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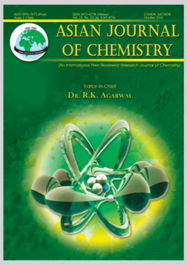

Kinetics Studies for the Adsorption of β-Carotene on Mesoporous Carbon Coated Monolith: Effect of Concentration and Temperature

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The adsorption kinetics for the removal of β-carotene as functions of temperature and initial β-carotene concentration onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solutions was investigated. The adsorption capacity increased as initial β-carotene concentration and temperature increased. Two kinetic models, pseudo-first-order and pseudo-second-order, were used to describe the adsorption kinetics. To identify the adsorption mechanism rate parameters for intraparticle diffusion model were evaluated. The results showed that the adsorption of β-carotene onto mesoporous carbon coated monolith followed pseudo-first-order model in isopropyl alcohol solution and pseudo-second-order model in *n*-hexane solution. The activation energies were 11.45 and 9.41 kJ/mol in isopropyl alcohol and *n*-hexane solutions, respectively.

Key Words: Mesoporous carbon coated monolith, β-Carotene, Adsorption kinetics, Thermodynamics, Isopropyl alcohol, *n*-Hexane.

INTRODUCTION

Crude palm oil usually contains 500-700 mg/L of carotenoids, mainly in the form of β-carotene. During conventional refining process majority of the carotenoids in palm oil destroyed. In an effort to reduce or to prevent these losses, methods of extraction and recovery of β-carotene have been developed by various researchers. These methods include solvent extraction[1], transesterification[2], adsorption using synthetic resins[3], silica gel[4], adsorption chromatography[5], supercritical carbon dioxide[6] and membrane technology[7].

Porous carbons are commonly used as adsorbent. The use of carbon for fixed bed process is associated with high pressure drops, potential channeling and several other disadvantages. These problems may 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[8]. 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[9, 10].

In previous studies, we have reported the equilibrium and thermodynamics of β-carotene adsorption onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solutions[11]. The objective of this study was to investigate the effects of initial β-carotene concentration and temperature on the adsorption kinetics of β-carotene onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solutions.

EXPERIMENTAL

Adsorbent: Cordierite monoliths (channel width 1.02 ± 0.02 mm or 400 channels per square inch and wall thickness 0.25 ± 0.02 mm) were obtained from Beihai Huihuang Chemical Packing Co. Ltd., China. The reported chemical composition of the cordierite monolith was SiO_2 50.9 ± 1 %, Al_2O_3 35.2 ± 1 %, MgO 13.9 ± 0.5 % and others < 1 %.

All the chemicals used were of analytical grade or as reported. Furfuryl alcohol (FA), pyrrole, poly(ethylene glycol) (PEG, m.w. 8000) were purchased from Fluka, Malaysia. Nitric acid (HNO_3, 65 %) was purchased from Fisher, Malaysia. 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 in solvents.

Preparation of mesoporous carbon coated monolith: Poly(ethylene glycol), a waxy solid at room temperature was ground. The poly(ethylene glycol) and furfuryl alcohol were then mixed in percentage volume ratio of 60:40. Nitric acid, a polymerization catalyst during the process, was added stepwise, after an interval of 5 min each with constant stirring for 1 h while maintaining temperature to approximately 21-23 ºC[12]. The monolith substrate was immersed for 20 min in a reactor with sufficient polymer solution to completely cover the surface. It was then dried at 110 ºC for 24 h. The dried coated monolith substrate precursor was carbonized in pure nitrogen flow at 650 ºC for 3 h with a heating rate of 10 ºC/min. The activation process was performed at 350 ºC for 4 h by flowing argon gas with 5 % oxygen.

Adsorption kinetics: A series of adsorption experiments were performed in a 500 mL conical flask containing 250 mL of β-carotene solution in water bath shaker (Stuart SBS40) at 150 rpm. The experimental temperature varied form 30 ± 1 ºC to 50 ± 1 ºC. The initial β-carotene concentration for the adsorption kinetics studies varied from 50 to 500 mg/L. The mesoporous carbon coated monolith mass was 3 g approximately. The samples from the reactor were collected at the specified time intervals using a digital micropipette (Rainin Instrument, USA). The supernatant solution was analyzed using a double beam UV/VIS spectrophotometer (Thermo Electron Corporation) at wavelength 446 nm. The amount of β-carotene adsorbed per g of mesoporous carbon coated monolith at time, q_t (mg/g), was determined by eq. (1):

$$q_t = \frac{V(C_0 - C_t)}{m} \qquad (1)$$

where, C_0 (mg/L) and C_t (mg/L) are initial β-carotene concentration and β-carotene concentration at time in the liquid phase, respectively, V is the volume of adsorbate (L) and m is the mass of adsorbent (g).

