

The kinetic parameters of drug compounds adsorption onto mesoporous materials

Masoud. Giahi^{1,*}, Abdollah. Falah Shojaie², Farkhondeh. Mirsfa Moqadam²

1. Department of Chemistry, Faculty of Science, Islamic Azad University, Lahijan Branch P.O. Box: 1616, Lahijan, Iran

2. Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box: 1914, Rasht, Iran

ABSTRACT

The discovery of mesoporous molecular sieves, MCM-41, which possesses a regular hexagonal array of uniform pore openings, aroused a worldwide resurgence in this field. This is not only because it has brought about a series of novel mesoporous materials with various compositions which may find applications in catalysis, adsorption, and guest-host chemistry, but also it has opened a new avenue for creating of the zeotype materials. This paper presents a comprehensive overview of recent advances in the field of MCM-41. Adsorption of drug molecules such as Pseudoephedrine hydrochloride onto mesoporous molecular sieves (MCM-41) from aqueous solution has been investigated systematically using batch experiments in this study. Results indicate that Pseudoephedrine hydrochloride adsorption is initially rapid and the adsorption process reaches a steady state after 2 min. The adsorption isotherms are well described by the Langmuir model. Based on the results, it suggests that the adsorption is primarily brought about by hydrophobic interaction between drug molecules and MCM-41 surface.

Keywords: MCM-41; Pseudoephedrine hydrochloride; Desorption; adsorption.

INTRODUCTION

Previously, Yanagisawa et al. (1990) reported the synthesis of the characteristic mesoporous materials of MCM-41. Through intercalation of long-chain, typically C16, alkyltrimethylammonium cations into the layered silicate kanemite followed by removing the organic species by calcination, a mesoporous material was obtained. The silicate layers were condensed to form a three-dimensional structure with "nanoscale pores". X-ray powder diffraction gave only an uninformative intensity centered at extreme low angles. Unfortunately, since no further

characterization data were available, Yanagisawa et al.'s results have been ignored.

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures (Beck et al., 1992a; Kresge et al., 1992).

The used template agent is no longer a single, solvated organic molecule or metal ion, but rather a self assembled surfactant molecular array as initially suggested by Beck et al. (1992a).

*. Corresponding author: Fax: +98 141 2228701, E-mail: giahi_m@yahoo.com

Three different mesophases in this family have been identified, i.e., lamellar (Dubois et al., 1993), hexagonal (Beck et al., 1992a), and cubic phases (Vartuli et al., 1994). The hexagonal mesophase, MCM-41, highly possesses regular arrays of uniform-sized channels whose diameters are in the range of 15 to 100 Å depending on the used templates, the addition of auxiliary organic compounds, and the reaction parameters. The pores of this novel material are considerably larger than those present in crystalline materials such as zeolites, thus offer new opportunities for applications in catalysis (Corma et al., 1995b; Kozhevnikov et al., 1995; Kloetstra and van Beckum, 1995; Armengol et al., 1995), chemical separation (Thomas, 1994), adsorption media (Rathousky et al., 1994, 1995; Llewellyn et al., 1995; Branton et al., 1993, 1994, 1995; Feuston et al., 1994), and advanced composite materials (Huber et al., 1994; Wu and Bein, 1994a-c; Abe et al., 1995). Accordingly, MCM-41 has been extensively investigated because the other members in this family are either thermally unstable or difficult to obtain (Vartuli et al., 1994).

Pseudoephedrine hydrochloride is a symptomatic amine found in plants of the genus *Ephedra* known in traditional medicine as Ma Huang. α -Adrenergic agonist: (+)-threo-isomer of ephedrine. The ephedrine groups are classified into narcotic compounds and since the desired molecule is a water soluble drug compound, it will be highly toxic in contact with skin and eyes causing various types of allergies. After use, Pseudo ephedrine hydrochloride in solution is generally discharged to waste water treatment plants where a larger proportion of it cannot be removed and finally is discharged into the surrounding aquatic environment persisting in the environment and posing a potential toxic threat to ecological and human health [1, 2]. Therefore, a variety of possible treatment technologies such as adsorption, photodegradation, advanced oxidation processes and conversions to ineffective complexes have been taken into account for the purification of waste waters [3, 5]. Adsorption of organic compounds onto siliceous materials has been intensively investigated by many researchers [6, 7]. In turn, adsorption isotherms are conducted

at batch experiments under different temperatures. Influencing parameters such as pH and desorption of Pseudoephedrine, HCl (PE, HCl) by MCM-41 have been studied to determine the reversibility of adsorption.

