Chemical Engineering Journal 166 (2011) 461–467

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Amine extraction from hexagonal mesoporous silica materials by means of methanol-enhanced supercritical CO_2: Experimental and modeling

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ARTICLE INFO

Article history:
Received 27 June 2010
Received in revised form 24 October 2010
Accepted 27 October 2010

Keywords:
Supercritical fluid extraction
Methanol
Hexagonal mesoporous silica
Amine removal
Diffusion-layer theory model

ABSTRACT

In this work, dodecylamine was extracted from freshly synthesized hexagonal mesoporous silica materials under pressure of 15.0–25.0 MPa and temperature of 50–105 °C with methanol-enhanced supercritical carbon dioxide. The effects of pressure, temperature, and solvent flow rate on the amine extraction recovery were studied. The experimental results show over 95% of the total amine used was extracted within 1 h at 25.0 MPa and 85 °C, and that the extraction recovery increased with pressure, supercritical solvent flow rate or methanol flow rate. The extraction data were described by an empirical model, a hot ball Crank model and a diffusion-layer theory model and the relative merits of the models were demonstrated. The calculations were compared with those experimentally obtained. Very nice agreement between the diffusion-layer theory model and our experimental measurements was achieved as reflected by the average absolute relative deviation being less than 6.0%. The empirical and hot ball Crank models both gave relatively poorer fit than the diffusion-layer theory model.

1. Introduction

Supercritical carbon dioxide ($SCCO_2$) has been extensively used for extraction of specialty chemicals from various matrices [1–15] since it has relatively low critical parameters, and it is non-toxic, non-flammable, non-corrosive, inexpensive and easy to handle. These advantages have rendered $SCCO_2$ extraction preferably attractive in selective separation of bioactive components from natural matters [1–4] or removal of certain undesirable components from solid matrices [5,6]. Currently, supercritical fluid has received ever-increasing interests in fabricating new mesoporous materials for specific applications [7–15]. For example, Chun et al. have evaluated the synthesis of mesoporous silicas using subcritical CO_2 and SCO_2 as solvents [7]. Their results show application of SCO_2 is much favorable for formation of mesopores with a pore size of 3.4 to 3.9 nm, and that mesoporous silicas with high mesopore volume and high specific surface area can be successfully achieved in $SCCO_2$ using tetraethylorthosilicate as a silica resource.

In present work, we have attempted to $SCCO_2$ extraction to remove the organic template from freshly synthesized hexagonal mesoporous silica (HMS). Conventionally, the organic template is directly burned off at high temperature to yield the void pores after the synthesis for any subsequent application investigations. The drawback of the calcination method is that the organic template cannot be recovered and meanwhile may also produce terrible smells and toxic gases. In addition, high temperature may have resulted in collapsed or distorted pore structures as evidenced by X-ray diffraction (XRD) results [16]. For that reason, SFE is advantageous in removing the organic template since is works at mild temperatures. Up to now, a numerous of studies have been performed on inorganic mesoporous materials by modified $SCCO_2$ extraction [11–15]. These works seem to suggest that modified $SCCO_2$ extraction is highly efficient in the template removal and usually leads to improved physical properties for the obtained mesoporous materials.

In this paper, the HMS materials investigated was synthesized by using dodecylamine as the templating agent, following the method described in the literatures [16,17]. The dodecylamine recovery was conducted by using methanol-modified $SCCO_2$ extraction. The effects of pressure, temperature, total solvent flow rate, and methanol flow rate on the extraction recovery were thus examined in detail. Extraction process may be mathematically modeled for better understanding the experimental observations from the systems studied and then promoting the development of scaling-up procedures for any subsequent extraction applications. Up to now, no modeling studies have been reported on the SFE process of the template removal from synthesized mesoporous materials. For that reason three mathematical models were used in this work to simulate the organic template extraction: (1) empirical

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doi:10.1016/j.cej.2010.10.072

