Optimization of sol-gel synthesis conditions for producing of silica monoliths promising for chromatography: sorption kinetics and mechanical stability

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The effect of porogen additives (polyethylene glycol and cetylpyridinium chloride) on the sorption kinetics and mechanical stability of silica monoliths was studied. Three kinetic models: (i) pseudo-first-order kinetic model; (ii) pseudo-second-order kinetic model; (iii) intra-particle diffusion model were applied for treatment of sorption kinetics of malachite green. The improving of sorption kinetics by introducing additives of polyethylene glycol and cetylpyridinium chloride into the reaction mixture for sol-gel synthesis was observed and discussed. The optimized composition of reaction mixture was used for producing of monolithic layers on the glass solid support, which were successfully used for separation of test mixture of dyes.

Изучено влияние порообразователей (полиэтиленгликоля и цетилпиридиний хлорида) на кинетику и механическую стойкость монолитов кремнезема. Для интерпретации данных по кинетике сорбции малахитового зеленого применено три модели: (i) кинетическая модель псевдо-первого порядка; (ii) кинетическая модель псевдо-второго порядка; (iii) модель диффузии внутри частиц. Установлено, что кинетика сорбции улучшается за счет введения порообразующих веществ, таких как полиэтиленгликоль и цетилпиридиний хлорид, в реакционную смесь при золь-гель синтезе. Оптимальный состав реакционной смеси использован для получения монолитных слоев на стеклянном носителе. Полученные пластины успешно применены для разделения тестовой смеси красителей.

1. Introduction

Monolith is the solid continuous block ("single-piece") of porous material with bimodal distribution dimensions of pores (macropores and mesopores) [1]. The problems of synthesis and application of monoliths have received much attention during last year's [1-5]. This is due to the fact that monolithic columns are a recent acquisition of analytical chromatography and solid-phase extraction [4, 5]. The essential advantages of monolithic materials, synthesized by sol-gel method, stem out from the possibility to control and optimize separately the average sizes of macro-, meso- and micro-

pores. Thus, the monolithic sorbents that have high permeability and can provide high efficiency and low retention times could be fabricated. The preparation of silica monolith suitable for chromatography or sample preparation is difficult problem due to low reproducibility of results that is caused by lot of factors affecting the structure and mechanical stability of sorbents [1].

As far as we know, there is only one single reliable commercial source of monolithic columns for high-performance liquid chromatography (Chromolith from Merck KGaA, Darmstadt, Germany; Onyx from Phenomenex, Torrance, CA, USA, is "based on mono-

lithic technology licensed from Merck KGaA"), as well as for thin-layer chromatography, which is called now ultra-thin layer chromatography [6, 7]. These sorbents have been under intensive investigation during last decade, however, due to the high cost of monolithic columns and plates their advantages and disadvantages are not fully investigated.

Several attempts are known in literature related with producing of monolithic thin-layers on the carrier [8-10]. However, the special equipment for disposition of monolithic layer on the carrier and long term for obtaining of layer with appropriate thickness are the limitations of these approaches. In work [11] more simple procedure for thin layers with monolithic sorbent have been proposed. Unfortunately, our efforts to reproduce this method were unsuccessful [12].

In our previous works we have concentrated our attention on the sol-gel synthesis conditions and investigation of properties of silica monoliths, which can be formed as thin-layer on the solid carrier [12-14]. The type of solid carrier and the procedure of its pre-treatment were chosen [12]. The type of precursor, control of drying additive, type of surfactant for increasing the adhesion between carrier and reaction mixture were selected [14]. The effect of drying regime and maximum temperature were studied by Fourier transform infrared spectroscopy and scanning electron microscopy [12-14]. Recently, the influence of the catalyst and pH of the reaction mixture on the sorption capacity of monolith were studied [13].

In this work the effect of amount of organic solvent additives in reaction mixture, the molecular weight and amount of polyethyleneglycol, concentration of cetylpyridinium chloride and the procedure of monoliths washing on the kinetics of malachite green adsorption and mechanical stability of produced monolith were investigated. The optimized sol-gel method of monoliths synthesis was used for preparation of monolithic thin-layers and separation of test mixture of dyes by ascending thin-layer chromatography (TLC).

