DOI: 10.6060/ivkkt.20186112.5542

УДК: 541.18.03 + 541.1

КИНЕТИКА АДСОРБЦИИ 4,4-ДИМЕТИЛ-1,3-ДИОКСАНА ИЗ ВОДНЫХ РАСТВОРОВ СИНТЕТИЧЕСКИМИ ЦЕОЛИТАМИ В ПРИСУТСТВИИ ФОСФОРНОЙ КИСЛОТЫ

Г.А. Овчинников, В.А. Горских, И.И. Фассалова, В.С. Тухватшин, Р.Ф. Талипов

Григорий Андреевич Овчинников, Валентина Андреевна Горских, Ильяна Ильдусовна Фассалова, Вадим Салаватович Тухватшин *, Рифкат Фаатович Талипов

Кафедра органической и биоорганической химии, Башкирский государственный университет, ул. З. Валиди, 32, Уфа, Российская Федерация, 450076

E-mail: defronzak@mail.ru, valushka.1.10.2012@yandex.ru, fassalova.ru@yandex.ru, vadimtukhvatshin@yandex.ru*, talipovrf@mail.ru

В работе нами изучена кинетика адсорбции 4,4-диметил-1,3-диоксана синтетическими цеолитами из водных растворов в присутствии фосфорной кислоты. Механизм адсорбции ДМД из водных растворов синтетическими цеолитами рассмотрен с позиций трех кинетических моделей: диффузионной модели (модель Бойда и Морриса-Вебера), Лагергерена (псевдо-первого порядка) и псевдо-вторвого порядка. В качестве сорбентов использовались синтетические цеолиты КА, NaA, CaA, CaX, NaX с диаметром пор 3-9Å. ДМД (температура кипения 113-114 °С) получен из изобутилена. Хроматографический анализ проводили на приборе Хроматек «Кристалл 5000.1» (Россия), длина колонки 2,0 м с неподвижной фазой силикона SE-30 (5%) (0,16-0,20 мм, рабочая температура 50-220 °С), газ-носитель - азот. Адсорбция ДМД из водных растворов изучалась при (75 ± 1) °С из ограниченного объема при постоянном перемешивании (лабораторная механическая мешалка 17 об/мин). Время контакта раствора с образцами сорбентов варьировалось от 120 до 3600 с. Концентрацию ДМД в растворе определяли хроматографическим методом (внутренний стандарт 4,4,5-триметил-1,3-диоксан). Получены значения коэффициентов диффузии внешнего и внутреннего массопереноса. Установлено влияние размера пор цеолитов на вклад внешнего или внутреннего диффузионного массопереноса в процесс адсорбции 4,4-диметил-1,3-диоксана. Определено время установления сорбционного равновесия. Нами обнаружено, что процесс адсорбции ДМД синтетическими цеолитами в присутствии фосфорной кислоты определяется значениями диаметра пор. Показано, что значение диаметра пор синтетических цеолитов не влияет на равновесное время адсорбции ДМД. Время равновесия адсорбции для всех используемых марок цеолитов составляют 900 с. Кинетика адсорбции ДМД на синтетических цеолитах может быть адекватно описана уравнением псевдо-второго порядка, что указывает на наличие взаимодействия сорбата (ДМД) с сорбентом (синтетическим цеолитом).

Ключевые слова: 4,4-диметил-1,3-диоксан, синтетические цеолиты, кинетика адсорбции

KINETICS OF ADSORPTION OF 4,4-DIMETHYL-1,3-DIOXANE FROM AQUEOUS SOLUTIONS BY SYNTHETIC ZEOLITES IN PRESENCE OF PHOSPHORIC ACID

G.A. Ovchinnikov, V.A. Gorskikh, I.I. Fassalova, V.S. Tukhvatshin, R.F. Talipov

Grygoriy A. Ovchinnikov, Valentina A. Gorskikh, Ilyana I. Fassalova, Vadim S. Tukhvatshin *, Rifkat F. Talipov

