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Characteristics of the Mass Transfer of Phosphatidylcholine during Its Sorption on Mesoporous Composites Based on MCM-41

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Abstract—The kinetic parameters of sorption of phosphatidylcholine on mesoporous composites based on MCM-41 are considered. It is noted that the possibility of both the diffusion and adsorption rate limitations of the process should be taken into account in the description of the kinetics of sorption of non-polar fat-soluble physiologically active compounds (PACs) from hexane solutions onto mesoporous materials of MCM-41 type. The adequacy of using the Boyd diffusion model and the Lagergren, Ho and McKay, and Elovich models to describe the kinetics of sorption of phosphatidylcholine on mesoporous composites based on MCM-41 is shown. The contributions from diffusion limitation (internal and external) and the rate of the chemical step of adsorption to the overall rate of the sorption process are determined. It is found that the sorption of the phospholipid is a mixed diffusion process.

Keywords: PAC, phospholipids, phosphatidylcholine, MCM-41, MMC-1, MMS-1, mesoporous composite, sorption kinetics, adsorption models.

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INTRODUCTION

Phospholipids (PLs) are the most important phosphorus-containing compounds of lipid nature and occur in all living organisms. The chemical structure of PLs, their amphiphilicity and the presence of charged groups determines the uniqueness of their physiological properties [1]. PLs are used as active components or additives in food products and drugs. The separation of PLs during their extraction from such natural products as vegetable raw materials and biological materials plays a crucial role in the transformation and utilization of biomass. The objects used for the isolation and purification of PLs have complex matrices that pose an obstacle to their use. The extraction [2] and chromatographic methods [3, 4] are currently used for separating and concentrating PLs. The use of sorption methods for sample preparation allows us to reduce the number of steps and the consumption of highly toxic solvents [5]. However, there is the problem of the limited number of sorbents for group or selective isolation [6]. Polymeric resins are usually employed as sorbents for extracting PLs [7]. In recent years, highly ordered nanostructured materials of hexagonal structure (MCM-41) have also been applied as effective sorbents [8–13]. The advantages of these materials are high values of their specific surface area (more than 1000 m^2 g^{-1}), a narrow pore size distribution, and opportunities to control structural characteristics by varying the conditions used in the synthesis of materials [14–17]. The above properties of nanostructured materials facilitate access of bulk PL molecules to sorption sites, thus affecting the kinetic parameters of the sorption process. The amphiphilic structure of PL molecules [1] and the presence of charged groups ensures surface activity and makes it possible to predict complex and specific interactions with sorbent, typical of these organic compounds [18].

The aim of this work was to examine the kinetics of sorption of phosphatidylcholine (PC) on mesoporous composites based on MCM-41. The obtained results can be used to plan the purification and concentration of PLs using mesoporous silica materials of the MCM-41 type.

EXPERIMENTAL

Phosphatidylcholine from soybeans (Sigma-Aldrich, Germany) containing 95% of the main substance was used as an object of the present study (Fig. 1).

The sorption of PC on mesoporous nanostructured MCM-41 material (Süd-Chemie, Germany) and its analogs synthesized by the methods reported in [19] (MMC-1 material with $S_{\text{sp}} = 996$ m^2 g^{-1}) and [20] (MMS-1 material with $S_{\text{sp}} = 638$ m^2 g^{-1}) was investi-

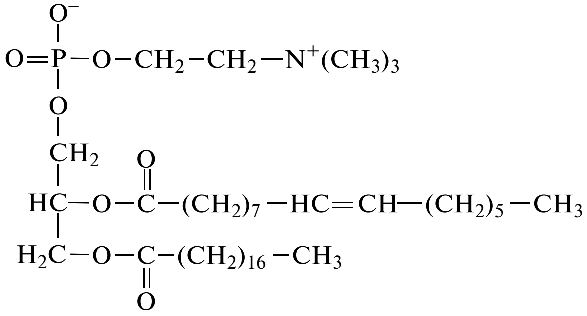

Fig. 1. Structural formula of PC (bipolar form).