2. Experimental

Tetraethoxysilane, ethanol (96.6 %), N,N-dimethylformaldehyde (DMFA, Merck, Germany), cetylpyridinium chloride (CPC, 98.6 %, Merck, Germany), polyethyleneglycol (PEG, M_r 300 and 1000, Fischamend, Austria) were used for synthesis of mono-

lithic sorbents. Acetonitrile (Reakhim, Russia) was used for washing of synthesized sorbent. Sorption properties of monoliths were investigated with respect to dye malachite green (malachite green oxalate, Shostkinsky plant of chemicals) at pH 4.3. Buffer solutions were prepared with sodium dihydrogen phosphate and potassium hydrogen phosphate. Bromocresol green (Reakhim, Russia), malachite green, methyl red (Reakhim, Russia) were used as test substances for TLC separations. Absorption spectra were registered by photometer KFK-3 (Zagorsky UEW, Russia). Glass cells of 0.3 cm length were used for photometric measurements.

Monolithic block sorbents were prepared by sol-gel method according to the procedure described in [13]. The monolithic layers for TLC were produced by the recently proposed procedure: the phosphate buffer with pH 7.4, DMFA and CPC dissolved in ethanol were mixed with PEG, and then the TEOS was added to reaction mixture. The reaction mixture was stirred intensively for 40 min and distributed on glass pre-treated by the previously described procedure. The mixture was dried at room temperature for 2 days, then, the glass plate was transferred to drying box. During 12 h the temperature was increased from 40°C to 60°C at 5°C/hour. After 12 h the temperature was increased from 60°C to 90–95°C at the same rate. Then, the layers were dried at 90–95°C for 24 h.

Three main kinetic models are commonly used for description of the adsorption kinetics: (i) pseudo-first-order kinetic model, called Lagergren equation [16]; (ii) pseudo-second-order kinetic model, which was proposed by Ho [17, 18]; (iii) intra-particle diffusion model, proposed by Weber et al. [15]. These three models have been used for description of kinetics of malachite green sorption on the monolithic sorbents synthesized by different procedures.

In the pseudo-first-order kinetic model the rate of adsoption is linearly proportional to the amount of sorbate :

$$\frac{dn_t}{dt} = k_1(n_{eq} - n_t), \qquad (1)$$

where n_{eq} and n_t are the amount of dye adsorbed at contact time t (sec) and at equilibrium, respectively; k_1 is the pseudo-first-order constant. After integration with boundary conditions $t = 0$ to $t = t$ and $n_t = 0$

to $n_t = n_t$, the following linear equation can be derived:

$$\log(n_{eq} - n_t) = \log n_{eq} - \frac{k_1}{2.303}t. \quad (2)$$

It is generally accepted that the pseudo-first-order kinetic model is related to diffusion-controlled process of adsorption.

The pseudo-second-order model is represented as follows:

$$\frac{dn_t}{dt} = k_2(n_{eq} - n_t)^2, \quad (3)$$

where k_2 is the pseudo-second-order constant. After integration for the boundary conditions $t = 0$ to $t = t$ and $n_t = 0$ to $n_t = n_t$ and linearization of the obtained equation, the following model can be obtained:

$$\frac{t}{n_t} = \frac{1}{k_2 n_{eq}^2} + \frac{t}{n_{eq}}. \quad (4)$$

The values of n_{eq} and k_2 are calculated from the intercept and slope of Eq. (4). The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption.

The intra-particle diffusion model is based on the following relationship between amount of adsorbed substance and time:

$$n_t = k\sqrt{t} + I, \quad (5)$$

where k is the intra-particle-diffusion rate constant. This model assumes that the sorption process consists of four steps: (i) migration of the adsorbate from the bulk phase to the surface of sorbent; (ii) diffusion through the boundary level; (iii) transport of the molecules from the surface to the interior pores; (iv) adsorption of molecules on the active centers of sorbent by chemical reaction.

3. Results and discussion

The force driving mobile-phase migration in ascending TLC is the decrease in the free energy of the solvent as it enters the porous structure of the layer. Thus, the transport mechanism is the result of capillary action [19–21]. Capillarity elution of solvents through the thin film media requires macrosized intercalated pores, with continuous channels throughout the porous chromatographic media. Regular, thin, sol-gel derived films have only nano-dimension pores which hinder eluent migration through the media [11]. Thus, the additives of templates are needed for formation of macropores in monolith for its application in chromatographic separations.