Department of Organic and Bioorganic Chemistry, Bashkir State University, Validi st., 32, Ufa, 450076, Russia
E-mail: defronzak@mail.ru, valushka.1.10.2012@yandex.ru, fassalova.ru@yandex.ru, vadimtukhvasin@yandex.ru *, talipovrf@mail.ru

In this paper we studied the kinetics of adsorption of 4,4-dimethyl-1,3-dioxane by synthetic zeolites from aqueous solutions in the presence of phosphoric acid. Kinetic mechanism of DMD adsorption from aqueous solutions by synthetic zeolites were considered from the position of three kinetic models: the diffusion model (Boyd and Morris-Weber model), Lagergeren (pseudo-first order), and pseudo-second order. As sorbents we have used synthetic zeolites KA, NaA, CaA, CaX, NaX with a pore diameter of 3-9 Å. DMD (boiling point is 113-114 ºC) was synthesized from isobutylene. Chromatographic analysis was performed on Chromatec Crystal 5000.1 instrument (Russia) using columns (2.0 m in length) with silicone SE-30 (5%) stationary phase (0.16–0.20 mm, operating temperature is 50–220 °C) with nitrogen as a carrier gas. An adsorption of DMD from aqueous solutions was investigated at (75±1) °C from a limited volume under constant mixing (laboratory mechanical stirrer, 17 rps). The contact time of the solution with samples of sorbents varied from 120 to 3600 s. The DMD concentration in solution was determined by the chromatographic method (the internal standard is 4,4,5-trimethyl-1,3-dioxane). The values of the external and internal mass transfer diffusion coefficients were obtained. The effect of the size of zeolite's pores on the contribution of the external or internal diffusion mass transfer in the process of adsorption of 4,4-dimethyl-1,3-dioxane was founded. The time of establishment of sorption equilibrium was determined. We have found that the process of adsorption of DMD by synthetic zeolites in the presence of phosphoric acid is determined by the values of the diameter of the pores. It is shown that the value of pore diameter of synthetic zeolites does not influence on the adsorption equilibrium time of DMD. The adsorption equilibrium time for all used family zeolites is 900 s. The kinetics of adsorption of DMD on synthetic zeolites can be correctly described by a pseudo-second-order equation, which indicates the presence of sorbate (DMD) interaction with the sorbent (synthetic zeolite).

Key words: 4,4-dimethyl-1,3-dioxane, synthetic zeolites, adsorption kinetics

Для цитирования:
Овчинников Г.А., Горских В.А., Фассалова И.И., Тухватшин В.С., Талипов Р.Ф. Кинетика адсорбции 4,4-диметил-1,3-диоксана из водных растворов синтетическими цеолитами в присутствии фосфорной кислоты. *Изв. вузов. Химия и хим. технология*. 2018. Т. 61. Вып. 12. С. 81–86

For citation:
Ovchinnikov G.A., Gorskikh V.A., Fassalova I.I., Tukhvatshin V.S., Talipov R.F. Kinetics of adsorption of 4,4-dimethyl-1,3-dioxane from aqueous solutions by synthetic zeolites in presence of phosphoric acid. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 12. P. 81–86

INTRODUCTION

The Prins reaction consists in the interaction of aldehydes with alkenes in the presence of a mineral acid and forms the basis for the industrial method of isoprene synthesis through 4,4-dimethyl-1,3-dioxane (DMD) [1-13]. DMD is obtained by condensation of the aqueous formaldehyde with isobutene in the presence of phosphoric acid. In the last decade, synthetic zeolites were used for the above process [4]. However, in these papers the interaction of products of Prins reaction with porous materials was not considered. Therefore, the aim of this work was to study the adsorption kinetics of DMD by synthetic zeolites in the presence of phosphoric acid.