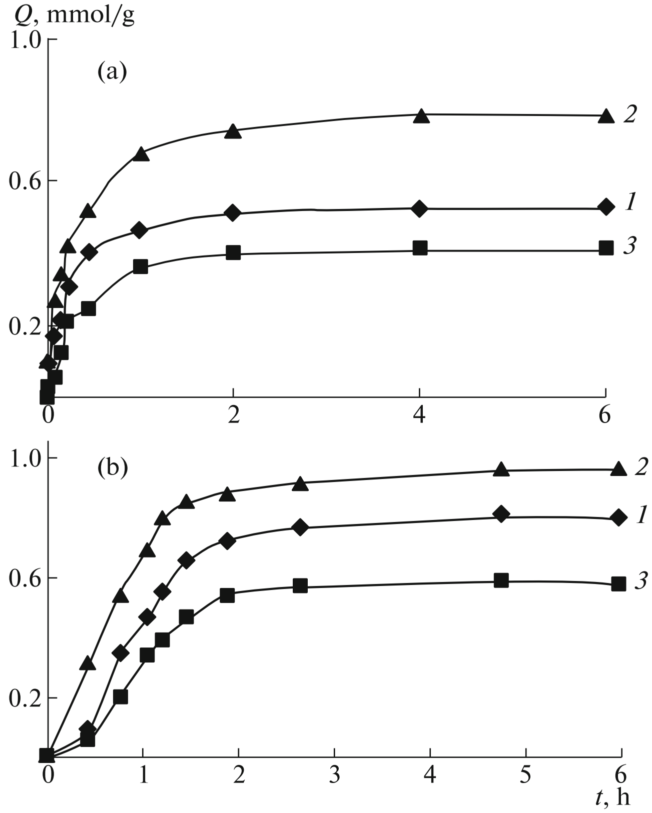

Fig. 2. Integral kinetic curves of sorption of PC from hexane solutions on (*1*) MCM-41 and such mesoporous composites based on it as (*2*) MMS-1 and (*3*) MMC-1, at (a) $C \ll$ CMC and (b) $C \gg$ CMC.

gated. The sorption of PC from hexane solutions at concentrations ranging between 0.1 and 5.0 mmol L^{-1} on previously fractionated (from 0.1 to 0.25 mm) and activated (at 130°C for 2 h) mesoporous sorbents was studied. The finite volume method was used to investigate the sorption kinetics [21]. Samples were collected at different time intervals after the beginning of contact between phases, and the content of PC in the external solution was controlled at the beginning of sorption (after 1–2 min) and then every 30 min for 4–8 h. The sorption of PC was observed upon stirring at a controlled temperature of 22 ± 2°C.

PC was quantitatively determined using a Shimadzu UV-1800 spectrophotometer (Japan–United States) at wavelength $\lambda_{max} = 273$ nm and a thickness of the absorbing layer of 1.00 cm. The concentration of PL in the contacting solution was found via the calibration curve method.

The kinetic curves of sorption of PC from hexane solutions onto mesoporous MCM-41 material and its synthesized analogs were presented as the dependences of the amount of PC adsorbed by the sorbent (Q, mmol g^{-1}) on the required time (t, min).

The process was considered complete if the content of compound in the liquid phase did not change over time.

The amount of adsorbed compound Q (mmol g^{-1}) was determined from the reduction of the PL concentration in the equilibrium solution and calculated using the equation

$$Q = \frac{(c_0 - c_t)V}{m} \times 1000, \qquad (1)$$

where c_0, mmol L^{-1}, is the initial concentration of the physiologically active compound (PAC) in the solution; c_t, mmol L^{-1}, is the concentration of PAC in the solution at time t; V, L, is the solution volume; and m, g, is the mass of the air-dried sample of sorbent.

RESULTS AND DISCUSSION

The use of nanostructured materials of the MCM-41 type as sorbents for the extraction of PACs was reported in [8–13, 22]. However, there have been few such studies because these materials are rather novel. The kinetics of sorption of fat-soluble PACs, particularly PLs, on silica inorganic materials remains poorly studied [23, 24] and requires that we consider the physical and chemical bases of the mechanism of sorption kinetics, allow for the nature of interactions in a sorbate–solvent–sorbent system, and determine the constants characterizing the affinity of sorbents to the target components. The surface activity of PLs is one of the factors that directly affects the magnitude and mechanism of their retention on the sorbent phase. One of the most common characteristics of surfactants, the critical micelle concentration (CMC), thus determines the rate of formation and the structure of adsorption layers [25]. The kinetics of sorption of PC from hexane solutions at concentrations above and below CMC (from 0.1 to 5.0 mmol L^{-1}) must therefore be examined to determine the form of the distribution of the adsorbed compound between the liquid and solid phases [26]. The kinetic curves of sorption of PC from hexane solutions at concentrations below CMC (0.1 mmol L^{-1}) are shown in Fig. 2a.