The molecules with high molecular weight or self-organized surfactant solutions, e.g. polyvinyl alcohol, polyethyleneglycol [22, 23], polyacrylic acid, cetylpyridinium chloride, [22, 24] lipase, egg albumin [25] etc, are often used as additives for formation of macropores in silica monolith.

In our previous work the next molar proportions of TEOS, H_2O, DMFA, EtOH, CPC were used for synthesis of monoliths $1.0{:}4.6{:}1.4{:}1.9{:}8{\cdot}10^{-4}$. The synthesis was performed at pH 7.4 maintained by phosphate buffer with concentration 0.067 M (the concentration is related to H_2O volume of reaction mixture). The additive of CPC was used mainly for increasing the adhesion between the pre-treated glass support and reaction mixture. Recently, we have examined the effect of polyethyleneglycol (M_r 300) on the specific surface area of monoliths. It was observed that polyethyleneglycol with M_r 300 improves the mechanical stability of monolithic blocks, formed in medical syringes, and increases the specific surface area of monolith up to molar ratio of PEG to TEOS equals to 0.31:1. The further increasing of PEG in reaction mixture leads to decreasing of the specific surface area. The important step of block monolith and thin-layer fabrication is the washing of sorbent from the components of reaction mixture. The acetonitrile was recognized as best solvent for static as well as dynamic washing of monolith among the following solvents: H_2O, mixture H_2O:acetonitrile (1:1 by volume), acetonitrile, ethanol, iso-pentanol, acetone and ethylacetate.

In this work we have studied the applicability of different kinetics models for the treatment of data on kinetics of malachite green adsorption on the monolithic blocks. The results of the modeling were used for the optimization of monolith synthesis. The addition of PEG to reaction mixture consisted of TEOS, H_2O, DMFA, EtOH, CPC (molar ratio $1.0{:}4.6{:}1.4{:}1.9{:}8{\cdot}10^{-4}$) results in some inhomogeneity of reaction mixture. Thus, we have investigated how the increasing of solvent (ethanol) amount in reaction mixture affects the gel formation process, kinetics of dye sorption and mechanical stability of monolith, synthesized in the presence of PEG with molar ratio to TEOS equals 0.31. The ratio of ethanol to TEOS was varied from 1.9 to 13.4 (Table). The pseudo-second-order model in general

Table. Parameters of kinetics models and correlation coefficients for linearized equations (2), (4), (5) for sorption of malachite green on monoliths, synthesized with using different molar proportions of components

X	n_{eq} (5 h)	Pseudo-first order			Pseudo-second order			Intra-particle diffusion		
		n_{eq}, $\mu mol \cdot g^{-1}$	k_1, $10^5 \cdot s^{-1}$	R^2	n_{eq}, $\mu mol \cdot g^{-1}$	k_2, $g \cdot \mu mol \cdot 10^6 \cdot s^{-1}$	R^2	I, $\mu mol \cdot g^{-1}$	k, $\mu mol \cdot 10^3 \times \times s^{-0.5} \cdot g^{-1}$	R^2
Molar proportions of reagents TEOS:H$_2$O:DMFA:EtOH:PEG (M$_r$ 300):CPC 1.0:4.6:1.4:X:0.31:8·10^{-4};										
1.9	6.34	5.1	14	–	7.9	25	0.991	0.68	43	0.992
3.8	3.99	3.2	15	0.98	4.8	50	0.992	0.70	25	0.990
7.7	11.5	10	18	0.99	14	15	0.997	1.6	77	0.980
9.6	9.21	7.8	16	0.99	11	19	0.99	1.4	60	0.997
11.5	9.62	8.7	17	0.98	12	16	0.996	1.1	66	0.980
13.4	9.67	8.9	16	0.98	12	15	0.99	0.87	67	0.997
Molar proportions of reagents TEOS:H$_2$O:DMFA:EtOH:PEG (M$_r$ 300):CPC 1.0:4.6:1.4:7.7:0.31:X;										
6·10^{-5}	5.04	3.8	13	0.998	6.2	34	0.99	0.70	33	0.998
2·10^{-3}	4.72	3.9	17	0.99	5.6	45	0.993	0.94	29	0.992
3·10^{-3}	5.59	4.5	17	0.991	6.7	39	0.994	1.1	34	0.991
5·10^{-3}	6.07	5.33	18	0.99	7.4	32	0.996	1.0	39	0.990
6·10^{-3}	6.23	5.6	18	0.99	7.4	32	0.994	0.88	41	0.990
8·10^{-3}	6.89	5.5	17	0.99	8.2	33	0.993	1.5	41	0.992
Molar proportions of reagents TEOS:H$_2$O:DMFA:EtOH PEG (M$_r$ 1000) : CPC 1.0:4.6:1.4:7.7:X:8·10^{-4};										
0.03	5.41	4.0	17	0.98	6.6	35	0.99	0.90	34	0.996
0.05	5.42	4.0	20	0.98	6.4	44	0.993	1.3	32	0.99
0.09	8.94	4.8	23	0.97	9.7	63	0.9994	4.3	38	0.87
0.13	10.29	4.2	40	0.992	11	216	0.9999	8.1	19	0.77
0.26	9.38	4.2	29	0.998	9.8	107	0.9999	6.0	28	0.89
0.52	5.67	5.3	23	0.996	7.1	30	0.9997	0.72	39	0.97