EXPERIMENTAL

As sorbents we have used synthetic zeolites KA, NaA, CaA, CaX, NaX with a pore diameter of 3-9 Å produced by the "Ishimbay Catalyst Plant" (Bashkor-

tostan, Ishimbay). For the preparation of aqueous formaldehyde we used the paraformaldehyde (brand C) (mass fraction of formaldehyde is 94-98%). DMD (boiling point is 113-114 °C) was synthesized from isobutylene. Chromatographic analysis was performed on Chromatec Crystal 5000.1 instrument (Russia) using columns (2.0 m in length) with silicone SE-30 (5%) stationary phase (0.16-0.20 mm, operating temperature is 50-220 °C) with nitrogen as a carrier gas.

An adsorption of DMD from aqueous solutions was investigated at (75±1) °C from a limited volume under constant mixing (laboratory mechanical stirrer, 17 rps).

Samples of a synthetic zeolites [weight (2,65±0,10) g] were introduced into the solutions containing 0.104-0.127 g of DMD, 50 ml of aqueous formaldehyde with the initial concentrations of 5.85-7.07 mol/l and 2.5 ml of 81% phosphoric acid (5% by weight). The contact time of the solution with samples of sorbents varied from 120 to 3600 s. The DMD concentration in solution was determined by the chromatographic method (the internal standard is 4,4,5-trimethyl-1,3-dioxane) [14].

RESULTS AND DISCUSSION

Experimental DMD adsorption kinetic curves from aqueous solutions by synthetic zeolites are shown in Fig. 1.

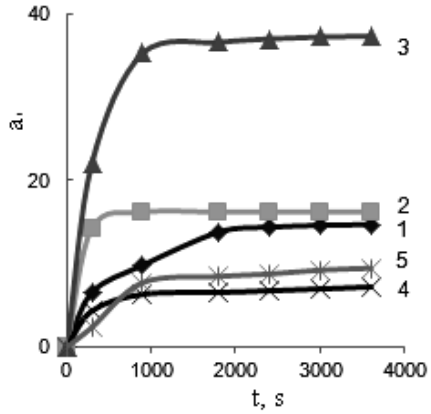

Fig. 1. Kinetic curves of DMD adsorption from solutions in the presence of phosphoric acid by synthetic zeolites at 75 °C (1 – KA; 2 – NaA; 3 – CaA; 4 – CaX; 5 – NaX)

Рис. 1. Кинетические кривые адсорбции ДМД из растворов в присутствии фосфорной кислоты синтетическими цеолитами при 75 °C (1 - KA, 2 - NaA, 3 - CaA, 4 - CaX, 5 - NaX)

For the study the kinetics mechanism of adsorption of DMD from aqueous solutions by synthetic zeolites, kinetic curves were considered from the position of three kinetic models: the diffusion model (Boyd and Morris-Weber model), Lagergeren (pseudo-first order), and pseudo-second order.

Adsorption of DMD (a) from aqueous solutions by synthetic zeolites was evaluated according to the equation (**1**) [15-18]:

$$a = [(c_0 - c_t)\cdot V] \cdot M_{DMD} \cdot 1000 / m, \quad (1)$$

c_t – adsorbate concentration at various time points, mol/l; c_0 – adsorbate concentration at the initial time, mol/l; V – solution volume, l; M_{DMD} = 116 g/mol, m – weight of synthetic zeolites.

Relative approach of the adsorption to equilibrium (γ) was calculated according to the equation (2) [15-18]:

$$\gamma = a/a_{eq}, \quad (2)$$

a_{eq} – adsorption at equilibrium, mg/g

Changing adsorbed DMD (T) at different times was calculated according to the equation (3) [15-18]:

$$T = -\ln(1-\gamma) \quad (3)$$

External diffusion mass transfer coefficients (βn) and internal diffusion of DMD from solution were calculated using the equation (4) [15-18]:

$$\beta_n = tg\alpha/T, \quad (4)$$

tgα – the tangent of linear portion of the graph according to the inclination angle T = *f* (t).