The dependences in Fig. 2a indicate that the curves of sorption of PC from hexane solutions at a concen-

Table 1. Kinetic parameters of the sorption of PC on MCM-41 and mesoporous composites based on it

Mesoporous material	$Q_{\max}$, mmol g^{-1}		
	t_e, h	at $C \ll$ CMC	at $C \gg$ CMC
MCM-41	4	0.05	0.80
MMC-1	6	0.04	0.58
MMS-1	8	0.08	0.96

tration of 0.1 mmol L^{-1} are characterized by the inflection points and subsequent plateau 1 h from the beginning of phase contact [27]. The inflections are due to the formation of an adsorption layer of PC on the surface of highly ordered silicas.

The inflection points are also observed on the kinetic curves at concentrations of PCs much higher than CMC (5 mmol L^{-1}), but the formation of inflections is shifted to longer times (Fig. 2b). The inflection shift is caused by both the interfering effect of micelles due to an increase in their number in the solution and the competing processes of association in the solution and sorbent. The amount of adsorbed compound grows substantially at concentration $C \gg$ CMC (5 mmol L^{-1}) owing to the formation of associates and their penetration into the pores of mesostructured samples (Table 1).

The sorption of ions and molecules on inorganic sorbents [23] and polymeric ion exchangers [28] characterized by diffusion kinetics is the most studied and mathematically described process.

The kinetic parameters of mass transfer of compounds in a sorption system must be considered in modeling sorption and chromatographic processes [29]. The process rate can be described in terms of validating the choice of the rate-limiting step, internal (gel) or external (film) diffusion. The sorption process is assumed to consist of four steps [28]:

(1) diffusion of ions and molecules in the volume of the solution in contact with the sorbent;

(2) the diffusion of sorbate through the surface layer;

(3) diffusion towards the sorption site (functional group) within a sorbent; and

(4) interaction between the sorbate and the functional group.

Sorption is a complex multi-step process and it is difficult to examine all its steps simultaneously. The concept of the rate-limiting step [28] which considered the slowest step as the rate-limiting is often used to simplify the description of complex sorption process. This approach allows us to estimate the kinetic coefficients and take them into account in describing the mass transfer of organic and mineral compounds during sorption on ion exchange materials [30]. Similar dependences can be also observed in the case of PLs. However, determination of the rate-limiting step is needed for rationally choosing the optimum parameters for the isolation of PLs by sorption. But this is difficult due to the complex form of the adsorption curves. It is possible only for the initial stages of the process.

Since the mass transfer of large organic molecules during the sorption of PC on mesoporous composites of the MCM-41 type is a rather fast process (Fig. 2a and Table 2), the rate-limiting step of the sorption cannot be clearly specified at degree of completion $F < 0.05$ [28].

The adsorption kinetics of compounds (chemical kinetics) is often observed along with diffusion kinetics. Describing kinetic curves by the chemical and diffusion kinetic models allows us not only to characterize the sorption mechanism and determine the rate-limiting step but also to optimize the sorption process [23].

The adsorption and diffusion of sorbate can be a rate-limiting step of sorption, with transport processes (the transfer of sorbate molecules from the solution to the active sites of the sorbent) playing a crucial role in the sorption system. The contribution from diffusion process to the sorption kinetics can be estimated using the Boyd diffusion model [31]. The sorption of organic compounds on polymeric materials is usually known from the literature [30] to be limited by the diffusion step.