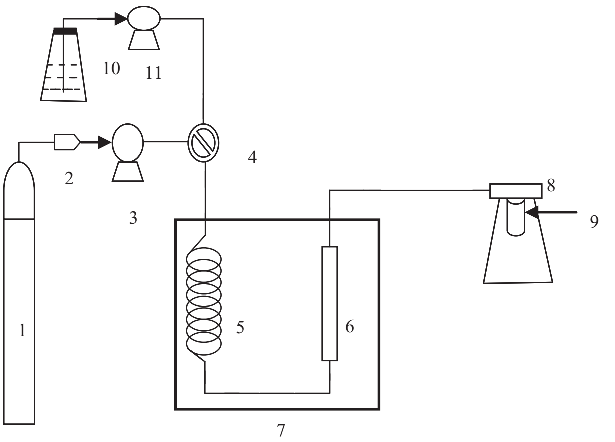

Fig. 1. Experimental setup used to remove the organic template from molecular sieves via the $SCCO_2$-modifier extraction: (1) CO_2 cylinder; (2) chiller; (3) liquid pump; (4) switching valve; (5) premixing coil; (6) extraction vessel; (7) oven; (8) back pressure regulator; (9) collection tube; (10) modifier reservoir; (11) modifier pump.

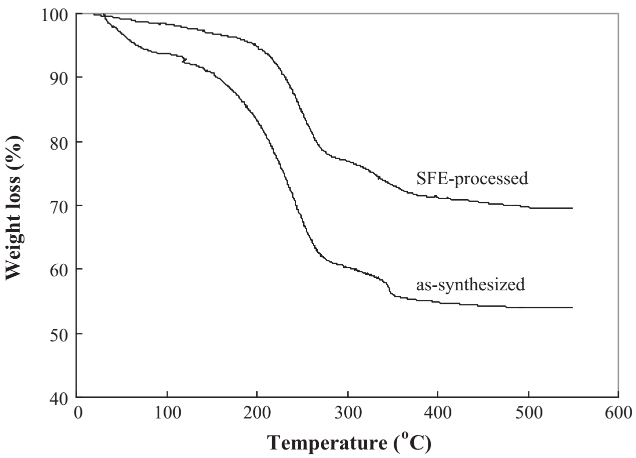

Fig. 2. Typical TGA curves of as-synthesized and SFE-processed HMS powders.

Naik model [18], (2) hot sphere Crank model [19–22], and (3) diffusion layer theory model [23]. The performances of these models are compared with experimental results.

2. Experimental

2.1. Preparation of HMS materials

Siliceous HMS was hydrothermally synthesized by using dodecylamine (99.5%, Fluka) as the organic template. 25.03 g of dodecylamine was put in a 1000 ml polypropylene bottle and mixed with 265 ml of ethanol (99.95%, Hayman) and 296 ml deionized water. After vigorously stirred for about 15 min to completely dissolve dodecylamine, 104.2 g of tetraethylorthosilane (98%, Aldrich) was then added into the solution under continuous stirring. The resultant synthesis gel has a mole ratio composition of tetraethylorthosilane:dodecylamine:H_2O:ethanol = 1:0.27:29.6:9.09. Agitation was stopped after 5 min and the obtained mixture was allowed to statically react under room temperature of around 22 °C for 18 h. The final solid product was washed with deionized water and recovered by filtration through a Buchner funnel. The washing and filtrating process was repeated for about 4 times. The moist solid was then put in an evaporation dish and dried in an oven at 30–40 °C for 2 days. The dried powder was then sieved into the desired particle size using mesh no. 40 (0.425 mm) and 60 (0.250 mm). The average particle size was taken to be the midpoint of the two dimensions, i.e., 0.338 mm.

2.2. Template removal and characterization

The template extraction from as-synthesized HMS powders was carried out using a continuous flow technique. Since pure supercritical CO_2 is not able to extract the template out of the matrix mesopores due to its low solvating power to polar organic surfactants [11,12,14,15], thus methanol (99.98%, Tedia) was selected as a polar liquid modifier to enhance the solvent strength of supercritical CO_2 to the amine template. The extraction was performed at temperature of 50, 85, 105 °C and pressure ranging from 15.0 to 25.0 MPa. The flow rates of liquefied CO_2 and liquid modifier investigated were in the span of 0.9–2.7 ml/min and 0.1–0.3 ml/min, respectively. A schematic of the experimental apparatus is shown in Fig. 1. The experimental procedure can be briefed as follows [11,12]. High purity carbon dioxide, after liquefied at −5 °C, was pumped into a sufficiently long premixing coil placed in a temperature-controlled oven. The liquid methanol was directly introduced into the system by a syringe pump at given flow rate. The modifier and CO_2, after thoroughly mixed in the coil, entered a 5 ml extraction vessel where approximately 0.5 g of as-synthesized powder was loaded for each run. A 0.5 μm filter was placed at each end of the vessel to eliminate entrainment. The template was then dissolved into the CO_2/modifier in the extraction vessel. The resultant fluid was directed to a backpressure regulator and depressurized to atmospheric pressure through a needle valve set in the regulator, resulting in the removal of the template from the parent matrix.