2. EXPERIMENTAL

2.1. Materials

Pseudoephedrine, HCl (99.8%; without further purification) was purchased from Behdashtkar bulk drug (Fig. 1). We used tetraethylorthosilicate (TEOS, Merck) as a source of silicon and decyltrimethylammonium bromide (CTMABr) as a surfactant template and ethylamine (EA, MERK) for preparation of the mesoporous materials (Fig. 2). The pH of solution was adjusted by introducing appropriate amounts of acid (HCl) solutions. Deionized distilled water was purified by Millipore Milli-Q system.

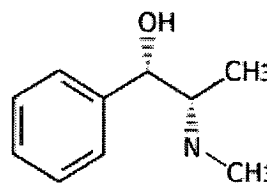


Fig.1. Pseudoephedrine molecular structure

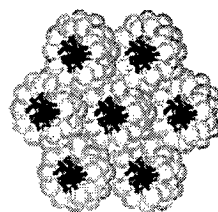


Fig.2. MCM-41 hexagonal structure after absorption

2.2. Preparation and Characterization of MCM-41

The MCM-41 material was synthesized by sol-gel method at room temperature with some modification of the described procedure in the literature [13] which details were described [14, 15]. X-ray diffraction (XRD) measurements were performed by Philips PW 1840 diffractometer with Cu-K α radiation (40 kV, 40 mA), scan rate 0.02 2 θ /s within a range of 2 θ of 1 to 10°. XRD patterns were recorded using an automatic divergence slit system. IR spectrum

was performed by Infrared spectrophotometer Shimadzu IR-470. Adsorption spectra were recorded by a 6405 UV/vis Spectrophotometer. All spectra were recorded at room temperature. The contents of the materials were determined by spectrophotometric method and conductivity measurement with using of calibration plot. The amount of the adsorbed material was calculated from the difference measurement of the concentration of drug compound in the solution before and after ion exchange treatments. The pH was adjusted by Jenway 3505 pH Meter, and the conductivity of Solution was recorded by Jenway 4510 Conductivity Meter.

2.3. Adsorption experiments

The PE,HCl adsorption data from water solutions were obtained by the immersion method [4]. PE,HCl was first dried at 105 °C for 3 h to remove moisture before usage. The adsorption experiments were carried out by mixing 0.5 g MCM-41 samples with a 200 ml aqueous solution in a 500-ml stirred flask at temperature of 298 K. The effect of contact time on PE,HCl adsorption onto MCM-41 was studied based on the Psudeoephedrine concentration in the range from 100 to 500 ppm. With respect to ionic structure of our proposed compound and cationic part adsorption on MCM-41 from the first to the end of procedure, a conductometric electrode was placed in the middle of reaction flask and we controlled conductivity changes whole adsorption procedure. The pH of the solution was adjusted by NaOH or HCl solution to maintain a constant value. The preliminary experiment revealed that about 20 min was required for the adsorption process to reach equilibrium. Solution and solid phase were separated by centrifugation at 8000 rpm for 5 min in a KOKUSUN H-11n centrifuge. After separation, the solution part was analyzed by UV-Visible spectroscopy and the solid part by XRD crystallography. The adsorption capacity of drug compound was then calculated using the relation of $q = \Delta C.V / M$, V is the volume of the liquid phase, M is the mass of the solid, and ΔC is the difference between the initial and final concentration of solutions obtained by UV. For the experiments

of adsorption kinetics, adsorption amounts were determined by analyzing the solution at appropriate time intervals, preliminary kinetic studies showed that adsorption could reach equilibrium state within a time of 2 min. The effects of temperature and pH on the adsorption data were carried out by performing the adsorption experiments at various temperatures (25, 45, 55 and 65 °C) and various pHs (5–12), respectively. To check reproducibility, Pseudoephedrine, HCl adsorption was carried out in duplicate which the relative deviations met with the requirement of less than 3%.

