and 50°C were higher compared to Freundlich model showing better applicability of Langmuir model (Table 1). These results were in good agreement with previously reported studies on β -carotene adsorption on acid-activated montmorillonite [4] and on silica-based adsorbent [5]. However, for β -carotene adsorption from crude maize and sunflower oil on acid-activated bentonite, applicability of Freundlich model was reported [6]. The values of b and K_L generally increased with increasing temperature. Table 2 compares β -carotene maximum adsorption capacity (b) with literature.

The separation factor (R_L) is a dimensionless parameter. It is defined as

$$R_L = \frac{1}{1 + K_L C_0}. \quad (4)$$

The R_L values for the present study were in range of favorable adsorption process (Table 1).

3.2. Effect of Temperature. The β -carotene adsorption increases with temperature (Figure 1) suggesting that the intraparticle diffusion rate of the adsorbate molecules into the pores increased with increase in temperature since diffusion is an endothermic process [7]. 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 [8]. 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 [9]. However, at higher temperature destruction of β -carotene may occur [5]. Therefore, the adsorption experiments were carried out up to 50°C.

FIGURE 1: Effect of temperature on β -carotene adsorption onto MCCM.

3.3. 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 Gibbs free energy change was calculated as

$$\Delta G = -RT \ln b, \quad (5)$$

where T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol·K). The ΔH and ΔS values were determined from the following equation:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT}. \quad (6)$$

The ΔG values at 30, 40, and 50°C were -7546.7 , -7951.23 , and -8345.7 J/mol, respectively. The decrease in ΔG values with temperature suggests that more β -carotene is adsorbed with increasing temperature [10]. This implies that the adsorption is favored at higher temperature. The positive ΔH value (4560.31 J/mol) indicates that the adsorption is endothermic. The positive ΔS value (39.96 J/mol·K) suggests increasing randomness at the solid/liquid interface during β -carotene adsorption on MCCM.

3.4. Effect of Contact Time. The experiments were performed varying temperature (i.e., 30, 40 and 50°C) at a fixed initial β -carotene concentration (500 mg/L). An increase in reaction temperature causes a decrease in solution viscosity leading to an increase in β -carotene molecules rate of diffusion across the external boundary layer and into the internal pores of the adsorbent. In addition, an increase in temperature increases MCCM equilibrium capacity for β -carotene. As shown in Figure 2, the recovery of β -carotene increased with increase in temperature. This may be the result of increase in the β -carotene molecules movement with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites. As presented

FIGURE 2: Effect of contact time on β -carotene adsorption on MCCM at different temperatures (initial β -carotene concentration—500 mg/L).

in Table 3 the β -carotene adsorption capacity onto MCCM increased from 8.218 to 10.775 mg/g with an increase in reaction temperature from 30 to 50°C, indicating that the process is endothermic [11]. The equilibration time at various temperatures was 200 min.

β -carotene adsorption on MCCM for various adsorbate concentrations was fast initially, thereafter, the adsorption rate decreased slowly as the available adsorption sites decreases gradually (Figure 3). The equilibration time increases from 165 to 200 min while the adsorption capacity increases from 3.099 to 10.775 mg/g with increase in concentration from 50 to 500 mg/L (Table 3).

3.5. Adsorption Kinetics. Lagergren rate equation is one of the most widely used adsorption rate equations to describe the adsorption kinetics. Linearized form is expressed as [12]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t, \quad (7)$$

where q_e and q_t are the adsorbed amount at equilibrium and at time t and k_1 is the pseudo-first-order rate constant (1/min).

The pseudo-second-order model in linearized form is expressed as [13]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t, \quad (8)$$

where k_2 is the rate constant of pseudo-second-order sorption (g/mg·min).

The values of R^2 for pseudo-second-order model were comparatively higher. The calculated adsorption capacity ($q_{e,calc}$) values for pseudo-second-order model were much

TABLE 3: Kinetics data for β -carotene adsorption on MCCM.

Temp ($^{\circ}\text{C}$)	C_0 (mg/L)	$q_{e,\text{exp.}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			$q_{e,\text{calc.}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,\text{calc.}}$ (mg/g)	k_2 (g/mg-min)	R^2
50	50	3.099	1.842	0.0221	0.9791	3.262	0.0249	0.9997
50	250	5.969	2.818	0.0235	0.9475	6.203	0.0187	0.9998
50	500	10.775	5.212	0.0237	0.9576	11.186	0.0105	0.9999
30	500	8.218	4.756	0.0196	0.9311	8.772	0.0073	0.9983
40	500	9.615	5.145	0.0216	0.9548	10.152	0.0081	0.9997

FIGURE 3: Effect of contact time on β -carotene adsorption on MCCM at different concentrations at 50°C .

closer to experimental adsorption capacity ($q_{e,\text{exp}}$) values (Table 3). Therefore, it is concluded that the pseudo-second-order kinetics model better describes β -carotene onto MCCM. Similar results were reported for β -carotene adsorption on acid activated bentonite [10, 14] and florilil [5].