gives the good fit of obtained experimental data for silica monolith synthesis with different additives of alcohol. The maximal n_{eq} and high value of k_2 was observed for the silica monolith synthesized with following molar proportions of TEOS, H$_2$O, DMFA, EtOH, PEG (M$_r$ 300), CPC 1.0:4.6:1.4:7.7:0.31:8·10^{-4}. The high goodness-of-fit was also observed for the intra-particle diffusion model. In both models the process of chemisorption is taken into account. Thus, it can be concluded that the interaction of monocationic form of malachite green with dissociated silanol groups is important process of sorption on fabricated silica monoliths. The increasing of alcohol content in the mixture results in formation of glassy and breakable monolith.

It is known that the additives of surfactants above the critical micelle concentration could be used for obtaining of monoliths with nanostructured pores. We have examined the affect of CPC additives on the sorption kinetics and mechanical stability of block monoliths as well as thin monolithic layers.

The molar ratio of CPC to TEOS was changed from 6·10^{-5} to 9.8·10^{-2}. However, only the monoliths synthesized by using molar proportion of CPC to TEOS up to approximately 8·10^{-3} were mechanically stable.

As can been concluded from comparison of R^2 values the pseudo-second-order model and intra-particle diffusion model gives the better description of experimental data than pseudo-first-order model (Table). According to the parameters of these models the highest n_{eq} and kinetic constant were observed for reaction mixture with molar proportion
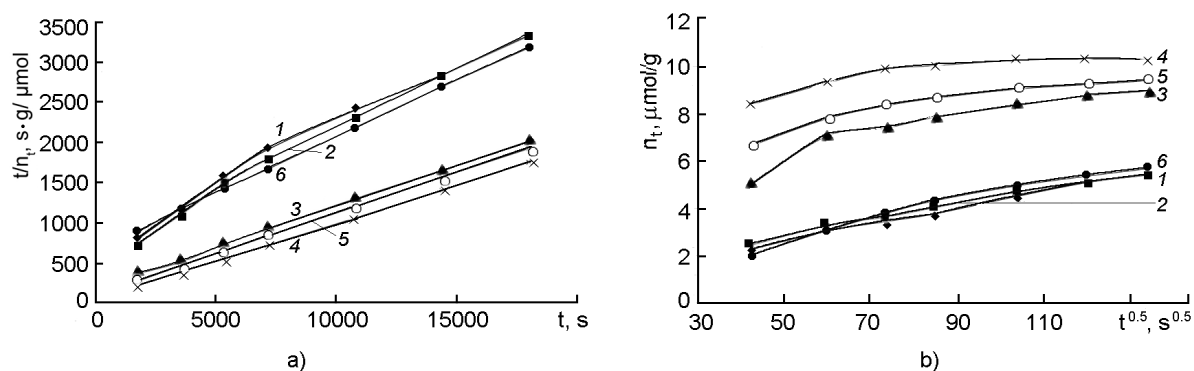
Fig. 1. Pseudo-second-order kinetic model (a) and intra-particle diffusion model (b) for adsorption of malachite green on monoliths synthesized using different ratios of PEG (M_r 1000) $X = (1)$ — 0.03, (2) — 0.05, (3) — 0.09, (4) — 0.13, (5) — 0.26, (6) — 0.52. Molar ratio of components in reaction mixture TEOS, H_2O, DMFA, EtOH, PEG (M_r 1000), CPC ($1.0{:}4.6{:}1.4{:}7.7{:}X{:}8{\cdot}10^{-4}$).