3. RESULTS AND DISCUSSION

3.1. Characterization of catalyst

Fig. 3 shows the obtained XRD pattern of the MCM-41 composite. A clear peak at $2\theta = 2.15^\circ$ was observed which was assigned to the (100) reflection of MCM-41 type materials. The (110) and (200) reflections from MCM-41 appeared as broad peaks at $2\theta \approx 4.1^\circ$. From the IR spectrum (Fig. 4), it was confirmed that the template was removed because of the absence of alkyl adsorptions of the template around 2900 cm^{-1} . IR spectra of the MCM-41 were dominated by strong characteristic bands of the support matrix. These bands are due to surface hydroxyl groups in the range of 3500 to 3100 cm^{-1} and lattice vibrations in the range of 1300 to 750 cm^{-1} . Two strong bands were presented at about 985 cm^{-1} and 800 cm^{-1} which can be assigned to $\nu_s(\text{Si-O-Si})$ and $\nu_s(\text{Si-O-Si})$, respectively. The band present at about 1000 cm^{-1} is attributable to $\nu(\text{Si-OH})$ vibrations.

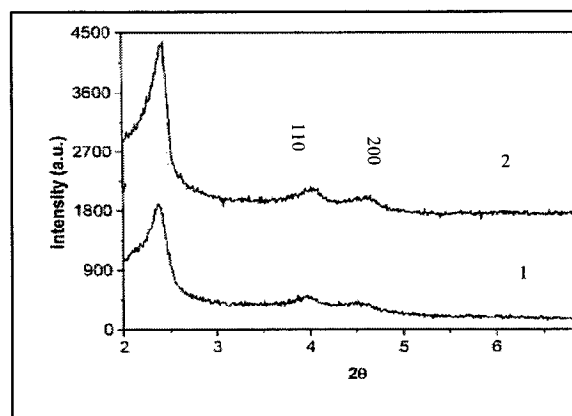


Fig.3. X-Ray diffraction pattern of the MCM-41 (1) before (2) after calcinations.

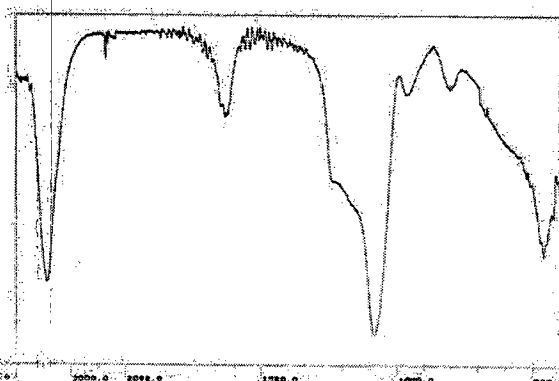


Fig.4. IR spectrum of the MCM-41 after calcinations

3.2. Effect of contact time on PE,HCl adsorption

As is illustrated in Fig. 5, apparent adsorption equilibrium is generally obtained within 2 min for the initial PE,HCl concentration of 100, 150 and 200 ppm, respectively. Thereafter, no notable concentration changes occur (< 20 min) after adsorption equilibrium (2 min) and the average removal efficiency of PE,HCl reaches to 87.06, 77.31, and 70.56 % when the initial concentrations of PE,HCl are 100, 150 and 200 ppm, during this period, respectively. It is assumed here that the adsorption primarily takes place at easily accessible surface sites, requiring no diffusion into micropores, and a hydrophobic interaction between adsorbent and organic compounds is may attributed to the rapid adsorption rate [16]. Additionally, Fig. 5 also illustrates that the removal of PE,HCl at adsorption equilibrium decreases by increasing of the initial concentration. The reason is the limited number of available adsorption sites for the uptake of our molecules at a fixed adsorbent dosage.