In the framework of the diffusion model, a quantitative approach is used for the primary demarcation of intra- and externally diffusion-limited adsorption, assuming an analysis of the kinetic data in the coordinates – T – t.

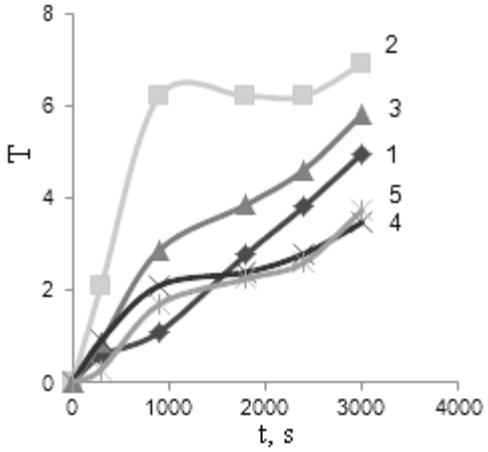

Fig. 2. Change in quantity the adsorbed substance during DMD adsorption from solution in the presence of phosphoric acid by synthetic zeolites at 75 °C (1 – KA; 2 – NaA; 3 – CaA; 4 – CaX; 5 – NaX)

Рис. 2. Изменение количества адсорбированного вещества при адсорбции ДМД из раствора в присутствии фосфорной кислоты синтетическими цеолитами при 75 °C (1 - KA, 2 - NaA, 3 - CaA, 4 - CaX, 5 - NaX)

For the all used synthetic zeolites there is a high rate of adsorption of DMD in the initial period (for up to 900 s). Adsorption rate decreases significantly with the increase of contact time. Adsorption equilibrium time for all used samples of zeolites is 900 s.

In the all period of time for KA the kinetic data (R = 0.996) depend only on the concentration of DMD in the solution (Fig. 2). In the case of used synthetic zeolites NaA, CaA, CaX, NaX kinetic data (R = 0.995) indicate a mixed-diffusion mechanism: the initial period of time (for up to 900 s) (Fig. 2) the process is characterized by the transfer of DMD molecules to the surface of the synthetic zeolite; the second section shows the diffusion of DMD molecules inside the sorbent. Mass transfer coefficients of external and internal diffusion were calculated by equations (**3**) and (**4**) (Table 1).

Table 1

Kinetic parameters of DMD adsorption from solutions by synthetic zeolites in the presence of phosphoric acid at 75 °C

Таблица 1. **Кинетические параметры адсорбции ДМД из растворов синтетических цеолитов в присутствие фосфорной кислоты при 75 °С**

Zeolite marks	Zeolite pore diameter, Å	External mass transfer coefficient ($\beta_n \times 10^3$) s^{-1}	Internal diffusion coefficient × 10^4, s^{-1}
KA	3	(1.63±0.08)	–
NaA	4	(6.89±0.39)	(5.77±0.31)
CaA	5	(3.21±0.17)	(6.31±0.28)
CaX	8	(2.29±0.11)	(6.38±0.32)
NaX	9	(1.96±0,09)	(909±0.45)

In the case of KA zeolite with the pore diameter of 3 Å the DMD adsorption process from an aqueous solution has been determined only by the mass transfer of the volume of the external solution. The values of the external mass transfer coefficient (β_n) is decreased and the values of internal diffusion coefficients increase with the change of pore diameter of the zeolites NaA, CaA, CaX, NaX (4-9 Å) (Table 1). Its facts can be explained by the value of diameter adsorbate molecule (value of critical diameter of the molecule DMD is 4.02 Å [19-21]).

For analyze the obtained kinetic curves of DMD adsorption on synthetic zeolites, two kinetic models were also used: pseudo-first (equation 5) and pseudo-second (equation 6) order.

$$\ln (a_{eq} - a) = \ln a_{eq} - k_1 t \quad (5)$$

$$t/a = 1/k_2 a_{eq}^2 + t/a_{eq}, \quad (6)$$

a_{eq}, a – adsorption at equilibrium and adsorption (mg/g) at the time point (sec); k_1 – the adsorption rate constant for the pseudo-first-order model; k_2 – the adsorption rate constant for the pseudo-second-order model.