RESULTS AND DISCUSSION

Effect of initial concentration and contact time: The effect of initial concentration on the extent of β-carotene adsorption on mesoporous carbon coated monolith as a function of time at 50 ºC is shown in Fig. 1. The rate of β-carotene adsorption for the initial 10 min was found to be fast. This is due to the adsorption of β-carotene on the exterior surface of the mesoporous carbon coated monolith. The adsorption rate gets slower as the β-carotene molecules diffuses into the pores of mesoporous carbon coated monolith. The equilibration time for the adsorption of β-carotene at different initial concentrations ranged from 80 to 135 min in isopropyl alcohol and 40 to 80 min in *n*-hexane system. In general, the equilibration time increases with increase in initial concentration.

The adsorption capacity increased with increasing initial β-carotene concentration. This could be attributed to the driving force of the concentration gradient being directly proportional to the initial concentrations. Table-1 showed that the adsorption capacity of β-carotene at 50 ºC increased from 3.474 to 18.542 mg/g in isopropyl alcohol and from 2.690 to 10.829 mg/g in *n*-hexane, for an increase in initial β-carotene concentration from 50 to 500 mg/L. The adsorption capacity of β-carotene on mesoporous carbon coated monolith was higher in isopropyl alcohol system.

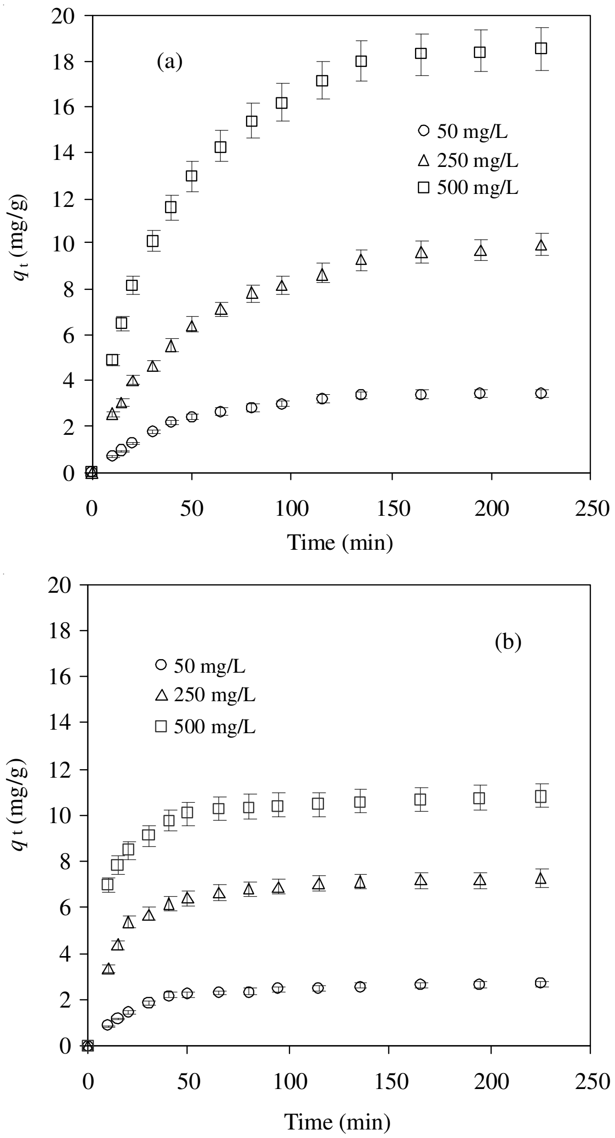


Fig. 1. Effect of initial concentration on the adsorption kinetics of β-carotene onto mesoporous carbon coated monolith in (a) isopropyl alcohol and (b) *n*-hexane solutions. (Conditions: temp. 50 ºC, agitation speed *ca.* 150 rpm)

For all cases under investigation, the β-carotene adsorption profile was a single, smooth and continuous curve leading to saturation, suggesting possible monolayer coverage of β-carotene on the surface of the adsorbent. This study is in good agreement with pervious study[11].

Effect of temperature: The effect of temperature on the adsorption of β-carotene (initial concentration 500 mg/L) was studied varying temperature form 30 to 50 ºC. The adsorption of β-carotene on mesoporous carbon coated monolith in both isopropyl alcohol and *n*-hexane as solvents increased with increase in temperature (Fig. 2). An increase in temperature increases the rate of diffusion of the β-carotene molecules across the external boundary layer and in the internal pores of the adsorbent, due to decrease in the viscosity of solution. This in turn results in increase in the adsorption capacity of the mesoporous carbon coated monolith for β-carotene as more the molecules acquire sufficient energy to undergo an interaction with the active sites. As observed, the adsorption of β-carotene onto mesoporous carbon coated monolith increased