Thermogravimetric analysis (TGA) was conducted on both as-synthesized and SFE processed samples to determine the extraction efficiency by comparing their weight losses. This allowed the determination of template recovery, which is defined as a ratio of the amount of the organic amine removed to the amount of the template originally existing in the powder. The samples were heated to 550 °C with a heating rate of 10 °C/min and at a flow rate of 35 ml/min air. Fig. 2 shows the typical TGA results of the as-synthesized HMS. As can be seen, the weight loss curve could be divided into three temperature ranges [16,17]. The first-stage before 150 °C with a weight loss of 9.2% can be assigned to the desorption of water or other volatile organics adsorbed in matrix apertures. The second range (150–300 °C), i.e., the greatest weight loss of 30.5%, is due to the decomposition and combustion of the organic amine template associated with Si–O in the sieve apertures. The third range (300–500 °C) is a gradual drop of 6.3% in weight, which is mostly attributed to a small amount of dehydroxylation of the surface of HMS mesoporous materials. Therefore, only about 54.0% of the actual mass can be truly attributed to that of the HMS. Neglecting the mass loss arising from the adsorbed water and organics, the template content calculated is about 33.6% of the dry mass of the tested sample. In the same way, the weight percentage of the retained template can be obtained for HMS samples having undergone SFE. By sheer comparison of the two percentages, the extraction recovery under various operating conditions could be determined.

2.3. Extraction model

For describing the extraction process of dodecylamine from HMS materials with $SCCO_2$, a few mathematical models are attempted in this work as described below. In 1991, Naik et al. have investigated perfume extraction from several vegetable materials by subcritical CO_2 [18]. They represented the extraction yield (y, kg extract/kg feed) against the extraction time (t, min) as a function of the type of a Langmuir gas adsorption isotherm, this empirical equation (denoted as the Naik model) may be generalized as follows:

$$y = \frac{y_\infty t}{b+t} \tag{1}$$

where y_∞ is the yield after an infinite extraction and the term (y_∞/b) is the initial slope of the specific yield as a function of time. In this work, the recovery (r) is then expressed as y/y_∞, giving

$$r = \frac{t}{b+t} \tag{2}$$

Hence the parameter b can be readily determined from the slope of plotting the inverse recovery against the inverse extraction time with experimental data.

Some researchers have argued that the SFE process may be possibly treated as a heat transfer phenomenon [19–22]. Following this idea, each single particle is considered as a hot ball in a uniform medium and the analyte to be extracted is uniformly distributed inside the particle. Applying Fick's second law of diffusion, the heat transfer analogy and the Fourier transforms, the materials balance across an internal surface of the particle can be solved analytically, giving [20]

$$\frac{q}{q_0} = \left(\frac{6}{\pi^2}\right)\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_e t}{r^2}\right) \tag{3}$$

where n is an integer, r is the radius of the sphere (m), D_e is the effective diffusion coefficient of the solute in the sphere (m^2/s), q is the concentration of the solute remaining in the sphere (kg/m^3), and q_0 is the initial concentration of the extractable material (kg/m^3). The extension of the results to the whole bed of particles is immediate since all the particles are assumed to be at the same extraction conditions. From Eq. (3), the amine recovery used here can be readily written as follows:

$$r = 1 - \left(\frac{6}{\pi^2}\right)\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_e t}{r^2}\right) \tag{4}$$

For simplicity, this equation is denoted as the Crank model. The parameter D_e is obtained by fitting the model against the experimental data.

In 1994, Veress assumed a diffusion-layer theory (DLT) model to quantify the extraction process of cannabinoids from marihuana and hashish by SCCO$_2$ [23]. Reasonably, the dynamic SFE may be simply composed of two simultaneous processes, i.e., transport of the analyte from the parent matrix to the bulk of the extraction fluid by dissolution and the flushing out of the dissolved analyte from the extraction vessel by the extraction fluid. Based on Fick's first law, a diffusion-layer mechanism may take control for the dissolution of a solid in a fluid. Thus the dissolution rate of the solute molecules is controlled by its diffusion across a diffusion layer of thickness h. Thus the dissolution rate (dm/dt), e.g., the mass of solute dissolved per unit time, is given as:

$$\frac{dm}{dt} = \left(\frac{AD}{h}\right)(c_s - c_t) \tag{5}$$

where A is the surface area of the solid particles, D is the efficient solute diffusivity, c_s and c_t are the concentration of the dissolving solute at the solid particle surface and in the bulk solution with time t, respectively.