When the internal diffusion limitation of the sorption process predominates, the equation proposed by Boyd can be used to calculate the effective diffusion coefficient [31]:

Table 2. Parameters of the kinetic models of sorption of PC on MCM-41 and mesoporous composites based on it

Mesoporous material	Pseudo-first order model [32]		Pseudo-second order model [33, 34]		Boyd diffusion model [31]	
	R^2	k_1, min^{-1}	R^2	k_2, g (mol min)$^{-1}$	R^2	$\overline{D} \times 10^9$, cm^2 s^{-1}
MCM-41	0.983	0.023	0.999	1.44	0.905	1.2
MMC-1	0.931	0.056	0.995	3.32	0.940	5.9
MMS-1	0.916	0.015	0.997	0.74	0.954	1.5

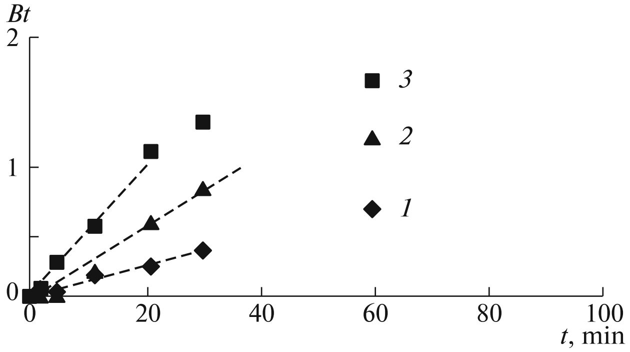

Fig. 3. *Bt–t* dependences obtained during the sorption of PC from hexane solutions on (*1*) MCM-41 and such mesoporous composites based on it as (*2*) MMS-1 and (*3*) MMC-1.

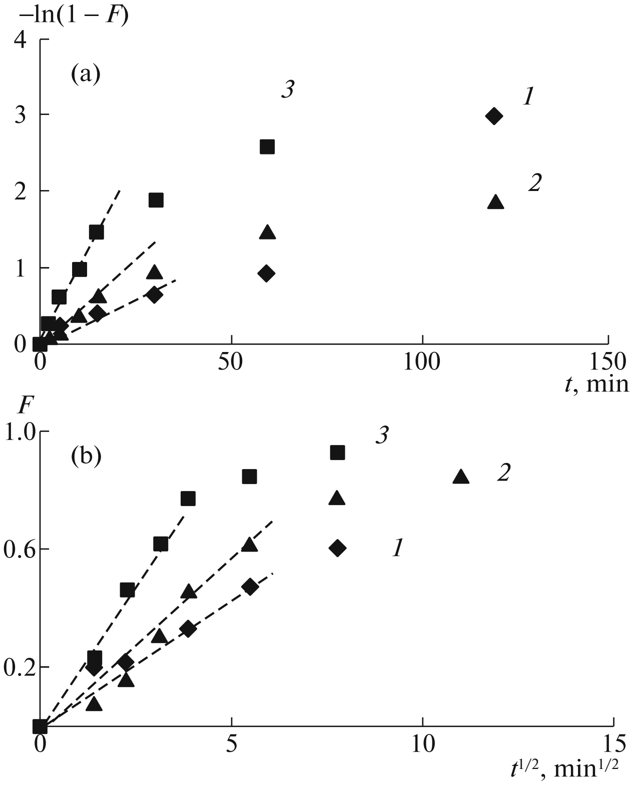

Fig. 4. (a) $-\ln(1 - F)$ versus *t* and (b) *F* versus $t^{1/2}$ dependences obtained during the sorption of PC from hexane solutions on (*1*) MCM-41 and such mesoporous composites based on it as (*2*) MMS-1 and (*3*) MMC-1.

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}\exp(-Dn^2\pi^2 t/r_0^2), \qquad (2)$$

where *F* is the degree of completion of the process:

$$F = \frac{Q_t}{Q_e}, \qquad (3)$$

and Q_e and Q_t, mmol g^{-1}, are the amounts of compound adsorbed by the mass unit of sorbent in the equilibrium state and at time *t*, respectively.

Degree *F* of the completion of the process is a function of parameter Dt/r_0^2, where *D*, cm^2 s^{-1}, is the effective diffusion coefficient; *t* is the time needed to achieve a given *F* value; *n*, integers 1, 2, 3..., is the number of terms; r_0, cm, is the average radius of sorbent grains; and ratio $B = D\pi^2/r_0^2$ is the kinetic coefficient.