3.6. Adsorption Mechanism. The rate-limiting step prediction is an important factor to be considered in sorption process. For solid-liquid sorption process, the solute transfer process was usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The mechanism for β -carotene removal by adsorption may be assumed to involve three successive transport steps: (i) film diffusion, (ii) intraparticle or pore diffusion, and (iii) sorption onto interior sites. The last step is considered negligible as it is assumed to be rapid. β -carotene uptake on MCCM active sites can mainly be governed by either liquid phase mass transfer or intraparticle mass transfer rate.

The most common method used to identify the mechanisms involved in the adsorption process is by fitting the

FIGURE 4: Weber and Morris plot for β -carotene adsorption at different temperatures (Initial β -carotene concentration was 500 mg/L).

experimental data to the intraparticle diffusion plot. The intraparticle diffusion equation can be expressed as [15]

$$q_t = k_{id} t^{1/2}, \quad (9)$$

where k_{id} is intraparticle diffusion rate constant (mg/g-min $^{1/2}$).

The Weber-Morris plots of q_t versus $t^{1/2}$ were presented in Figures 4 and 5, for the β -carotene adsorption onto MCCM as a function of temperature and initial concentration. For the adsorption process to be intraparticle diffusion controlled, the plots of q_t versus $t^{1/2}$ should pass through the origin and the R^2 should be sufficiently close to unity. The intraparticle diffusion parameters, k_{id} , for these regions were determined from the slope of the plots.

The adsorption data for q_t versus $t^{1/2}$ for the initial period show curvature, attributed to boundary layer diffusion effects or external mass transfer effects [16]. As shown in Figures 4 and 5 the adsorption process followed two phases, suggesting that the adsorption process proceeded first by surface adsorption and then intraparticle diffusion. This demonstrated that, in the initial stages, adsorption was due

TABLE 4: Intraparticle diffusion parameters for β -carotene adsorption on MCCM.

Temp. ($^{\circ}\text{C}$)	Conc. (mg/L)	$q_{e,\text{exp.}}$ (mg/g)	$k_{\text{id},1}$ (mg/g-min $^{1/2}$)	R^2	$k_{\text{id},2}$ (mg/g-min $^{1/2}$)	R^2
50	50	3.099	0.2448	0.9505	0.0675	0.9160
50	250	5.969	0.3542	0.9439	0.0706	0.8241
50	500	10.775	0.7540	0.9445	0.1133	0.9537
30	500	8.218	1.0631	0.9490	0.1239	0.9204
40	500	9.615	0.8993	0.9372	0.1190	0.9530

FIGURE 5: Weber and Morris plot for β -carotene adsorption at different initial concentrations and temperatures 50°C .

to the boundary layer diffusion effect and subsequently due to the intraparticle diffusion effect [17].

The Weber-Morris plots did not pass through the origin (Figures 4 and 5), implying that the mechanism of adsorption was influenced by two or more steps of adsorption process. This also indicates that the intraparticle diffusion is not the sole rate-controlling step. The values of rate parameters of intraparticle diffusion ($k_{\text{id},1}$ and $k_{\text{id},2}$) and correlation coefficients (R^2) were presented in Table 4. The intraparticle diffusion rate increases with increase in initial β -carotene concentration and reaction temperature. The driving force of diffusion was very important for adsorption processes. Generally driving force changes with β -carotene concentration in bulk solution. The increase in β -carotene concentration and reaction temperature result in increase of the driving force, which in turn increases the diffusion rate of β -carotene molecules in monolith pores.

3.7. Determination of Activation Energy. The values of rate constant found from adsorption kinetics could be applied in the Arrhenius form to determine the activation energy.

The relationship between the rate constants and solution temperature is expressed as

$$k_2 = k_0 \exp\left(-\frac{E_a}{RT}\right), \quad (10)$$

where k_0 is the temperature independent factor, E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol K), and T is the solution temperature (K). Equation (10) could be transformed into a linear form as

$$\log k_2 = \log k_0 - \frac{E_a}{2.303RT}. \quad (11)$$

The values of E_a and k_0 were obtained from the slope and intercept of the plot $\log k_2$ versus $1/T$ (figure not shown).

As shown in Table 3, the values of rate constant for pseudo-second-order (k_2) were found to increase from 0.0073 to 0.0105 g/mg-min, with increasing solution temperature from 303.15 (30°C) to 323.15 K (50°C). The magnitude of activation energy could provide information on type of adsorption, either physical or chemical. The value of activation energy for β -carotene adsorption was 14.73 kJ/mol. This value was <42.0 kJ/mol and is therefore consistent with physical adsorption process [18]. Adsorption of β -carotene by an acid-activated bentonite [6], sorption of β -carotene and chlorophyll onto acid-activated bentonite [10], and the sorptions of β -carotene on tonsil [19] have been reported to be controlled by physical adsorption.

4. Conclusions

β -carotene adsorption studies onto MCCM from methyl ester solution were conducted. Langmuir was the best applicable isotherm model with maximum monolayer adsorption capacity 22.37 mg/g at 50°C . The adsorption process was endothermic and followed physisorption mechanism. Kinetics studies showed applicability of pseudo-second-order kinetics model. The activation energy was 14.73 kJ/mol, suggesting that β -carotene adsorption onto MCCM is via physical adsorption.

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