For the flushing out process of the dissolved analyte, solute concentration c_0 may be assumed at the beginning of the extraction without mass transfer from the matrix to the fluid, so the analyte concentration can be differentially expressed as follows.

$$\frac{dc_t}{dt} = \left(\frac{F}{V}\right)(c_0 - c_t) \tag{6}$$

where c_t is the solute concentration in the bulk solution at time t, F is the flow-rate of the extraction fluid and V is the void volume of the extraction chamber.

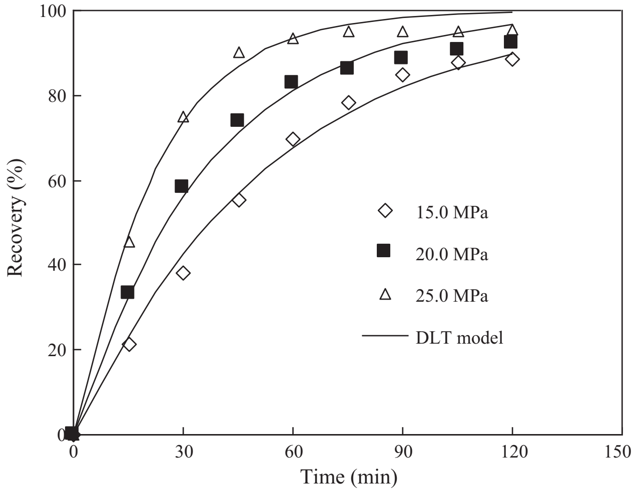

Fig. 3. Effect of pressure on the amine recovery from as-synthesized HMS powders: liquefied CO$_2$ with flow rate = 1.8 ml/min, methanol modifier with flow rate = 0.2 ml/min, T = 50 °C.

Derived from Eqs. (4) and (5), the time dependence of the analyte concentration in dynamic SFE can be given as below:

$$c_t = \frac{M\beta}{\beta V - F}(e^{-Ft/V} - e^{-\beta t}) \tag{7}$$

where β is defined by $\beta = AD/Vh$, and M is the mass of analyte to be extracted and present in the matrix.

Thus the recovery r in dynamic SFE process can be obtained from the integral of the product of c_t and F by taking into consideration that the full recovery could only be achieved after an infinite time of extraction, resulting in

$$r = 1 - \frac{\beta F}{\beta V - F}\left[\frac{V}{F}e^{-(F/V)t} - \frac{1}{\beta}e^{-\beta t}\right] \tag{9}$$

3. Results and discussion

3.1. Experimental results

The effects of several process parameters like extraction pressure, temperature, total solvent flow rate and cosolvent flow rate on the extraction rate have been experimentally studied in present work.

Fig. 3 shows the effect of pressure on the template removal rate where the experimental data were obtained at pressures of 15.0, 20.0 and 25.0 MPa, temperature of 80 °C, methanol flow rate of 0.2 ml/min and liquefied CO$_2$ feed rate of 1.8 ml/min. The dodecylamine extraction efficiency steadily increases with the processing time, then slows down and asymptotically levels off for matrix exhaustion. It can be seen that the extraction rate and the maximum efficiency obtained are strongly affected by pressure and both increase with pressure. The dependence on pressure is typical since the higher pressure, the higher is the SCCO$_2$ density, and thus higher is the solvating power for solving substances. As can be seen, a faster extraction rate at low-extraction period can be observed when pressure increases. The results reflect that increase in pressure from 15.0 to 25.0 MPa the efficiency increases from 38.3 to 80.1% in 30 min and 69.5 to 93.5% in 60 min.