Substituting the kinetic coefficients into Eq. (2) leads to the dependence

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}\exp(-Btn^2). \qquad (4)$$

Dimensionless parameter *Bt* proposed by Boyd is the solution to the diffusion problem for a solid of a certain shape. Parameters *Bt* calculated for different values of degree of completion *F* are tabulated as $Bt = f(F)$.

The *Bt* versus *t* and $-\ln(1 - F)$ versus *t* dependences are used to confirm the diffusion limitation of the sorption process (Figs. 3 and 4).

Analysis of the type of dependences of *Bt* on *t* obtained during the sorption of PC on mesoporous MCM-41 silica materials shows that the dependences are linear in the initial stages, where pores are filled with adsorbate molecules, and the slope of the curves then fall. The mass transfer of PC in the pores of sorbent is thus hindered, resulting in lower values of the diffusion coefficients (Table 2).

Figure 4a shows that only the initial region of the $-\ln(1 - F) = f(t)$ function is linear. External diffusion kinetics predominate at the beginning of the sorption process on the studied mesoporous materials, with the effect of external diffusion falling and that of internal diffusion rising along with the degree of completion. The sorption kinetic curves in the *F* versus $t^{1/2}$ coordinates are linear at short phase contact times and then deviate from linearity (Fig. 4b). According to [28], this indicates the mixed diffusion nature of the process, with both steps (film and gel diffusion) significantly affecting the overall rate of the process.

Attributing the kinetic curves to one type of kinetics allows us to calculate the effective diffusion coefficients from the experimental curves. The effective diffusion coefficients are kinetic coefficients that include both the diffusion characteristics of molecular transport in a sorption system and the simultaneous processes of ion exchanger swelling, protolysis, and sorbate solvation. The diffusion coefficients can be calculated using the equation

$$D = \frac{Btr_0^2}{\pi^2 t}. \qquad (5)$$

Fast mass transfer of PC in the sorption system indicates that diffusion is not the only rate-limiting step of

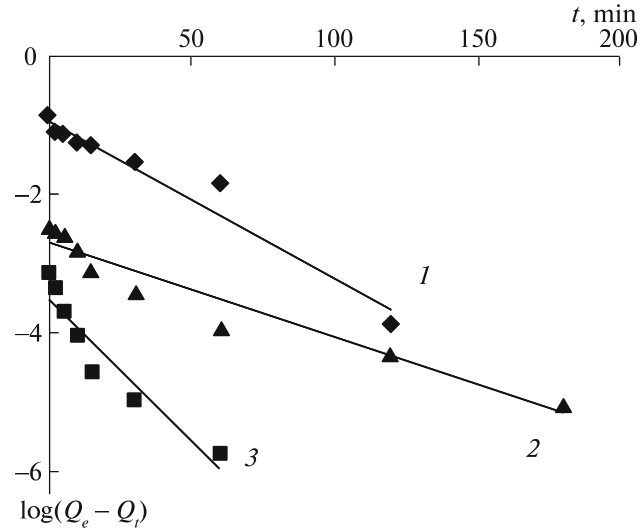

Fig. 5. $\log(Q_e - Q_t)$ versus t dependences obtained during the sorption of PC from hexane solutions on (*1*) MCM-41 and such mesoporous composites based on it as (*2*) MMS-1 and (*3*) MMC-1.

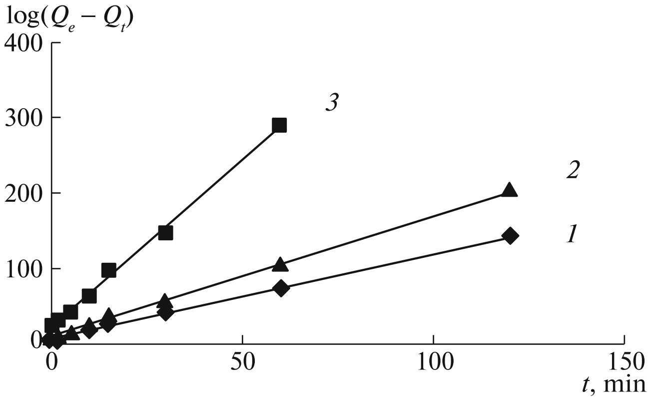

Fig. 6. $1/(Q_e - Q_t)$ versus t dependences obtained during the sorption of PC from hexane solutions on (*1*) MCM-41 and such mesoporous composites based on it as (*2*) MMS-1 and (*3*) MMC-1.

sorption on mesoporous materials, as is generally assumed for sorption on disordered polymeric sorbents. Since sorbent of the MCM-41 type and its analogs are characterized by nanostructured natures, we must consider not only the rate of diffusion but the rate of chemical kinetics (the adsorption step and sorbate–sorbate interactions) as well.

