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Desorption of β-carotene from mesoporous carbon coated monolith: Isotherm, kinetics and regeneration studies

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ABSTRACT

β-carotene, a natural antioxidant, beneficial form human health prospective. In this study we had examined the recovery of β-carotene form mesoporous carbon coated monolith (MCCM) by batch process. Desorption kinetics and isotherm studies were carried out by using *n*-hexane as an eluent. Isotherm studies showed better applicability of Langmuir model. The first-order two-compartment three-parameter kinetics model as a function of initial loading concentration and reaction temperature was applied. It was observed that β-carotene desorption process is controlled by both rapid and slow desorption. Results showed that the slow desorption fraction increases from 0.8446 to 0.9007 with increase in initial loading concentration from 10.83 to 39.72 mg/g while, the slow desorption fraction decreases from 0.9261 to 0.8684 with increase in reaction temperature form 30 to 50 °C. The activation energies for rapid and slow desorption were 7.88 and 44.47 kJ/mol, respectively. The regeneration studies were carried out by both chemical and thermal process. The regeneration efficiency (RE%) for the three consecutive cycles reduced from 96.24 to 60.04% and 94.51 to 81.62% for chemical and thermal regeneration processes, respectively.

1. Introduction

β-carotene ($C_{40}H_{56}$), a precursor of vitamin A, belongs to a class of fat-soluble vitamins. It is abundantly present in crude palm oil. The antioxidant property of β-carotene has drawn considerable attention [1]. Studies revealed the effectiveness of β-carotene and other carotenoids to reduce the risk of certain cancers and cardiovascular disorders [2].

The conventional refining processes cause major loss of carotenoids present in palm oil. In an effort to reduce or to prevent these losses, methods of extraction and recovery of β-carotene like solvent extraction [3], transesterification [4], adsorption using synthetic resins [5], silica gel [6], adsorption chromatography [7], supercritical carbon dioxide treatment [8], and membrane treatment technology [9] have been developed.

Porous activated carbon (AC) is a conventionally used adsorbent. High pressure drop specifically in fixed bed columns and potential channelling are some of the demerits of AC. Carbonaceous monoliths could be utilized to overcome these issues. Compared to conventionally used AC, carbonaceous monolith has large external surface area. The pressure drop across fixed bed monolith column is very less [10]. The carbonaceous monolith can also be placed in vertical or horizontal position and in mobile system without deformity in shape and is easier to be scaled up due to its simple design and uniform flow distribution [11,12].

In our previous work we had reported adsorption equilibrium and thermodynamics studies of β-carotene on mesoporous carbon coated monolith (MCCM) [13]. To our knowledge none of the studies have reported recovery of β-carotene from MCCM. In this study we had explored desorption equilibrium and kinetics of β-carotene from MCCM. To check the economic feasibility of MCCM as an adsorbent, regeneration studies were also carried out by using chemical and thermal methods.

2. Experimental

2.1. Adsorbent

Cordierite monoliths with channel width 1.02 ± 0.02 mm and wall thickness 0.25 ± 0.02 mm were purchased from Beihai Huihuang Chemical Packing Co. Ltd., China. The reported chemical

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composition of monolith was SiO_2 – 50.9 ± 1%, Al_2O_3 – 35.2 ± 1%, MgO – 13.9 ± 0.5%, and others <1%.

2.2. Chemical and reagents

β-carotene, isopropyl alcohol (IPA), *n*-hexane, acetone, cyclohexane, and petroleum ether were purchased from Sigma–Aldrich, Malaysia. Furfuryl alcohol (FA), pyrrole, poly(ethylene glycol) (PEG) were purchased from Fluka, Malaysia. Nitric acid was purchased from Fisher, Malaysia. All the chemicals and reagents used were of analytical regent (AR) grade or as specified.

2.3. Preparation of MCCM

Polyethylene glycol, a waxy solid was grounded to powder. It was then dispersed in FA. The mixing ratio of FA and PEG was 40:60 by percentage volume. Nitric acid was added drop wise after each 5 min. The mixture was continuously stirred for 1 h while maintaining temperature at 21–23 °C [14]. The monolith was fully immersed in this mixture forming a coat over the surface. It was then dried and carbonized in a furnace at 650 °C with heating rate of 10 °C/min for 3 h under nitrogen atmosphere. The carbonized monolith was then activated with argon (containing 5% oxygen) at 350 °C for 4 h. Surface studies of the MCCM showed BET surface area 61.13 m^2/g. The pore size studies showed bimodal distribution [13].