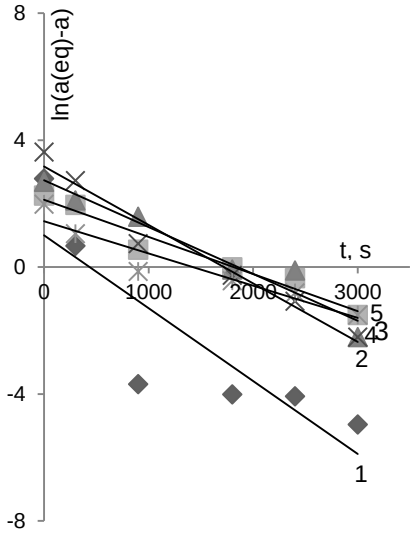

Fig. 3. Kinetic curves of adsorption of DMD from aqueous solutions by synthetic zeolites in the presence of phosphoric acid at 75 °C in the framework of pseudo-first order model

Рис. 3. Кинетические кривые адсорбции ДМД из водных растворов синтетическими цеолитами в присутствии фосфорной кислоты при 75 °С в рамках моделей псевдо-первого порядка

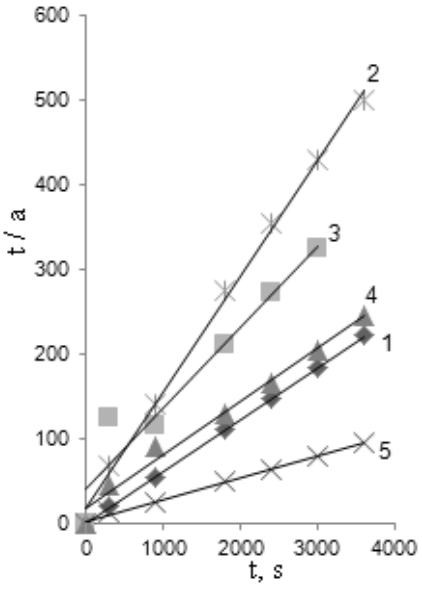

Fig. 4. Kinetic curves of adsorption of DMD from aqueous solutions by synthetic zeolites in the presence of phosphoric acid at 75 °C in the framework of pseudo-second order model

Рис. 4. Кинетические кривые адсорбции ДМД из водных растворов синтетическими цеолитами в присутствии фосфорной кислоты при 75 ° С в рамках модели псевдо-второго порядка

Table 2

Kinetic constants of adsorption of DMD from aqueous solutions by synthetic zeolites in the presence of phosphoric acid at 75 °C in the framework of pseudo-first and pseudo-second order models

***Таблица 2*. Кинетические константы адсорбции ДМД из водных растворов синтетическими цеолитами в присутствии фосфорной кислоты при 75 °С в рамках моделей псевдо-первого и псевдо-второго порядка**

Zeolite mark		$\ln(a_{eq}-a) = \ln a_{eq} - k_1 t$			$t/a=1/k_2a^2_{eq}+t/a_{eq}$		
	$a_{exp.\ eq.}$, mg/g	$k_1 \cdot 10^3$, s^{-1}	$a_{eq.}$, mg/g	R	$k_2 \cdot 10^3$, mg/g×s	$a_{eq.}$, mg/g	R
KA	14.73±0.74	1.48±0.09	14.90±0.90	0.973	2.12±0.13	15.87±0.80	0.992
NaA	16.23±1.14	2.30±0.12	2.83±0.14	0.872	3.78±0.16	16.33±0.98	0.999
CaA	37.32±2.22	1.84±0.13	23.20±1.20	0.982	1.72±0.09	41.54±2.10	0.990
CaX	7.22±0.40	0.68±0.034	3.36±0.14	0.777	4.04±0.04	7.36±0.37	0.984
NaX	9.50±0.50	1.17±0.06	8.20±0.40	0.978	2.12±0.11	10.57±0.53	0.981