The effect of temperature has been studied for experiments performed from 50 to 105 °C, pressure of 25 MPa, methanol flow rate of 0.2 ml/min and liquefied CO$_2$ feed rate of 1.8 ml/min. The exper-

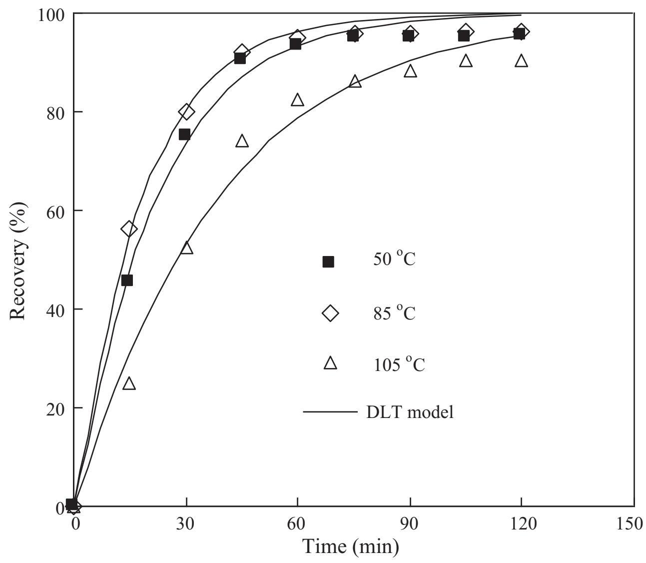

Fig. 4. Effect of temperature on the amine recovery from as-synthesized HMS powders: liquefied CO_2 with flow rate = 1.8 ml/min, methanol modifier with flow rate = 0.2 ml/min, P = 20.0 MPa.

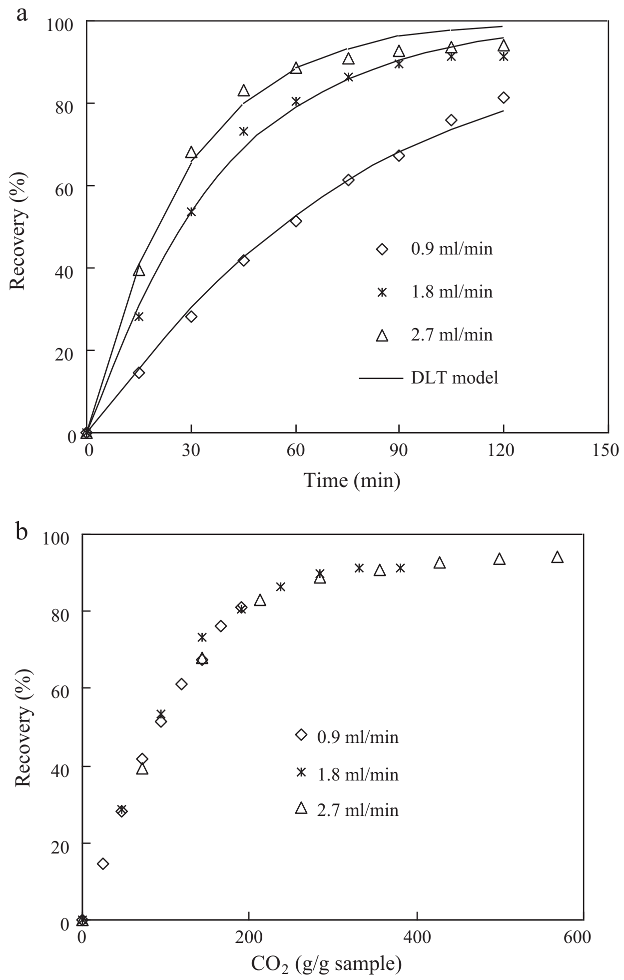

Fig. 5. Effect of flow rate of liquefied CO_2 on the amine recovery from as-synthesized HMS powders (a) and dependence of extraction recovery on the total amount of CO_2 consumed (b): methanol modifier with flow rate = 0.2 ml/min, T = 85 °C and P = 20.0 MPa.

imental results are presented in Fig. 4. It can be observed that at 20.0 MPa the increase of temperature from 50 to 80 °C results in the increase of the extraction rate whereas the increase of temperature from 80 to 105 °C leads to the decrease of the extraction rate. This observation may be related to the effect of temperature on the amine solubility. Note that the effect of temperature on the amine solubility is usually realized through two competing factors of amine sublimation and SCF solvent density. As temperature increases, the amine vapor pressure also increases while the solvent density decreases. An increase of the extract vapor pressure makes the extract more soluble whereas a decrease of solvent density renders the extract less soluble. These two temperature-dependent factors affect the extraction recovery in the opposite ways. Therefore, as extraction temperature is higher than 80 °C, the decrease of the modified CO_2 density obviously dominates over the increase amine vapor pressure, consequently leading to the considerable decrease of the extraction recovery. But as temperature increases from 50 to 80 °C the increase in the amine vapor pressure is still dominant over the decrease of the modified CO_2 density, hence resulting in the slight increase of the extraction recovery. Similar observations have been reported several studies [1,4,24].