2.4. Desorption equilibrium and desorption kinetics

In 250 mL stopper cork conical flask, adsorbent (MCCM, 0.8 g) was initially saturated with different concentrations (*i.e.* 100, 300 and 500 mg/L) of β-carotene solution in IPA. The saturation reaction occurs in a temperature controlled water bath shaker (Stuart SBS40) at 50 °C and 150 rpm for 48 h. To elute β-carotene form saturated MCCM, 100 mL of *n*-hexane was added as an eluent under nitrogen atmosphere to avoid degradation of β-carotene in presence of oxygen. To avoid photolytic degradation of β-carotene the flask was wrapped with aluminium foil. The flask was shaken in a temperature controlled water bath shaker at 50 °C and 150 rpm. At equilibrium, sample was withdrawn and analysed by UV–vis Spectrophotometer (Thermo Electron Corporation) at λ_{max} – 446 nm.

The equilibrium loading of β-carotene on MCCM, q_e (mg/g) was calculated using a mass balance equation as:

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

where q_i is the initial solid phase β-carotene concentration (mg/g), C_i is the initial β-carotene concentration in solution (mg/L), C_e is the β-carotene concentration in solution (mg/L) at equilibrium and V is the volume of solution and m is the adsorbent mass.

Desorption efficiency was calculated as:

$$\text{Efficiency}\,(\%) = \frac{q_i - q_e}{q_i} \times 100\% \tag{2}$$

For desorption kinetics, 100 mL of *n*-hexane solution was taken in 250 mL of stopper corked conical flask. It was then heated in a temperature controlled water bath shaker to certain temperature range (30–50 °C) and 150 rpm. After attaining the required experimental temperature β-carotene saturated MCCM was put into the flask. The samples were withdrawn at the specified time intervals and were analysed by UV–vis Spectrophotometer (Thermo Electron Corporation) at λ_{max} – 446 nm. The amount of β-carotene remaining on the adsorbent, q_t (mg/g) was calculated using a mass balance equation:

$$q_t = q_i - \frac{V(C_t - C_i)}{m} \tag{3}$$

where C_t is the β-carotene concentration in solution (mg/L) at any time.

2.5. Regeneration studies

To make a comparative approach, MCCM was regenerated by both chemical and thermal processes. Initially, 100 mL of β-carotene solution with 500 mg/L initial concentration was treated with 0.8 g MCCM. The equilibration time for the reaction was 40 h. The saturated MCCM was then washed with distilled water to remove the unadsorbed traces of β-carotene. The chemical regeneration was carried out for 5 h by using *n*-hexane as an eluent while, the thermal regeneration process was carried out for 3 h in a furnace at 650 °C under nitrogen atmosphere. Both processes were repeated for three consecutive cycles. The regeneration efficiency (RE%) of the MCCM was calculated as:

$$\text{RE\%} = \frac{\text{adsorption capacity of regenerated MCCM}}{\text{adsorption capacity of fresh MCCM}} \times 100 \tag{4}$$

3. Results and discussion

3.1. Desorption isotherms

The linear, Freundlich and Langmuir isotherms were applied to describe desorption of β-carotene from MCCM. The linear isotherm model assumes that all of the sites on the adsorbent have equal affinity for the solute [15]. The linear isotherm model is given as:

$$q_e = K_d\, C_e \tag{5}$$

where q_e (mg/g) is the β-carotene concentration remaining on the MCCM at equilibrium, C_e (mg/L) is the β-carotene concentration at equilibrium in liquid phase, and K_d (mL/g) is the distribution coefficient, can be calculated from the plot q_e versus C_e.

Freundlich isotherm describes equilibrium on heterogeneous surface where adsorption energies are not equal for available adsorption sites. The heterogeneity might be caused by the differences in pore size, pore shape, and adsorbate–adsorbent interaction. The linear form of Freundlich isotherm is given as [16]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where Freundlich constants K_F $(mg/g)(L/mg)^{1/n}$ can be used as an alternative measure of sorption capacity, and $1/n$ is the surface heterogeneity factor (sorption intensity). The more heterogeneous the surface, the more it will bring the $1/n$ value closer to zero [17]. The values of these parameters were obtained from the slope and intercept of a plot of log q_e versus log C_e.