The process of PC sorption on mesoporous silicas can be presented as

$$\mathrm{A} + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{AM},$$

where A denotes the sorption sites on the sorbent's surface; M is the free sorbate in the solution; AM is the compound bound to the sorbent; and k_1 and k_2 are the adsorption and desorption rate constants, respectively.

In this case, one of the earliest sorption kinetic models, the pseudo-first order rate model proposed by Lagergren and based on sorption capacity, may be used [32]. The equation for describing sorption from a liquid medium onto solid sorbents can be presented as

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t), \tag{6}$$

where k_1, min^{-1}, is the pseudo-first order rate constant of the kinetic model.

Integrating Eq. (6) from $t = 0$ to $t = t$ and from $Q_t = 0$ to $Q_t = Q_t$ (the boundary conditions) yields [32]

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{k_1}{2.303}t. \tag{7}$$

It should be noted that the equation of the pseudo-first order model is similar to the one of film diffusion. In the case of the latter, however, the rate of the process depends on the particle size of the sorbent and the film thickness. Since the chemical kinetics are the rate-limiting step, the rate of sorption depends only on concentration and temperature rather than the above-mentioned factors. If the kinetics of the process is described by the pseudo-first order model, the PL molecules therefore must diffuse to their adsorption site.

Analysis of the kinetic curves of the sorption of PC on mesoporous MCM-41 material and its synthetic analogs plotted in $\log(Q_e - Q_t)$ versus t coordinates (Fig. 5) shows the linear dependences in the initial stages of the process. The slopes of the curves then gradually fall, indicating the contribution from diffusion in the film of the solution to the overall rate of the process. This form of the dependences shows that the sorption process cannot be clearly described by the limits of internal or external diffusion. The high determination coefficients of these dependences (Table 2) suggest the great thermodynamic advantage of sorbate–sorbent interactions. However, the deviation from linearity indicates us to consider sorbate–sorbate interactions. The PL molecules therefore must diffuse to the sites of their attachment, and this process could also limit the rate of PC sorption during its mass transfer within the systems of mesopores of ordered MCM-41 material and its synthesized composite analogs.

The pseudo-second order rate equation (the Ho and McKay model [33, 34]) was used to determine the contribution from sorbate–sorbate interactions to the overall rate of the process during the multimolecular adsorption of PC. The integral form of the classical equation of the pseudo-second order rate is [33, 34]

$$Q_t = \frac{t}{\dfrac{1}{k_2 Q_e^2} + \dfrac{t}{Q_e}}, \tag{8}$$

where k_2, g (mmol min)$^{-1}$ is the rate constant of sorption according to the pseudo-second order model, and t, min, is the time.

This equation allows us to avoid the problem of finding the Q_e effective parameter. If the model of the pseudo-second order kinetics can be used to describe the sorption process, the linear dependence in the t/Q_t versus t coordinates should be observed and the Q_e and k_2 values can be calculated as the slope and intercept, respectively [33, 34].

Equation (8) can be presented as a curve plotted in the $1/(Q_e - Q_t)$ versus t coordinates (Fig. 6).

Figure 6 shows that the $1/(Q_e - Q_t) = f(t)$ dependences are linear throughout the time interval of sorption. The high values of the coefficients of determination ($R^2 > 0.9$) suggest the applicability of the pseudo-second order model for describing the adsorption kinetics step and consider the intermolecular interactions in the studied systems.

The rate constants of the process were calculated using the pseudo-second order model of sorption via the graphical interpretation of Eq. (8) (Table 2).

In contrast to the previous model, the pseudo-second order model generally describes the sorption process throughout the studied time interval and there is no need to know in advance the values of the equation parameters.