The effect of CO_2 flow rate is shown in Fig. 5a and b. Fig. 5a is a plot of the extraction yield versus the extraction time while Fig. 5b is a plot of the extraction yield versus the total weight of $SCCO_2$ that has been passed through the extraction bed. It is seen that the extraction rate is significantly influenced by the CO_2 flow rate. The extraction rate increases with the increase in CO_2 flow rate and this increase in extraction rate with time is almost linear in the early stages of fast extraction. The slope of the initial line is seen to become steeper as the flow rate increases. The duration of the fast extraction period, decreased from 120 to 45 min as the solvent flow rate increased from 0.9 to 2.7 g/min. At the end of the fast extraction period approximately the about 80% of the amine template can be recovered but at the cost of roughly 200 g of CO_2 per gram sample.

Interestingly, Fig. 5b shows that the extraction curve is not affected by $SCCO_2$ flow rates and all the data points for all the flow rates fall on a single curve. This result seems to suggest that the amine extraction recovery is not dependent on the flow rate but the total amount of CO_2 consumed per fixed amount of raw materials in a given time. Thus, it is the amount of modified supercritical solvent consumed accounts for the success of extraction. This observation may indicate that the exit concentration of the extracted amine is independent of $SCCO_2$ flow rate, and that the early extraction process is in dissolution equilibrium and the mass transfer resistance is not dominant in the fast extraction period. At the end of the fast extraction, the modified $SCCO_2$ is less saturated with the amine template after passing through the extraction bed. Similar observation has also been reported in the literature by several researchers [23,25]. However in the other studies [2,3], obvious mass transfer resistance can be observed during the whole extraction process, since at different flow rates the plots of the extraction yield versus the total amount of supercritical CO_2 consumed are totally different from each other in the slopes of the initial straight lines and the final extraction yield.

It has been reported that pure $SCCO_2$ cannot extract the polar template from freshly prepared mesoporous materials, due to the low solubility of the polar organic template in CO_2 [11,12,14,15]. For that reason, methanol was used as a polar modifier in this study to enhance the solvating power of CO_2 to the amine template. Fig. 6 shows the effect of the methanol flow rate on the amine recovery at temperature of 85 °C and pressure of 20.0 MPa and a flow rate of liquefied CO_2 of 1.8 ml/min, respectively. The flow rate of liquid modifier added varies in the span of 0.1–0.3 ml/min.

Data presented in Fig. 6 show the effect of methanol flow rate on amine recovery. The time required to reach the recovery of 80%

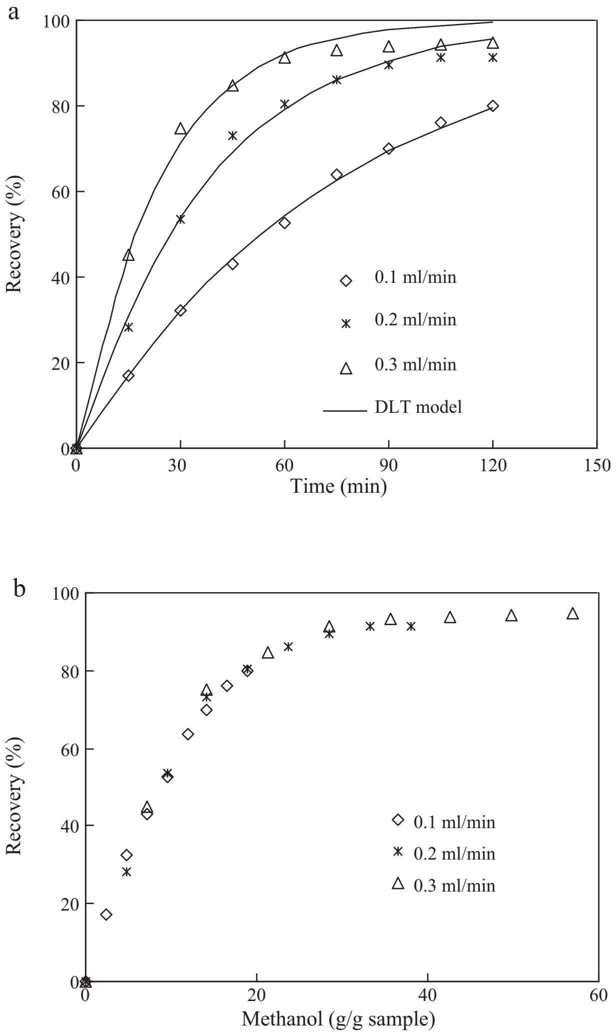

Fig. 6. Effect of methanol flow rate on the amine recovery from as-synthesized HMS powders (a) and dependence of extraction recovery on the total amount of methanol consumed (b): liquefied CO_2 with flow rate = 1.8 ml/min, T = 85 °C and P = 20.0 MPa.