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

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{1}{b} \times C_e \tag{7}$$

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

The desorption isotherm data was applied to the linear, Freundlich and Langmuir isotherm models (Fig. 1). The regression coefficient (R^2) value for Langmuir model was comparatively higher (Table 1) suggesting that desorption of β-carotene form MCCM is well described by Langmuir model. The applicability of Langmuir model confirms that homogenous sites were actively involved for the desorption process. These results were in agreement with our previous study on β-carotene adsorption on MCCM [13]. Contrary to these results, Chu et al. [18] reported the applicability of

Table 1
Isotherm parameters for β-carotene desorption from MCCM at 50 °C.

Freundlich model			Linear model		Langmuir model		
K_F	n	R^2	K_d	R^2	K_L	b	R^2
4.701	3.769	0.9308	0.054	0.7888	0.0718	18.25	0.9983

Freundlich model for desorption of Vitamin E from silica-based adsorbent.

3.2. Effect of contact time on β-carotene desorption

The extent of β-carotene desorption from MCCM was studied as a function of time under different conditions, *i.e.* initial β-carotene concentration and reaction temperature. It was observed that the ratio of desorption capacity at any time t (q_t) and initial desorption capacity (q_i) *i.e.* q_t/q_i under different conditions decreases with an increase in time and finally reaches equilibrium. The studies showed rapid desorption phase initially, becoming slower as it proceeds towards equilibrium (Figs. 2 and 3). The trend of β-carotene desorption profiles was similar for all systems. The slow desorption step was the rate-limiting step for the recovery of β-carotene. As can be seen from Fig. 2, an increase in temperature from 30 to 50 °C results in an increase of β-carotene recovery (initial loading – 26 mg/g), indicating that desorption of β-carotene from MCCM was an endothermic process.

The amount of β-carotene desorbed decreases with increase in initial loading concentration (Fig. 3). As the concentration of β-carotene gradually increases, it increases desorption resistance of β-carotene from the MCCM to aqueous phase leading to decrease in β-carotene desorption rate. Similar results were reported by Chefetz et al. [19]. However, Gao et al. [20] and Gunasekara and Xing [21] found that at high solute concentration, more molecules were

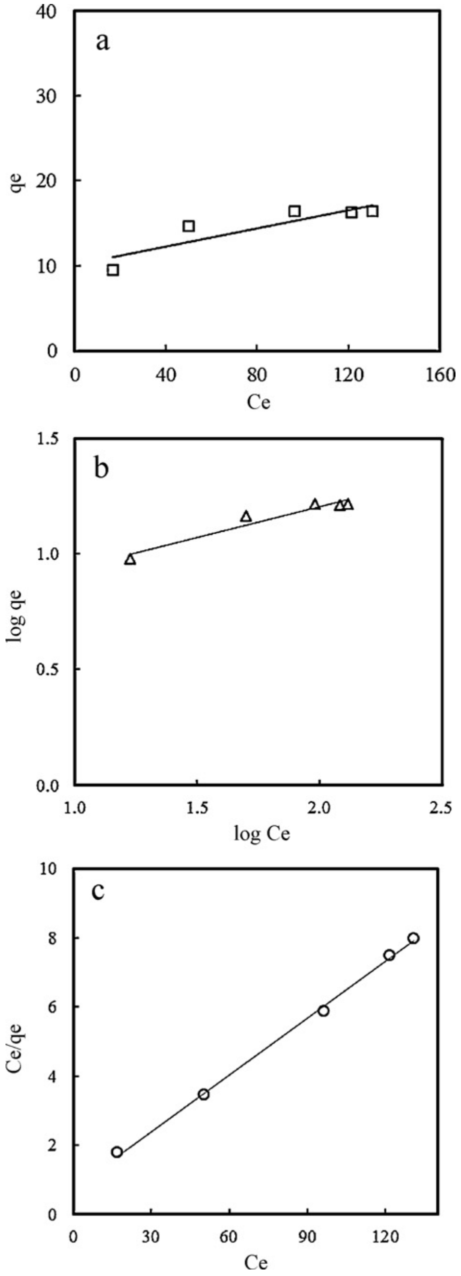

Fig. 1. Desorption isotherm models of β-carotene from MCCM (a) Linear, (b) Freundlich, and (c) Langmuir.