of CPC $8{\cdot}10^{-3}$. This amount of CPC was used for further investigations.

The volume of meso- and macropores can be increased by additives of porogens with high molecular weight. The additives of PEG with M_r 1000 instead of PEG with M_r 300 were used for synthesis of monoliths. The ratios of PEG to TEOS were varied from 0.03 to 0.52. It is interesting that in the case of additives of PEG with M_r 1000 only the pseudo-second-order model provides high quality of results description (Table, Fig. 1). The high values of n_{eq} were observed for monolith synthesized with the reaction mixture containing 0.09, 0.13 and 0.26 moles of PEG per 1 mol of TEOS (Table). The kinetic constant, k_2, for this monoliths equals 63, 216 and 107 correspondingly. However, for monoliths obtained by using reaction mixture with 0.09 and 0.13 moles of PEG per mol of TEOS the curvature of intra-particle diffusion model is more pronounced than for 0.26 mol of PEG 1000 per 1 mol of TEOS (Fig. 1b). This fact is also confirmed by comparison of correlation coefficients for intra-particle diffusion model (Table). The presence of two straight lines for intra-particle diffusion model can be interpreted as simultaneous occurring of two processes during adsorption on the monolith: fast diffusion through the boundary layer and intra-particle-diffusion through pores [15].

Thus, the monoliths synthesized with the ratio of PEG (M_r 1000) to TEOS equals 0.13 and 0.26 gives the best sorption kinetics characteristics (Table) according to pseudo-second order model. However the data obtained for PEG (M_r 1000) to TEOS ratio 0.13 were unsuccessfully described by intra-parti-

cle diffusion model. The composition with molar ratio PEG (M_r =1000) to TEOS equals 0.26 was used for producing monolithic layers on the glass support.

The fabricated thin monolithic layers were tested for TLC separation of the mixture of dyes: bromocresol green (0.7 g/l), malachite green (0.4 g/l), methyl red (0.4 g/l). The TLC plates were of $3{\times}3$ cm^2 area. After drying, the TLC plates were washed with acetonitrile and dried again. The separations were performed in ascending mode by using the mobile phase toluene:methanol (80:20 by volume). 0.3 μl of the dyes mixture solution was brought at the start line by using chromatographic microsyringe. The three dyes were completely separated in 5 min; the distance from the start to front line equals 2 cm. It is interesting that the same mixture of dyes could not be separated on the commercial normal-phase plates Sorbfil (PKB Plastmash, Krasnodar, Russia) using the same mobile phase even after 30 min.

4. Conclusions

The analysis of sorption kinetics on the monolithic sorbents can be useful for optimization of sol-gel synthesis and investigation of mechanism of sorption process. The pseudo-second-order kinetic model gives the better goodness-of-fit for treatment of experimental data obtained for sorption of malachite green on different monoliths in comparison with pseudo-first-order model and intra-particle diffusion model. The analysis of kinetic models results in conclusion of chemisorption process on the monolithic sorbents. The optimal amounts of polyethylene glycol and cetylpyridinium

chloride were selected for fabrication of monolithic thin layer on the solid glass support on the basis of sorption kinetic investigation. Better selectivity and lower separation time of the test mixture of dyes was observed for TLC plates with monolithic sorbent in comparison with classical normal-phase TLC plates.