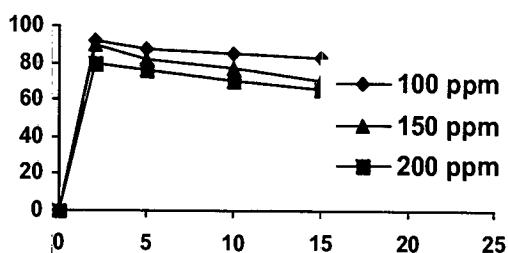


Fig.5. Effect of contact time on PE, HCl adsorption by MCM-41 (adsorption conditions: adsorbent dosage = 1.6 g/L, pH 5.11, and temperature = 298 K).

3.3. Adsorption isotherms

Adsorption equilibrium data, expressed by the mass of adsorbate per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate, are usually represented by adsorption isotherm which is important in the adsorption systems designing. The Langmuir equation (1) is applicable to homogeneous adsorption system while the Freundlich empirical equation (2) is employed to describe heterogeneous systems not restricted to the formation of the monolayer.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \quad (1)$$

$$Q_e = K_F C_e^{1/n} \quad (2)$$

Q_e is the equilibrium concentration on the adsorbent (mg/g), C_e is the equilibrium concentration in solution (mg/l), Q_{max} is the monolayer capacity of MCM-41 (mg/g), and K_L is the Langmuir adsorption constant (l/mg). K_L is a measure of the affinity between adsorbate and adsorbent and its reciprocal value gives the concentration at which half the maximum adsorption capacity of the adsorbent is reached. A plot of C_e/Q_e vs C_e will give a straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}K_L$ if Langmuir model is held. K_F (l/g) and $1/n$ are the Freundlich constants corresponding to adsorption capacity and adsorption intensity, respectively. It is noteworthy that $1/n < 1$ (> 1) corresponds to favorable adsorption (unfavorable adsorption) and to an increase (a decrease) in the adsorption capacity. The plot of $\ln Q_e$ vs $\ln C_e$ is employed to generate K_F as intercept and $1/n$ as slope. In Fig. 7, Langmuir model is fitted into the measured adsorption isotherms at different temperatures. The values of $Q_{max}K_L$, and the linear regression correlations for Langmuir (r_L^2) is given in Table 1.

Table1. Langmuir isotherm constants for the adsorption of PE,HCl on MCM-41

Temperature (K)	Q_{max} (mg/g)	K_L (l/mg)	r_L^2
298	2.45	$1.41 \cdot 10^{-2}$	0.9738
318	6.33	$7.2 \cdot 10^{-1}$	0.9992
328	11.86	$2.3 \cdot 10^{-2}$	0.9985
338	8.43	1.41	0.9998

As listed in Table 1, the coefficients for fitting are $0.9738 < r_L^2 < 0.9998$ for Langmuir equation indicating that Langmuir model should describe the adsorption on the MCM-41, especially at 328 K.

The effect of contact time on the amount of PE,HCl adsorbed onto MCM-41 was measured at the optimum initial concentration and different temperatures. A simple kinetic analysis was performed with the aid of pseudo-second-order equation (3) (Wang et al., 2004a,b). In this equation, the average value of the rate constant k is calculated.

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \quad (3)$$

k is the rate constant, and Q_e and Q_t are the amount of drug adsorbed per unit mass of the adsorbent at equilibrium and time t , respectively. After definite integration by applying the initial conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, Eq. (3) turns into (4).

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \quad (4)$$

Linear plots of t/Q_t vs t (Fig. 8) with linear regression coefficient of about 0.99 indicates the applicability of this kinetic equation and the pseudo-second nature of the adsorption process of PE,HCl onto MCM-41.