From the data obtained, it follows that the values of the equilibrium adsorption (a_{eq}) of DMD on synthetic zeolites calculated using equation **5** differ significantly from the experimentally calculated values. Therefore, the application of the pseudo-first-order model to describe the kinetics of DMD adsorption on synthetic zeolites is not correct (Fig. 3, Table 2). The values of the equilibrium adsorption (a_{eq}) of DMD on synthetic zeolites calculated using equation **6** are close to experimentally determined parameters (Fig. 4, Table 2). Therefore, the pseudo-second-order equation is applicable for describing the kinetics of DMD adsorption on synthetic zeolites.

CONCLUSIONS

We have found that the process of adsorption of DMD by synthetic zeolites (KA, NaA, CaA, CaX, NaX) in the presence of phosphoric acid is determined by the values of the diameter of the pores. With increase in pore diameter of the zeolite the internal diffusion effect on the adsorption process is increased. It is shown that the value of pore diameter of synthetic zeolites does not influence on the adsorption equilibrium time of DMD. The adsorption equilibrium time for all used stamps zeolites is 900 s. The kinetics of adsorption of DMD on synthetic zeolites can be correctly described by a pseudo-second-order equation.

ЛИТЕРАТУРА

1. **Yamabe S., Fukuda T., Yamazaki S.** A new intermediate in the Prins reaction. *Beilstein J. Org. Chem.* 2013. V. 51. N 9. P. 476-485. DOI: 10.3762/bjoc.9.51.
2. **Yadav J.S., Subba Reddy B.V., Jayasudhan Reddy Y., Phaneendra Reddy B., Adinarayana Reddy P.** A novel Prins-alkynylation reaction for the synthesis of 4-phenacyl tetrahydropyrans. *Tetrahedron Lett.* 2010. V. 51. N 8. P. 1236-1239. DOI: 10.1016/j.tetlet.2009.12.117.
3. **Pastor I.M., Yus M.** Focused update on the Prins reaction and the Prins cyclization. *Current Org. Chem*. 2012. V. 16. N 10. P. 1277-1312. DOI: 10.2174/138527212800564196.
4. **Dumitriu E., Hulea V., Fechete I., Catrinescu C., Auroux A., Lacaze J.F., Guimon C.** Isoprene by Prince condensation over acidic molecular sieves. *Appl. Catal. A: Gen.* 1999. V. 181. N 1. P. 15-28.
5. **Платэ Н.А., Сливинский Е.В.** Основы химии и технологии мономеров. М: Наука. 2002. 696 с.
6. **Тухватшин В.С., Насыров И.Ш., Беланогов И.А., Талипов Р.Ф.** Синтез изопрена. РИЦ БашГУ. 2017. 72 с.
7. **Telalović S., Maheswari J. F., Ramanathan R., Chuah A., Hanefeld U.** Synergy between Bronsted acid sites and Lewis acid sites. *Chem. Commun. (Cambridge, England).* 2008. V. 7345. N 38. P. 4631. DOI: 10.1039/b807953f.
8. **Ордомский В.В., Сушкевич В.Л., Иванова И.И.** Патент РФ № 2412148. 2011.
9. **Мазина Л.А.** Патент РФ № 2459790. 2012.
10. **Ордомский В.В., Сушкевич В.Л., Иванова И.И.** Патент РФ № 2446138. 2012.
11. **Котельников Г.Р., Сиднев В.Б., Качалов Д.В., Луговкин С.Н., Комаров С.М., Чуркин В.Н., Глушаков М.И.** Патент РФ № 2448939. 2012.