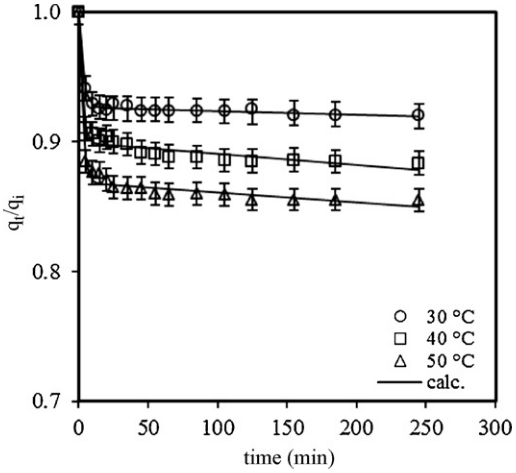

Fig. 2. Effect of contact time on β-carotene desorption from MCCM at various temperatures.

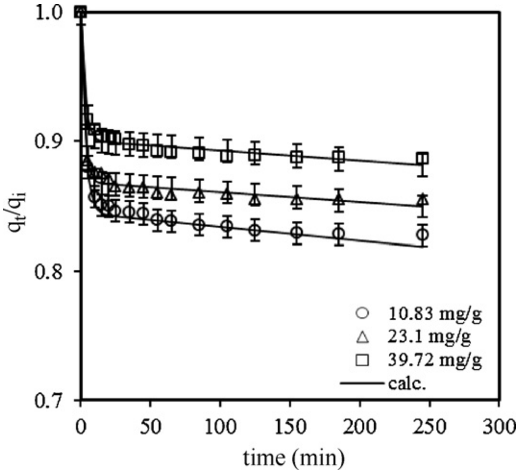

Fig. 3. Effect of contact time on β-carotene desorption from MCCM at various initial loading concentrations.

taken up by low-energy binding sites and therefore can readily be desorbed. There results were contrary to our findings.

3.3. Desorption kinetics

A first-order two-compartment three-parameter model [22] was used to describe the β-carotene desorption rate from MCCM. Assuming a slowly desorbing fraction, Φ_S, and a rapidly desorbing fraction, $(1-\Phi_S)$:

$$\frac{q_t}{q_i} = \Phi_S \exp(-k_s t) + (1-\Phi_S)\exp(-k_r t) \qquad (7')$$

where k_s and k_r are the apparent first-order rate constants for the slow and rapid desorbing fractions, respectively.

This model was fitted to desorption kinetics data using the non-linear regression method. The best estimated values of k and Φ were obtained by minimizing the sum of the squares of the differences between experimental and calculated values of (q_t/q_i) in Microsoft Excel using the generalized reduced gradient algorithm (SOLVER).

Desorption kinetics data for the studied systems were successfully described by a first-order two-compartment three-parameter model. Desorption kinetics parameters determined from the model are listed in Tables 2 and 3. Both rapid (k_r) and slow (k_s) desorption rates and slow desorption fractions (Φ_S) were the functions of initial loading concentrations and reaction temperature. In terms of initial loading effect, the values of Φ_S are proportional to the initial loading concentrations applied while, the values of Φ_S decreases with increase in temperature. The results showed that β-carotene desorption process is controlled by both rapid and slow desorption which is related to its specific bimodal property of the pore size distribution on MCCM. Furthermore the values of k_s decreases with increase in initial loading this might be due to gradual increase in desorption resistance of β-carotene form MCCM. When the reaction temperature increases, the value of the Φ_S decreases while, an increase in temperature causes an increase in β-carotene desorption. This shows that heterogeneities in pore size and pore characteristics of MCCM could possibly the reason of presently observed occurrence of the decrease in Φ_S with temperature. The intra-particle diffusion may be retarded through narrow pores. The small pore size might cause entrapment and slow down the diffusion of adsorbates through voids within the adsorbents [23]. Cylindrical molecular geometry of β-carotene might also be the possible reason of blocking diffusion pathways to some extent.