at the end of the fast extraction period decreased from over 120 to less than 45 min when the flow rate of methanol added to $SCCO_2$ (kept at a feed rate of 1.8 ml/min) increased from 0.1 to 0.3 g/min. Similar to the case of CO_2 flow rate, the extraction rate increases as the methanol flow rate increases. The increase in extraction recovery with time is almost linear in the initial stage of fast extraction. The slope of the linear part becomes steeper as the methanol flow rate increases. Obviously, the increase in methanol flow rate has the same effect on the increase of extraction rate as compared with the increase in CO_2 flow rate whereas the former seems more effectively than the latter, as reflected by the experimental results.

Likewise, Fig. 6b shows that all the data points for all the flow rates coincide on a single extraction recover curve. This result further suggests that the extraction recovery is not dependent on the flow rate but the total amount of methanol consumed in a given time. Thus it may be deduced that the amine solubility instead of the mass transfer resistance controls the extraction process over the range of experimental conditions investigated here. In this sense, the modified $SCCO_2$ solvent at the exit seems to be fully saturated by the extracted amine template during the early stage of extraction process but becomes unsaturated after the fast extraction period. Therefore, the increase in the methanol flow rate or the $SCCO_2$ flow rate could aid to shorten the whole extraction process.

3.2. Modeling studies

In the calculations, the objective function used is the average absolute relative deviation (AARD) between the calculated and experimental data:

$$\mathrm{AARD} = \frac{1}{N} \times \sum_{i=1}^{N} \frac{|r_{\mathrm{cal}} - r_{\mathrm{exp}}|}{r_{\mathrm{exp}}} \times 100\% \tag{8}$$

where N is the number of experimental data points. The r_{cal} and r_{exp} are the calculated and experimental values, respectively. A single least square process was used to simulate data by using the three different models. The model parameters and AARD values regressed for these models are displayed in Table 1.

Among these three models, the Naik model is very simple and readily for simulating the extraction process. It performs very well in modeling the extraction rate of a few natural maters like cardamom, clove, cumin, ginger sandalwood, and vetiver [18]. However, Table 1 shows that the Naik model has not resulted in satisfactory calculations in modeling the amine recovery from HMS materials, as reflected by the AARD values ranging from 6.8 to 19.2%. This may be probably due to that this model fails to take into account the interactions between the solute and the solid matrix. Thus, it can only be used for fitting experimental data. On the other hand, the model parameter b obtained will permit to estimate the extraction time to achieve a 50% recovery even if the full recovery extraction is still far from accomplishment. It is seen from the parameter b values given in Table 1 that the time used for a 50% recovery is greatly shortened as pressure, CO_2 flow rate or methanol flow rate increases.

Table 1 shows that the hot ball Crank model can describe the experimental results fairly well with an AARD value less than 8% for half of the extraction recovery curves obtained here. Similar model performances have also been reported in the literatures [19,21,22]. Reverchon et al. have applied this model to describe the yield curves of essential oils from various vegetable matrices like basil, rosemary and marjoram, resulting in a fairly good agreement between the model and yield dada [21]. Further, Bartle et al. have ever applied this model to monitor the SFE of rosemary leaves by analyzing the cineole content in the extracts [22].

Table 1 also shows the effective diffusivity D_e obtained by fitting Eq. (5) against the experimental data. As can be seen, D_e reflects no dependence on system temperature but it does increase with pressure, CO_2 flow rate and methanol flow rate. But it still remains in the same order of magnitude and varies in the range of 1.20–5.50 m^2/s. Esquível et al. have observed that for SFE of olive husk oil the D_e obtained from the Crank model exhibits no dependence on CO_2 flow rate but increases significantly with extraction pressure as it is 6.4×10^{-13} m^2/s at 10 MPa and 2.5×10^{-12} m^2/s at 18 MPa, respectively [19].