The Elovich model was applied to consider the contribution from the adsorption and desorption of PC on mesoporous materials to the kinetics [35]. The Elovich equation is often used to describe the adsorption kinetics of compounds in heterogeneous systems, based on the sorption capacity. An exponential decrease in the rate of sorption of carbon monoxide on manganese(II) oxide as the amount of adsorbed gas grew was reported by Zel'dovich in [35]. This dependence is also known as the Elovich equation:

$$\frac{dQ}{dt} = \alpha e^{-\beta Q_t}, \tag{9}$$

where Q_t, mmol g^{-1} is the amount of compound adsorbed at time t; α, g (mmol min)$^{-1}$ is the initial rate of the sorption process; and β, g mmol^{-1} is the desorption constant. Chien and Clayton assumed that $\alpha\beta t \gg 1$ to simplify the Elovich equation [36]. The integral form of Eq. (9) derived with boundary conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$ is

$$Q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t). \tag{10}$$

The kinetic parameters can thus be calculated on the basis of Q_t versus linear dependence ln$t$. The constants of the equation can be determined as the slope and y-intercept of the Q_t versus $\log(t + t_0)$ line.

MCM-41 and its analogs are characterized by highly ordered pore systems, and their surfaces can be considered homogeneous. On the other hand, if there are disturbances in the pore systems of the materials during the adsorption process, their surface can be considered heterogeneous systems [37]. The region of the linear dependence obtained during the sorption of PC on mesoporous MCM-41 material and its synthetic analogs ranged from 0 to 5 at t_0 (Table 3). This testifies to the homogeneity of the structures of mesoporous MCM-41 material and its synthetic analogs.

Table 3. Kinetic constants of the sorption of PC on MCM-41 and mesoporous composites based on it, calculated using the Elovich model [35, 36]

Mesoporous material	t_0	α, g (mol min)$^{-1}$	β, g mmol^{-1}	R^2
MCM-41	0	–	96	0.978
	1	0.010	96	0.978
MMC-1	0	–	131	0.939
	1	0.008	131	0.939
MMS-1	0	–	72	0.916
	1	0.014	72	0.916

The kinetic constants derived from the Elovich equation are summarized in Table 3. A comparison of the coefficients of determination obtained from our description of the sorption kinetics of PC shows that the Elovich equation is characterized by lower R^2 values than the other two models, due to the highly ordered structure of the sorbent allowing us to consider a material's surface as a homogeneous system.

CONCLUSIONS

Examination of the kinetic curves of sorption of PC on mesoporous MCM-41 material and its analogs thus reveals a multi-step mechanism of sorption, with both the structure and properties of the sorbent and the studied compound, and the interactions between them, affecting the process. The structured mesoporous materials are characterized by a high adsorption capacity with respect to the test PL. The high rate of mass transfer during sorption on mesoporous silicas is due to the highly ordered structure and presence of mesopores, with the equilibrium in the PL solution—sorbent system being established in several hours, while in the case of classical sorbents, equilibration can take from several tens of hours to several days.

Both the limitation of diffusion (internal and external) and the rate of the adsorption step contribute to the overall rate of the sorption process. The film diffusion and internal diffusion that allow the compounds to reach available sorption sites and be adsorbed on them are not the rate-limiting steps of the sorption of PL on these materials.

The use of chemical kinetic equations shows that to some degree, the adsorption kinetics step also contributes to the overall rate of the process. The use of chemical kinetics models shows that the polymolecular interactions in the sorbate–solution–sorbent system must be considered in the sorption of PC on mesoporous materials of the MCM-41 type.

Examination of the adequacy of our kinetic models to characterize the sorption of PC on mesoporous composites reveals that the pseudo-second order rate equations are better for describing the sorption of PC on MCM-41 and its synthesized analogs.

The overall rate of sorption of PL turns out to be controlled by the adsorption kinetics. This suggests that the contribution from the adsorption rate to this process is higher than that of diffusion. The large pore size of the sorbent (d_p = 4.2 nm [14]) facilitates the transfer of PC molecules within pores and helps them to reach active sorption sites without the diffusion rate limitation of sorption. It should be noted that the pseudo-second order model describes not only the limitation of sorption on these materials but also the other kinetic mechanisms affecting the process rate.

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