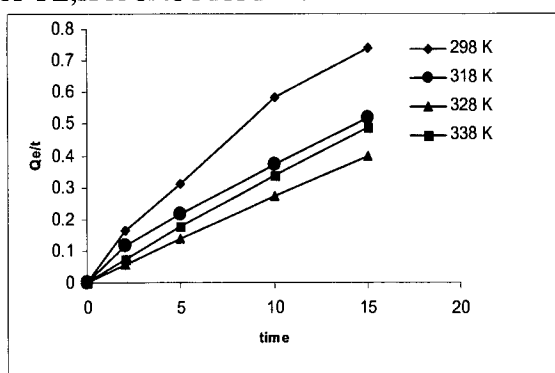


Fig.6. The pseudo-second-order kinetics plots for the adsorption of PE, HCl on MCM-41. Conditions: adsorbent dosage = 1.6 g/L, pH=5.11).

The calculated k values from these plots are $5.12 \cdot 10^{-2}$, $3.6 \cdot 10^{-2}$, $2.35 \cdot 10^{-2}$, $1.54 \cdot 10^{-2}$ g $\text{mg}^{-1} \text{min}^{-1}$ for 25, 45, 55 and 65 °C, respectively.

Because the k values have been determined, several thermodynamic parameters including the Arrhenius activation energy (E_a), activation free energy change (ΔG^*), activation enthalpy change (ΔH^*) and activation entropy change (ΔS^*) can be calculated by using the following equations (Stumm and Morgan, 1996; O' zcan and O' zcan, 2004):

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$k = \frac{k_B T}{h} K^*$$

$$\Delta G^* = -RT \ln K^*$$

$$\Delta H^* = E_a - RT$$

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$

A is the Arrhenius factor, k_B and h are Boltzmann's and Planck's constants, respectively, R is the gas constant, and K^* is the equilibrium constant at temperature T . A linear plot of $\ln k$ vs. $1/T$ for the adsorption of PE, HCl onto MCM-41 is constructed to generate the E_a value from the slope. The amount of E_a is obtained by a straight line with regression coefficient of about 0.998. Moreover, the values of ΔG^* , ΔH^* and ΔS^* in term of KJmol^{-1} are given in Table 2.

The slightly high ΔH^* values for PE, HCl/MCM-41 give clear evidence that the interactions between PE, HCl and the surface hydroxyl groups of MCM-41 are strong. On the other hand, the positive values of ΔG^* indicate the presence of an energy barrier in the adsorption process. The positive value for this parameter is quite common because the activated complex in the transition state is in an excited form. The negative values of ΔS^* suggest decreased randomness at the solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption of PE, HCl onto MCM-41.

Table 2. Thermodynamical parameter of adsorption process

Temperature (K)	Rate constant (k)	Equilibrium constant (K*)	Activation free energy change (ΔG^*)	Activation enthalpy change (ΔH^*)	Activation entropy change (ΔS^*)
298	5.12×10^{-2}	8.22×10^{-4}	17.600	-2.597	-0.67
318	3.6×10^{-2}	5.41×10^{-4}	19.887	-2.772	-0.71
328	2.35×10^{-2}	3.42×10^{-4}	21.763	-2.859	-0.75
338	1.54×10^{-2}	2.18×10^{-4}	23.692	-2.946	-0.78

CONCLUSIONS

We examined the possible effects of interaction between small molecules of drug and MCM-41 on the pore structure of MCM-41 and the potential of MCM-41 for removing of these molecules. The adsorption capacity of PE, HCl on MCM-41 was firstly measured and the changes in surface characteristics and pore structure of MCM-41 during the adsorption processes were then characterized with the analysis of the XRD patterns and the IR spectra. It was concluded that although MCM-41 might be a good adsorbent for the removal of these pollutants from effluents, but the effects of the interaction between these small molecules and surface hydroxyl groups of MCM-41 on the pore structure stability of MCM-41 must be considered because it might induce a sharp decrease in the adsorption capacity.

Moreover, the Langmuir model was found to provide better description for the adsorption on MCM-41. On the other hand, the adsorption kinetics data could be well described by the pseudo-second-order kinetics model.

The activation parameters could be evaluated with the pseudo-second-order rate constants. The slightly high values of ΔH^* confirmed the strong interaction between large PE, HCl molecule and the surface hydroxyl groups of MCM-41.

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