Apparently, the DLT model performs the best among three models and it can satisfactorily simulate the amine extraction process by methanol modified $SCCO_2$, as reflected by the AARD value obtained for each experimental condition. As can be seen from Table 1, the AARD value varies from 1.5 to 6.0%, considerably lower than those obtained by either the Naik model or Crank model. The calculated recovery results by this model are also graphically demonstrated in Figs. 3–6. From these figures, it is clearly seen that the DLT model can excellently describe the recovery during the fast extraction period where the amine solubility takes control as discussed previously about the effect of the flow rate. Actually, the D_e value obtained shows small difference over the wide conditions considered, suggesting that the amine extraction from the parent porous matrix is the solubility control instead of the mass transfer resistance control. On the other hand, the DLT model overestimates the recovery achieved during the leveling-off extraction period. This is

Table 1
Regressed results by using three different models.

No.	T	P	F_{CO_2}	$F_{methanol}$	Naik model		Crank model		DLT model		
	(°C)	(MPa)	(ml/min)	(ml/min)	b (min)	AARD%	D_e (10^{-12} m^2/s)	AARD%	β (10^{-2} min^{-1})	h (nm)	AARD%
1	50	15.0	1.8	0.2	49.33	16.91	2.08	20.01	1.92	11.7	4.65
2	50	20.0	1.8	0.2	25.57	11.79	3.25	7.84	2.84	12.3	3.13
3	50	25.0	1.8	0.2	14.24	10.76	5.50	6.04	4.62	12.8	3.05
4	80	25.0	1.8	0.2	9.55	6.86	6.72	3.41	5.64	12.8	2.45
5	105	25.0	1.8	0.2	36.21	19.21	2.98	14.96	2.62	12.2	6.00
6	80	20.0	0.9	0.1	80.03	17.12	1.19	25.83	1.30	9.8	3.46
7	80	20.0	1.8	0.2	31.56	15.7	3.04	11.98	2.66	12.3	3.19
8	80	20.0	2.7	0.3	18.81	11.49	4.31	6.27	3.65	12.7	3.26
9	80	20.0	1.8	0.1	67.05	12.79	1.26	20.44	1.33	10.2	1.59
10	80	20.0	1.8	0.3	14.83	9.66	5.01	5.43	4.29	12.6	2.93
Overall AARD%						13.23		12.22			3.37

possibly due to that the amine extraction after the fast extraction period is controlled by the diffusion through the pores instead of the interfacial dissolution mechanism, and subsequently the analyte transport is affected in a different way.

The regressed parameter β values for the DLT model are also shown in Table 1, which range from 1.30 to 5.64 min^{-1}, depending on the extraction conditions. Similar to the trend observed for D_e, the β value reflects no dependence on system temperature but increases with pressure, CO_2 flow rate and methanol flow rate. Based on these β values, along with two measurable process parameters V and F, the extraction time required to reach a predefined level of extraction recovery may be estimated accordingly [23]. More interestingly, the thickness (h) of the diffusion layer can be calculated from the β value. Note that the D for the DLT model is not experimental available and thus the D_e obtained from the Crank model is used. The h values obtained for each extraction condition are displayed in Table 1. As seen, the thickness of the diffusion layer is in the order of 10 nanometers, spanning from 9.8 to 12.8 nm.

4. Conclusion

The application of supercritical CO_2/methanol extraction has been performed on freshly synthesized mesoporous HMS powders with dodecylamine as the organic template. The effects of various extraction conditions on the amine recovery from these mesoporous materials are investigated. The experimental results show that up to 95% of the total amine template employed for HMS synthesis can be successfully recovered within 1 h extraction, and that the extraction rate is greatly influenced by extraction pressure, temperature, CO_2 flow rate and methanol flow rate.

Three different models are used to describe the dynamic amine extraction process. The models used include an empirical model, a hot ball Crank model and a diffusion-layer theory model, respectively. Among these models, the empirical model is very simple to use but leads to the poorest agreement with the experimental data. Similarly, the hot ball Crank model results in not very satisfactory performance. The amine effective diffusivity obtained by this model ranges from 1.20 to 5.50 m^2/s. The diffusion-layer theory model performs the best to describe the experimental measurements, leading to an overall AARD value of 3.4%. These calculations indicate that the extraction process is mainly the amine solubility control.

Acknowledgements

The authors would like to thank the financial support of National Natural Science Foundation of China (NNSFC-20676107) and of State Education Ministry of China (SRF Project for ROCS, SEM). The authors would also like to thank Prof. S. Kawi for at National University of Singapore for his comments on our work.

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