The rapid rate constant (k_r) was studied as a function of initial β-carotene loading at 50 °C. It was observed that k_r increases from 0.3009 to 0.3880 l/min with increase in initial loading from 10.83 to 23.10 mg/g (Table 2). Further increase in initial loading leads to decrease in k_r. Similar to initial β-carotene loading studies, k_r as a function of temperature at 27 mg/g initial β-carotene loading increases from 0.3208 to 0.4095 l/min as temperature increases from 30 to 40 °C (Table 3). Further increase in temperature causes decrease in k_r. This indicates that k_r is rather insensitive to initial β-carotene loading and reaction temperature.

3.4. Effect of temperature on desorption kinetics

The energy of activation measures the magnitude of the forces required to overcome during desorption process. The rate constants determined for desorption kinetics could be applied to Arrhenius equation to determine the activation energy. The relationship between the rate constants and solution temperature is expressed as:

$$k_{\text{rapid}}\ or\ k_{\text{slow}} = k_0 \exp\left(-\frac{E_{\text{des}}}{RT}\right) \qquad (8)$$

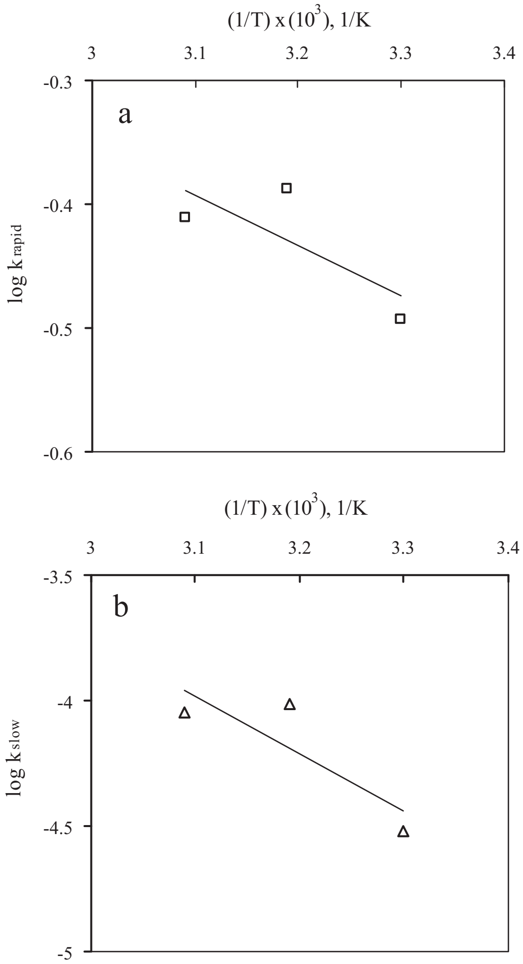

Fig. 4. Arrhenius plot for (a) rapid desorption, and (b) slow desorption of β-carotene from MCCM.

where k_0 is the temperature independent factor, E_{des} is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol K) and T is the solution temperature (K). Eq. (8) could be transformed into a linear form:

$$\log k_{\text{rapid}}\ or\ \log k_{\text{slow}} = \log k_0 - \frac{E_{\text{des}}}{2.303RT} \qquad (9)$$

The energy of activation (E_{des}) was determined from the slope of Arrhenius plot, $\log k_{\text{rapid}}$ or $\log k_{\text{slow}}$ versus $1/T$, as shown in Fig. 4(a) and (b). The values of E_{des} obtained for the rapid and slow desorption were 7.88 and 44.47 kJ/mol, respectively. The activation energy values were strongly depended on the adsorbent characteristics [22]. According to Werth and Reinhard [24], and Wang and Grathwohl [25], the activation energies for the diffusion in liquids and gases were larger in micropores than in mesopores or macropores. In the present study, higher activation energy was observed for slow rate constant (k_{slow}) confirming diffusion might occur through micropores.

3.5. Regeneration studies

The reutilization potential of an adsorbent can be elucidated though regeneration studies. A decrease in MCCM regeneration efficiency (RE%) for β-carotene was observed for successive regeneration steps (Fig. 5). For the first cycle, the RE% values for chemical and thermal process were 96.24 and 94.51%, respectively. The efficiency for chemical process was further reduced to 68.10 and 60.04% for second and third cycles, respectively. While for ther-

Table 2
Desorption rate parameters for β-carotene as a function of initial loading at 50 °C.