REFERENCES

1. **Yamabe S., Fukuda T., Yamazaki S.** A new intermediate in the Prins reaction. *Beilstein J. Org. Chem.* 2013. V. 51. N 9. P. 476-485. DOI: 10.3762/bjoc.9.51.
2. **Yadav J.S., Subba Reddy B.V., Jayasudhan Reddy Y., Phaneendra Reddy B., Adinarayana Reddy P.** A novel Prins-alkynylation reaction for the synthesis of 4-phenacyl tetrahydropyrans. *Tetrahedron Lett.* 2010. V. 51. N 8. P. 1236-1239. DOI: 10.1016/j.tetlet.2009.12.117.
3. **Pastor I.M., Yus M.** Focused update on the Prins reaction and the Prins cyclization. *Current Org. Chem*. 2012. V. 16. N 10. P. 1277-1312. DOI: 10.2174/138527212800564196.
4. **Dumitriu E., Hulea V., Fechete I., Catrinescu C., Auroux A., Lacaze J.F., Guimon C.** Isoprene by Prince condensation over acidic molecular sieves. *Appl. Catal. A: Gen.* 1999. V. 181. N 1. P. 15-28.
5. **Plate N.A., Slivinskii E.V.** The basics of chemistry and monomers technologies. M.: Nauka. 2002. 696 p. (in Russian).
6. **Tukhvatshin V.S., Nasyrov I.Sh., Belanogov I.A., Talipov R.F.** Synthesis of isoprene. Ufa: Bashkir State University. 2017. 72 p. (in Russian).
7. **Telalović S., Maheswari J. F., Ramanathan R., Chuah A., Hanefeld U.** Synergy between Bronsted acid sites and Lewis acid sites. *Chem. Commun. (Cambridge, England).* 2008. V. 7345. N 38. P. 4631. DOI: 10.1039/b807953f.
8. **Ordomskii V.V., Syhkevich V.L., Ivanova I.I.** RF Patent N 2412148. 2011 (in Russian).
9. **Mazina L.A.** RF Patent N 2459790. 2012.
10. **Ordomskii V.V., Sushkevich V.L., Ivanova I.I.** RF Patent N 2446138. 2012 (in Russian).

12. **Бикбулатов И.Х., Даминев Р.Р., Юнусов Д.Ш., Бачонина Е.И.** Патент РФ № 2417977. 2011.
13. **Бикбулатов И.Х., Даминев Р.Р., Юнусов Д.Ш., Бачонина Е.И.** Патент РФ № 2417979. 2011.
14. **Фадеева В.И., Шеховцова Т.Н., Иванов В.М.** Основы аналитической химии. Практическое руководство. М.: Высш. шк. 2003. 463 с.
15. **Краснова Т.А., Голубева Н.С., Беляева О.В.** Извлечение фенола из органоминеральных смесей. *Актуал. пробл. современ. науки.* 2006. № 4. С. 143-146.
16. **Неудачкина Л.К., Петрова Ю.С., Засыхин А.С., Осипова В.А., Горбунова Е.М., Ларина Т.Ю.** Кинетика сорбции ионов тяжелых металлов пиридилэтилированными аминопропилполисилоксанами. *Аналитика и контроль*. 2011. Т. 15. № 1. С. 87-95.
17. **Крижановская О.О., Синяева А.А., Карпов С.И., Селеменев В.Ф., Бородина Е.В., Росснер Ф.** Кинетические модели при описании сорбции жирорастворимых физиологически активных веществ высокоупорядоченными неорганическими кремнийсодержащими материалами. *Сорбцион. и хроматографич. процессы*. 2014. Т. 14. № 5. С. 784-794.
18. **Романцова И.В., Бураков А.Е., Кучерова А.Е.** Изучение кинетики процесса жидкофазной адсорбции органических веществ на гибридных наноструктурированных углеродных сорбентах. Тез. докл. VI Всерос. науч.-практич. конф. "Современные наукоемкие инновационные технологии". Самара: Самарский научный центр Российской академии наук. 2014. С. 611-614.
19. **Kupova O.Yu., Vakulin I.V., Talipov R.F.** Ab initio study of 1,3-dioxanes formation from formaldehyde dimer and alkenes. *Computat. Theor. Chem.* 2013. V. 1013. P. 57-61. DOI: 10.1016/j.comptc.2013.02.024.
20. **Купова О.Ю., Вакулин И.В., Талипова Г.Р., Талипов Р.Ф.** Квантовохи-мическое изучение образования 1,3-диоксанов из димера формальдегида и алкенов. *Бутлеров. сообщ*. 2012. Т. 32. № 13. С. 123-127.
21. **Вакулин И.В., Купова О.Ю., Талипов Р.Ф.** Квантовохимическое изучение особенностей присоединения олигомеров формальдегида к алкенам. *Вестн. Башкир. ун-та*. 2010. Т. 15. № 2. С. 294-297.