TABLE-1
KINETIC DATA FOR THE ADSORPTION OF β-CAROTENE ON MESOPOROUS CARBON COATED MONOLITH

Temp (°C)	C_0 (mg/L)	$q_{e,exp.}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			$q_{e,calc.}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,calc.}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
Isopropyl alcohol								
50	50	3.474	3.887	0.0251	0.9880	4.286	0.0053	0.9940
50	250	9.979	9.473	0.0191	0.9923	11.905	0.0020	0.9984
50	500	18.542	19.494	0.0253	0.9886	21.739	0.0014	0.9987
40	500	16.986	16.932	0.0216	0.9960	20.367	0.0012	0.9973
30	500	16.067	15.926	0.0191	0.9967	19.724	0.0011	0.9968
n-hexane								
50	50	2.690	1.732	0.0200	0.9628	2.924	0.0181	0.9986
50	250	7.284	3.451	0.0212	0.9381	7.610	0.0130	0.9998
50	500	10.829	3.691	0.0210	0.9010	11.074	0.0153	0.9999
40	500	10.154	4.624	0.0251	0.9717	10.493	0.0131	0.9999
30	500	9.538	4.340	0.0223	0.9604	9.881	0.0121	0.9998

from 16.067 to 18.542 mg/g in isopropyl alcohol solution and 9.538 to 10.829 mg/g in *n*-hexane solution (Table-1), with an increase of solution temperature from 30 to 50 °C, indicating that the process is endothermic[13].

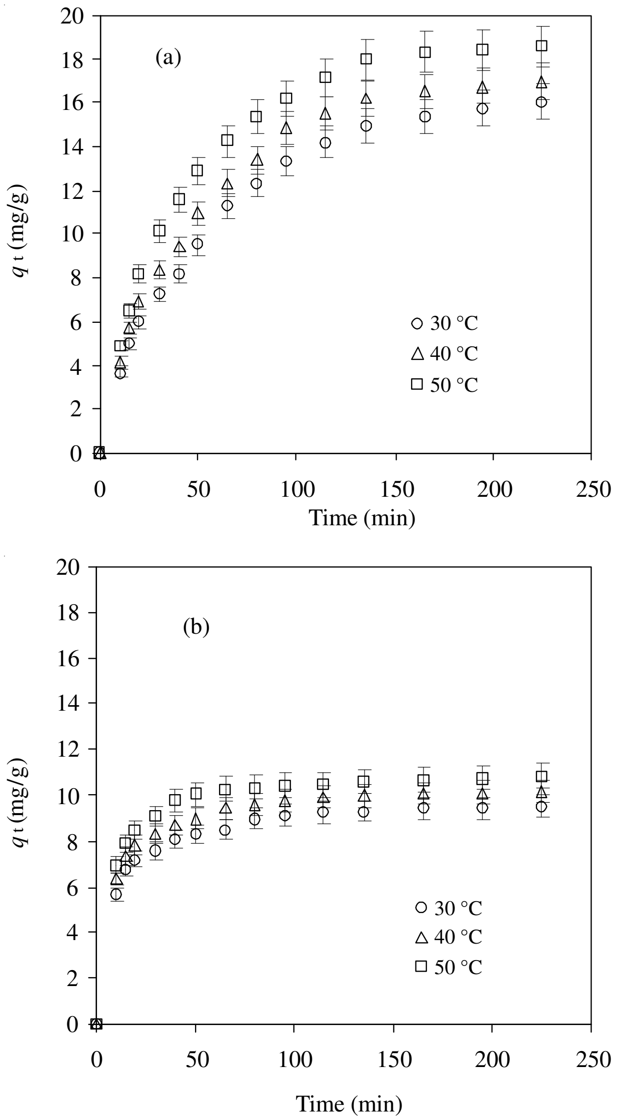


Fig. 2. Effect of temperature on the adsorption kinetics of β-carotene onto mesoporous carbon coated monolith in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: Initial β-carotene concentration -500 mg/L, agitation speed *ca.* 150 rpm)

Adsorption kinetics: The Lagergren-first-order (pseudo-first-order) and pseudo-second-order kinetics models were applied to the kinetics data. The Lagergren-first-order model[14] is expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{2}$$

where, q_e is the adsorbed amount (mg/g) at equilibrium and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of eqn. (2) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{3}$$

The values of k_1 and q_e can be obtained from the slope and intercept of the plot of log (q_e-q_t) *versus* t.