Initial loading, q_i (mg/g)	Φ_S	k_r (l/min)	k_s (l/min)	SSE[a]	R^2
10.83	0.8446	0.3009	0.000130	0.00026	0.9904
23.10	0.8684	0.3880	0.000089	0.00020	0.9890
39.72	0.9007	0.3363	0.000087	0.00015	0.9869

[a] SSE – Sum of square error.

Table 3
Desorption rate parameters for β-carotene as a function of temperature at 27 mg/g initial loading.

Temperature (°C)	Φ_S	k_r (l/min)	k_s (l/min)	SSE[a]	R^2
30	0.9261	0.3208	0.000030	0.000036	0.9935
40	0.8991	0.4095	0.000097	0.000227	0.9807
50	0.8684	0.3880	0.000089	0.000204	0.9890

[a] SSE – Sum of square error.

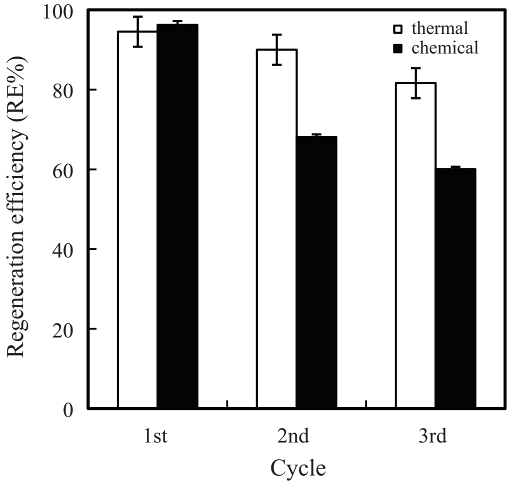

Fig. 5. Regeneration efficiency plot of MCCM using chemical and thermal regeneration processes.

mal process the RE% for second and third cycles was 89.99 and 81.62%, respectively. The decrease in β-carotene uptake on MCCM by chemical process indicates a loss in RE% for continuous regeneration steps. This could be due to a decrease in the number of binding sites over MCCM [26]. The degradation of MCCM surface might be the other reason [27]. For thermal regeneration, shrinking of pores on carbon surface might occur, resulting decrease in total surface area reducing the accessible surface for β-carotene binding [28]. The loss in capacity due to thermal regeneration was also reported Misra et al. [29], Magne and Walker [30] and Ferro-Garcia et al. [31]. Widening of mesopores due to thermal treatment might also be the possible cause for reduction in capacity [29].

Comparing the regeneration processes it was observed that the efficiency decreases with regeneration steps. For first cycle, chemical process showed better results, while for second and third cycle thermal process showed better results. These results showed that MCCM could be repeatedly used for the β-carotene adsorption, indeed, slightly detectable decrease in adsorption capacities. Recovery of β-carotene is an issue with thermal process proving chemical process as a better alternative.

4. Conclusions

β-carotene desorption potential from MCCM was testified. The equilibrium and kinetics parameters were studied. To check the economic feasibility of the process regeneration studies were carried out by chemical and thermal process. The applicability of Langmuir model to experimental data confirms active involvement of homogenous sites in desorption process. The contact time studies profile as a function of initial loading concentration and reaction temperature showed rapid desorption phase initially, becoming slower as it proceeds towards equilibrium. The variation in temperature from 30 to 50 °C during contact time studies result in an increase in β-carotene recovery from MCCM indicating an endothermic process. First-order two-compartment three-parameter kinetics model for β-carotene desorption from MCCM showed that k_r is rather insensitive to initial loading and reaction temperature. The higher value of activation energy (44.47 kJ/mol) for slow rate constant (k_{slow}) confirms that diffusion might occur through micropores. The regeneration studies showed loss in RE% by both chemical and thermal process. The RE% after three consecutive cycles was reduced to 60.04% and 81.62% for chemical process and thermal processes, respectively. The recovery of β-carotene is an issue by thermal process which could be achieved through chemical process. This proves the efficiency of chemical over thermal process.

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