References

1. G. Guiochon, *J. Chromatogr.*, 168, 101, (2007).
2. C.J.Brinker, in: Sol-gel Science. The Physics and Chemistry of Sol-gel Processing, ed. by C.J.Brinker, G.V.Scherer, Academic, Boston (1990).
3. S.Sakka, H.Kozuka, Sol-gel Science and Technology. Processing Characterization and Application. Sol-gel Processing, ed. by H.Kozuka, Kluwer Academic Publishers, Boston, Dordrecht, London (2005), v.1.
4. A-M.Siouffi, *J. Chromatogr. A*, **1000**, 801 (2003).
5. K.K.Unger, R.Skudas, M.M.Schulte, *J. Chromatogr. A*, **1184**, 393 (2008).
6. H.Hauck, M.Schulz, *J. Chromatogr. Sci.*, **40**, 550 (2002).
7. H.Hauck, M.Schulz, *Chromatogr. Suppl.*, **57**, 313 (2003).
8. M.Yin, X.Yao, L.Zhang, *J. Zhejiang Univ. SCI.*, **5**, 422 (2004).
9. J.M.Berquier, L.Teyssedre, C.Jacquiod, *J. Sol-Gel Sci. and Techn.*, **13**, 739 (1998).
10. L.Bezuidenhout, M.Brett, *J. Chromatogr. A*, **1183**, 179 (2008).
11. M.Tsionsky, A.Vanger, O.Lev, *J. Sol-Gel Sci. and Techn.*, **2**, 595 (1994).
12. A.M.Frolova, M.A.Chukhlieb, A.V.Drobot et al., *The Open Surf. Sci. J.*, **1**, 40 (2009).
13. A.M.Frolova, A.P.Boichenko, O.Yu.Konovalova, *Kharkov University Bulletin. Chemical Series*, **17**, 157 (2009).
14. A.M.Frolova, M.A.Chukhlieb, A.V.Drobot et al., *Kharkov University Bulletin. Chemical Series*, **16**, 160 (2008).
15. B.K.Nandi, A.Goswami, M.K.Purkait, *J. Hazardous Mat.*, **161**, 387 (2009).
16. Yu Liu, L.Shen, *Langmuir*, **24**, 11625 (2008).
17. Y.S.Ho, G.McKay, *Process Biochemistry*, **34**, 451 (1999).
18. Y.S.Ho, G.McKay, *Chem. Engin. J.*, **70**, 115 (1998).
19. Sz.Nyiredy, Planar Chromatography. A Retrospective View for the Third Millennium, ed. by Sz.Nyiredy, Budakalasz, Springer, Hungary, (2001), p.614.
20. J.C.Giddings, G.H.Stewart, A.L.Ruoff, *J. Chromatogr.*, **3**, 239 (1960).
21. A.L.Ruoff, J.C.Giddings, *J. Chromatogr.*, **3**, 438 (1960).
22. Y.W.Sun, Y.J.Wang, W.Guo et al., *Micropor. and Mesopor. Mater.*, **88**, 31 (2006).
23. T.Hara, H.Kobayashi, T.Ikegami et al., *Anal. Chem.*, **78**, 7632 (2006).
24. K.Nakanishi, *J. Por. Mater.*, **4**, 67 (1997).
25. S.Sato, T.Murakata, T.Ohgawara, *J. Mater. Sci.*, **25**, 4800 (1990).

Оптимізація умов золь-гель синтезу для одержання монолітних сорбентів на основі кремнезему, перспективних для хроматографії: кінетика сорбції та механічна міцність

О.П.Бойченко, А.М.Фролова, О.Ю.Коновалова, Л.П.Логінова

Вивчено вплив пороутворювачів (поліетиленгліколю та цетилпіридиній хлориду) на кінетику та механічну міцність монолітів кремнезему. Для інтерпретації даних щодо кінетики сорбції малахітового зеленого застосовано три моделі: (і) кінетична модель псевдо-першого порядку; (іі) кінетична модель псевдо-другого порядку; (ііі) модель дифузії всередині часток. Встановлено, що кінетика сорбції покращується за рахунок введення порогенних речовин, таких як поліетиленгліколь та цетилпіридиній хлорид, у реакційну суміш при золь-гель синтезі. Оптимальний склад реакційної суміші використано для отримання монолітних шарів на скляному носії. Отримані пластини успішно застосовано для розділення тестової суміші барвників.