The pseudo-second-order model is expressed as follows[15,16]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{4}$$

where, k_2 is the rate constant of pseudo-second-order sorption (g/mg-min). Integrating eqn. (4) with the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the linear form is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

The values of k_2 and q_e can then be obtained from the slope and intercept of the plot of t/q_t *versus* t. For the applicability of the model, the correlation coefficient R^2 needs to be sufficiently high and $q_{e,exp}$ must be sufficiently close to $q_{e,calc}$. Figs. 3-6 present the plots of log (q_e-q_t) *versus* t and plot of t/q_t *versus* t, respectively. As presented in isopropyl alcohol system, the values of R^2 for both the models are very high (> 0.98) (Table-1). However, the values of $q_{e,calc}$ obtained from pseudo-first-order model are closer to $q_{e,exp.}$, as compared to $q_{e,calc.}$ obtained from pseudo-second-order model. It could therefore be concluded that the adsorption of β-carotene onto mesoporous carbon coated monolith in isopropyl alcohol system was better described by pseudo-first-order model. Christidis and Kosiari[17] also reported the applicability of pseudo-first-order kinetics model for the adsorption of β-carotene onto acid-activated bentonite.

For *n*-hexane system, the values of $q_{e,calc.}$ determined from pseudo-second-order kinetics model are closer to the experi-

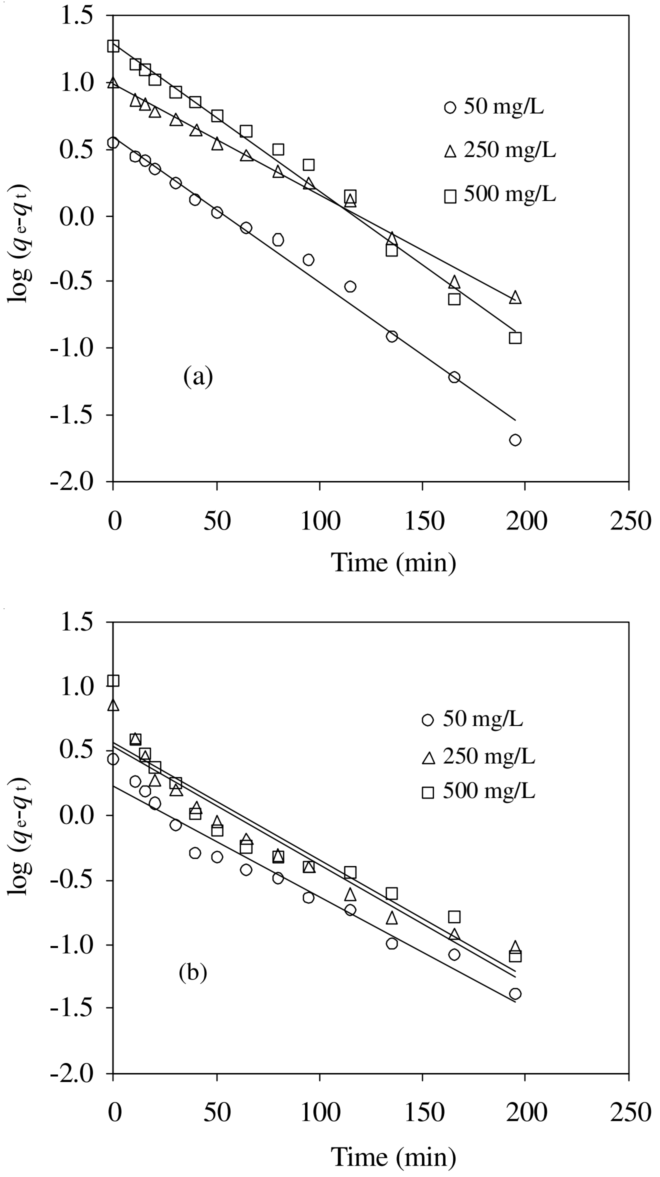
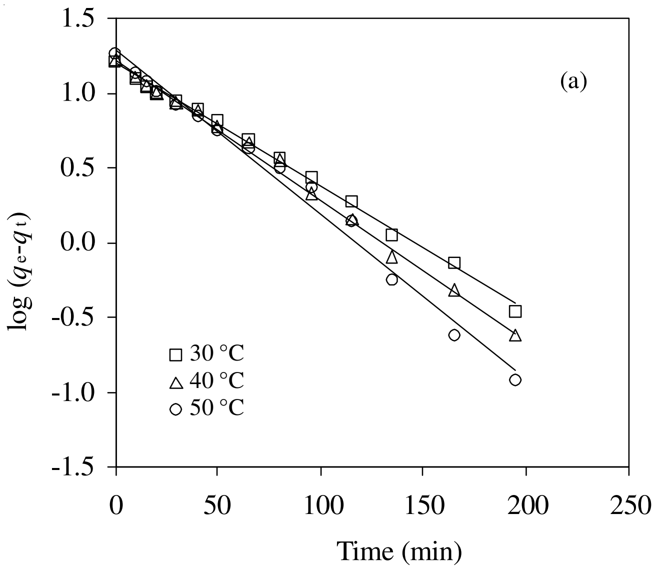


Fig. 3. Pseudo-first-order kinetics plot for the adsorption of β-carotene at different initial concentrations in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: temp. 50 ºC, agitation speed *ca.*150 rpm)