11. **Kotelnikov G.R., Sidnev V.B., Kachalov D.V., Lygovkin S.N., Komarov S.M., Churkin V.N., Glushakov M.I.** RF Patent N 2448939. 2012 (in Russian).
12. **Bikbulatov I.Kh., Daminev R.R., Yunusov D.Sh., Bachonina E.I.** RF Patent N 2417977. 2011 (in Russian).
13. **Bikbulatov I.Kh., Daminev R.R., Yunusov D.Sh., Bachonina E.I.** RF Patent N 2417979. 2011 (in Russian).
14. **Fadeeva V.I., Shekhovtsova T.N., Ivanova V.M.** The basics of analytical chemistry. Practical course. M.: Vyssh. shk. 2003. 463 p. (in Russian).
15. **Krasnova T.A., Golybeva N.S., Belyaeva O.V.** Extraction of phenol from organo-minerals mixtures. *Akt. Probl. Sovrem. Nauki.* 2006. N 4. P. 143-146 (in Russian).
16. **Neudachkina L.K., Petrova Yu.S., Zasykhin A.S., Osipova V.A., Gorbunova E.M., Larina T.Yu.** Kinetics of sorption of heavy metal ions by pyridylethylated aminopropylpolysiloxane. *Analitika Kontrol*. 2011. V. 15. N 1. P. 87-95 (in Russian).
17. **Krizhanovskaya O.O., Sinyaeva L.A., Karpov S.I., Selemenev V.F., Borodina E.V., Ressner F.** Kinetic models in describing the sorption of fat-soluble physiologically active substances by highly ordered inorganic siliceous materials. *Sorpts. Khromatogr. Protsessy.* 2014. V. 14. N 5. P. 784-794 (in Russian).
18. **Romantsova I.V., Burakov A.E., Kucherova A.E.** Study of the kinetics process of the liquid-phase adsorption of organic substances on hybrid nanostructured carbon sorbents. Abstracts of VI Russian scientific-practical conference "Modern science-intensive innovative technologies". Samara: Samara Scientific Center of the Russian Academy of Sciences. 2014. P. 611-614. (in Russian).
19. **Kupova O.Yu., Vakulin I.V., Talipov R.F.** Ab initio study of 1,3-dioxanes formation from formaldehyde dimer and alkenes. *Computat. Theor. Chem.* 2013. V. 1013. P. 57-61. DOI: 10.1016/j.comptc.2013.02.024.
20. **Kupova O.Yu., Vakulin I.V., Talipova G.R., Talipov R.F.** Quantum-chemical study of the formation of 1,3-dioxanes from formaldehyde dimer and alkenes. *Butlerov Soobshch.* 2012. V. 32. N 13. P. 123-127 (in Russian).
21. **Vakulin I.V., Kupova O.Yu., Talipov R.F.** Quantum-chemical study of the features of addition of oligomers of formaldehyde to alkenes. *Vest. Bashkir Gos. Un-ta.* 2010. V. 15. N 2. P. 294-297 (in Russian).

Поступила в редакцию 06.12.2016
Принята к опубликованию 25.10.2018

Received 06.12.2016
Accepted 25.10.2018