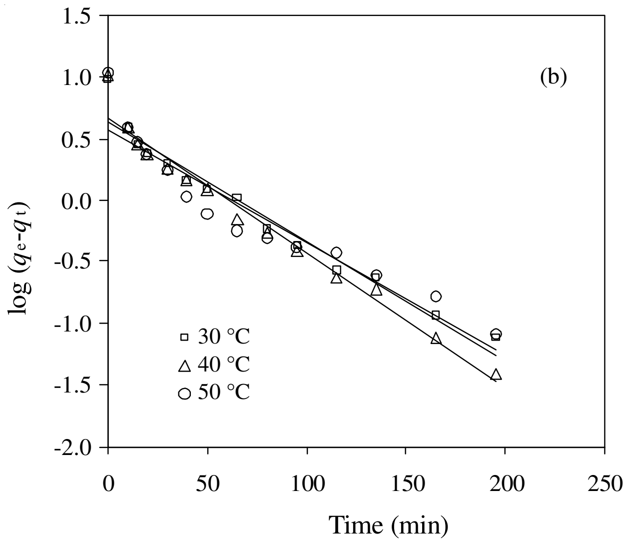


Fig. 4. Pseudo-first-order kinetics plot for the adsorption of β-carotene at different temperatures in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: Initial β-carotene concentration 500 mg/L, agitation speed *ca.* 150 rpm)

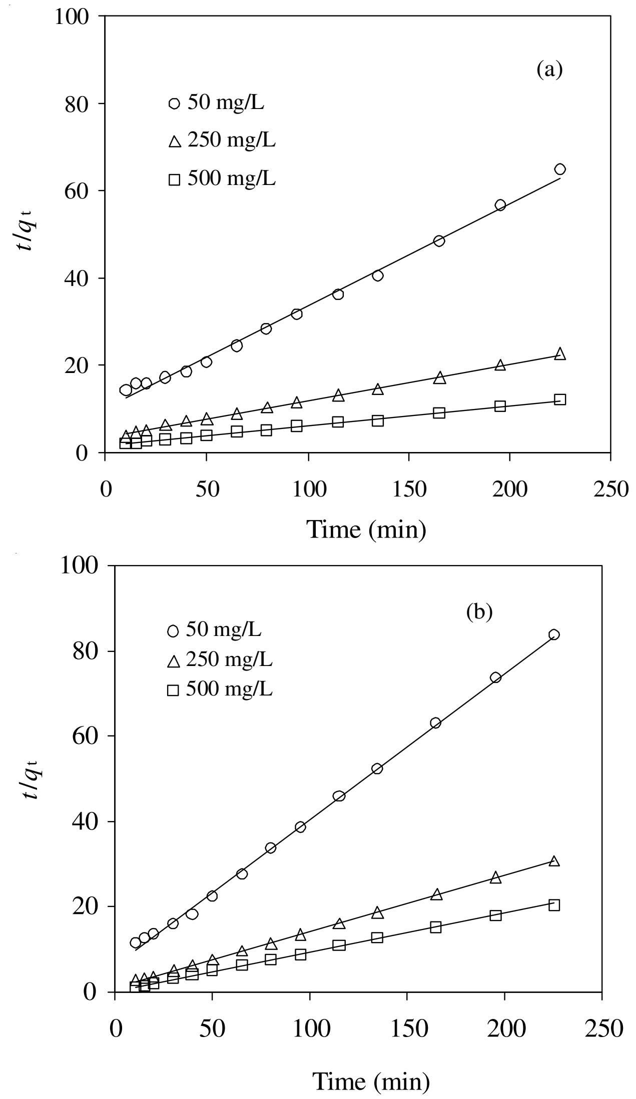


Fig. 5. Pseudo-second-order kinetics plot for the adsorption of β-carotene at different initial concentrations in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: temp. 50 ºC, agitation speed *ca.* 150 rpm)

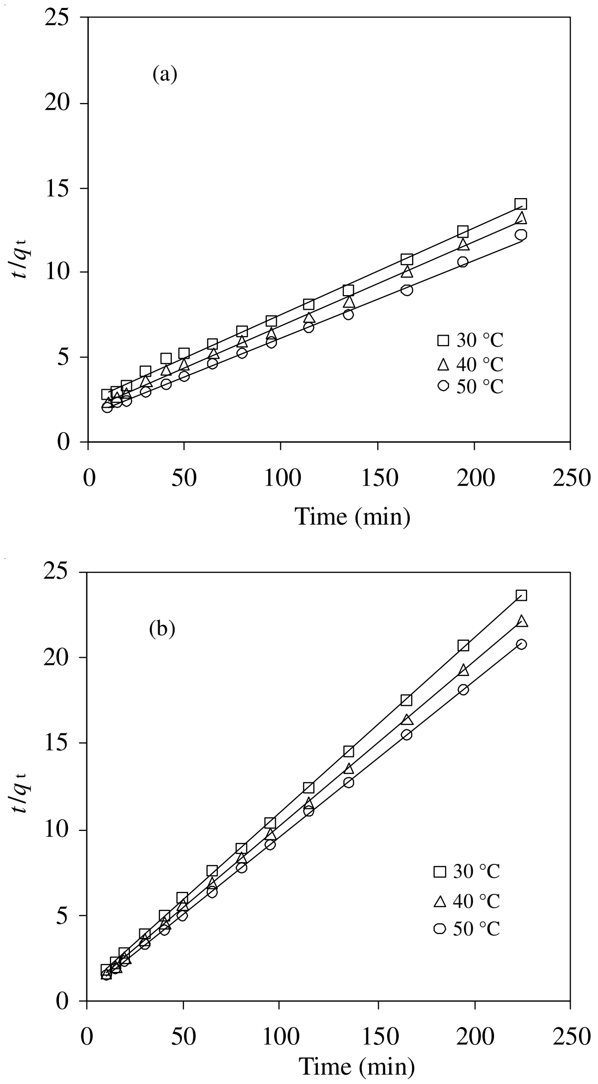


Fig. 6. Pseudo-second-order kinetics plot for the adsorption of β-carotene at different temperatures in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: Initial β-carotene concentration 500 mg/L, agitation speed *ca.* 150 rpm)

mental values ($q_{e,exp.}$) and the correlation coefficient values for pseudo-second-order ($R^2 > 0.99$) are considerably higher than the pseudo-first-order model (Table-1). Therefore, it can be concluded that the adsorption of β-carotene onto mesoporous carbon coated monolith in *n*-hexane system obeys pseudo-second-order model. These results are in good agreement with results reported elsewhere[18-20].

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

The most common method used to identify the mechanisms involved during the adsorption process is by matching the experimental data in the intraparticle diffusion plot. The intraparticle diffusion equation can be expressed as[21]:

$$q_t = k_{id}\, t^{0.5} \tag{6}$$

where, k_{id} is intraparticle diffusion rate constant (mg/g-min $^{0.5}$).

The Weber-Morris plots for the adsorption of β-carotene onto mesoporous carbon coated monolith as a function of initial concentration and temperature in isopropyl alcohol and *n*-hexane solutions were presented in Figs. 7 and 8. For the adsorption process to be intrapaticle diffusion controlled the plots should pass through the origin and the R^2 should be sufficiently close to unity. As shown in Figs. 7 and 8 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 to the boundary layer diffusion effect and subsequently due to the intraparticle diffusion effect[22-24].

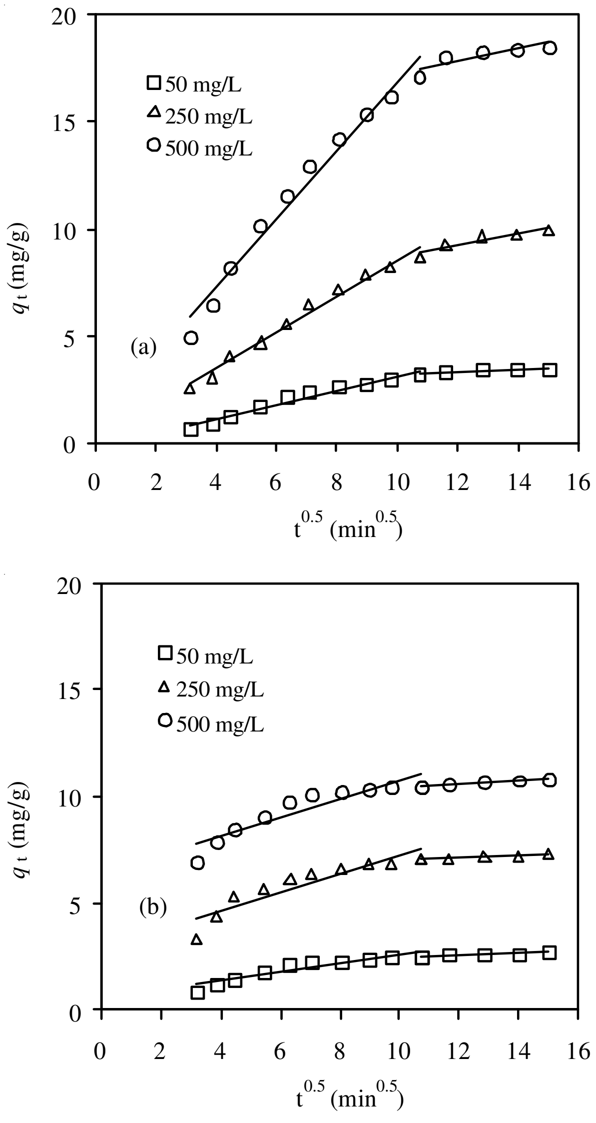


Fig. 7. Weber and Morris intraparticle diffusion plots for the adsorption of ß-carotene at different initial concentration in (a) isopropyl alcohol and (b) *n*-hexane solutions; (Conditions: temp. 50 °C, agitation speed *ca.* 150 rpm)

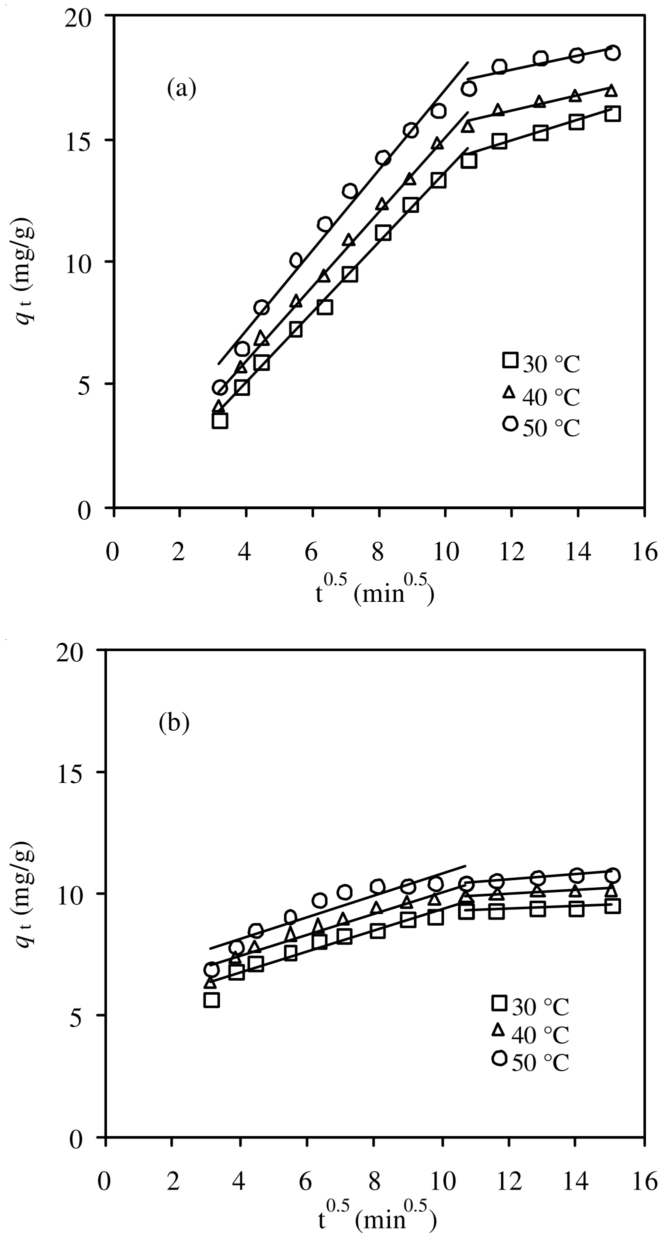


Fig. 8. Weber and Morris intraparticle diffusion plots for the adsorption of β-carotene at different temperatures in (a) isopropyl alcohol and (b) *n*-hexane solutions. (Conditions: Initial β-carotene concentration 500 mg/L, agitation speed *ca.* 150 rpm)

The Weber-Morris plots did not pass through the origin, 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 ($k_{id,1}$ and $k_{id,2}$) and R^2 were presented in Table-2.

Determination of activation energy: The values of rate constant determined from adsorption kinetics could be applied in the Arrhenius equation to determine the activation energy. The relationship between the rate constants and solution temperature is expressed as:

$$k_1 \quad \text{or} \quad k_2 = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

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 (7) could be transformed into a linearized form:

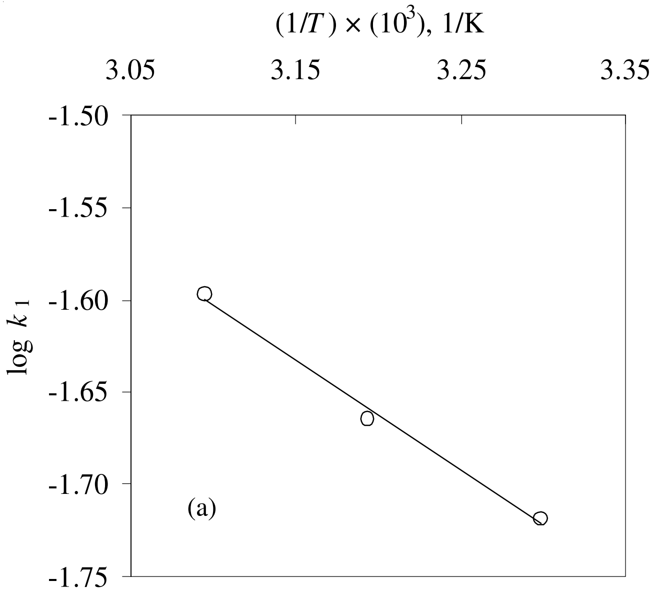
$$\log k_1 \quad \text{or} \quad \log k_2 = \log k_0 - \frac{E_a}{2.303RT} \qquad (8)$$

The values of E_a and k_0 were obtained from the slope and intercept of the straight line in the plot of log k_1 or log k_2 *versus* 1/T, as shown in Fig. 9.

TABLE-2
WEBER-MORRIS'S MODEL PARAMETERS FOR THE ADSORPTION OF β-CAROTENE ON MESOPOROUS CARBON COATED MONOLITH

C_0 (mg/L)	$k_{id,1}$ (mg/g-min$^{0.5}$)	R^2	$k_{id,2}$ (mg/g-min$^{0.5}$)	R^2
Isopropyl alcohol				
50	0.3381	0.9651	0.0611	0.8393
250	0.8426	0.9844	0.2753	0.8925
500	1.6164	0.9775	0.2935	0.8057
500	1.5108	0.9933	0.3134	0.9328
500	1.4185	0.9949	0.4118	0.9569
n-Hexane				
50	0.2102	0.8652	0.0395	0.9407
250	0.4271	0.8371	0.0510	0.9497
500	0.4404	0.8474	0.0815	0.9839
500	0.4385	0.9187	0.0569	0.9641
500	0.4289	0.9231	0.0639	0.9828

As shown in Table-1, the values of rate constant were found to increase from 0.0191 to 0.0253 1/min in isopropyl alcohol solution (pseudo-first-order) and 0.0121 to 0.0153 g/mg-min in *n*-hexane solution (pseudo-second-order), with increasing solution temperature from 30 to 50 ºC. The magnitude of activation energy (E_a) could provide information on the type of adsorption, either physical or chemical. The E_a for β-carotene adsorption onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solutions was found to be 11.45 kJ/mol and 9.41 kJ/mol, respectively. The magnitude of E_a in both the solutions was < 42.0 kJ/mol, it is therefore more consistent with the physical adsorption process[25]. The adsorption of β-carotene onto acid-activated bentonite[17,18] and on tonsil[26] has been reported to be controlled by physical adsorption.



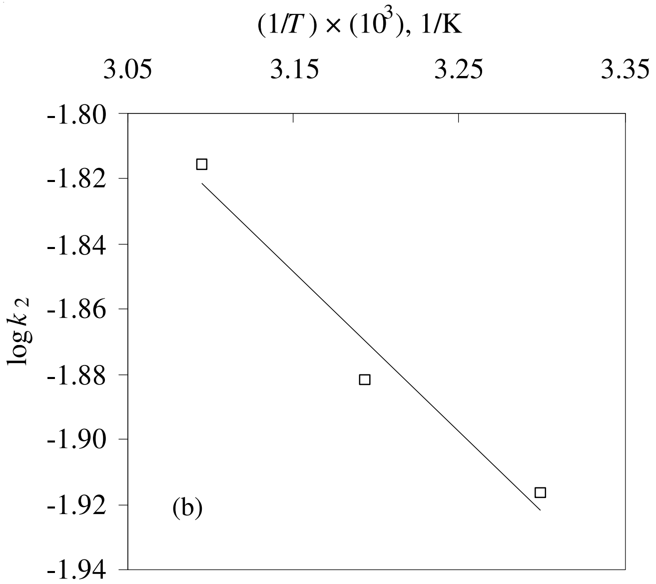


Fig. 9. Relationship between rate constant and solution temperature in (a) isopropyl alcohol and (b) *n*-hexane solutions. (Conditions: Initial β-carotene concentration 500 mg/L, agitation speed *ca.* 150 rpm)

Conclusion

The present study showed that mesoporous carbon coated monolith is an effective adsorbent for the recovery of β-carotene from organic solutions. The adsorption of β-carotene was found to vary with initial β-carotene concentration, solvent system and temperature. The increase in solution temperature increased the rate of diffusion of β-carotene molecules through the external boundary layer and in the interior pores of the mesoporous carbon coated monolith.

Adsorption kinetics were modeled using the pseudo-first-order, pseudo-second- order and intraparticle diffusion models. It was concluded that the pseudo-first-order kinetic model could describe well the adsorption kinetics in isopropyl alcohol solution and pseudo-second-order in *n*-hexane solution.

The activation energies were 11.45 kJ/mol and 9.41 kJ/mol in isopropyl alcohol and *n*-hexane solutions, respectively. The lower values of the activation energy suggest that the adsorption process of β-carotene onto mesoporous carbon coated monolith is *via* physical adsorption.

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