CINÉTICA DA IMPREGNAÇÃO DE POLÍMEROS POR TRIALQUILAMINA

KINETICS OF POLYMER CARRIER IMPREGNATION BY TRIALKYLAMINE

КИНЕТИКА ИМПРЕГНИРОВАНИЯ ПОЛИМЕРНОГО НОСИТЕЛЯ ТРИАЛКИЛАМИНОМ

TROSHKINA, I. D.^{2*}; OBRUCHNIKOVA, J. A.²; VESELOVA, O. A.²; PESTOV, S. M.¹

¹Dmitry Mendeleev University of Chemical Technology of Russia, Department of Expert Examination in Drug Testing and Narcoanalysis
20 Geroyev Panfilovtsev St., Moscow, 125480, Russian Federation

²Moscow Technological University, Department of Physical Chemistry
86 Vernadsky Ave., Moscow, 119454, Russian Federation

* *Corresponding author*
tid@rctu.ru

Received in 20 September 2018; received in revised form 02 December 2018; accepted 13 December 2018

RESUMO

O imediatismo do problema em estudo deve-se à falta de dados sobre a cinética de impregnação de transportadores de polímeros com agentes de extração. O objetivo deste artigo é obter as características cinéticas da impregnação de um transportador macroporoso polimérico - uma resina catiônica fracamente ácida com grupos carboxila - com trialquilamina e suas soluções em acetona. As curvas cinéticas integrais da adsorção do agente extrator no transportador foram obtidas. Isso permitiu estimar o tempo de equilíbrio pelo método de volume de solução limitado. Esse tempo foi de 25 a 30 horas, diminuindo com a aplicação de um agente de diluição e com o aumento da temperatura. As características cinéticas de impregnação foram calculadas por meio dos modelos de pseudo-segunda ordem, Elovich e difusão interna. O modelo de pseudo-segunda ordem descreve os dados cinéticos experimentais com alto grau de correlação (R^2 0,995-0,997) e aponta que a interação com dois centros de sorção possivelmente ocorre com a adsorção de uma única molécula de trialquilamina. As constantes de taxa de impregnação através de um agente de extração foram calculadas usando todos os modelos cinéticos. Com base na magnitude da energia de ativação aparente (37 ± 14 kJ/mol), pode-se assumir que a difusão é o passo limitante do processo de impregnação. Este artigo pode ser útil para criar impregnados contendo agentes de extração de várias classes.

Palavras-chave: cinética, impregnação, transportador polimérico macroporoso, trialquilamina, modelos cinéticos.

ABSTRACT

The immediacy of the problem under study is due to the lack of data on the kinetics of polymer carrier impregnation with extraction agents. The article is aimed at obtaining the kinetic characteristics of the impregnation of a polymeric macroporous carrier—a weakly acidic cation resin with carboxyl groups—with trialkylamine and its solutions in acetone. The integral kinetic curves of the extraction agent adsorption on the carrier were obtained. This allowed estimating the time of equilibrium by the limited solution volume method. This time was 25-30 hours, decreasing with the application of a dilution agent and with the increase in temperature. The kinetic impregnation characteristics were calculated by means of the pseudo-second-order, Elovich, and internal diffusion models. The pseudo-second-order model describes the experimental kinetic data with a high correlation degree (R^2 0.995-0.997) and points out that interaction with two sorption centres possibly takes place with the adsorption of a single trialkylamine molecule. The impregnation rate constants via an extraction agent were calculated using all kinetic models. Based on the apparent activation energy magnitude (37 ± 14 kJ/mol), it can be assumed that diffusion is the rate-limiting step of the impregnation process. This article can be useful for creating impregnates containing extraction agents of various classes.

Keywords: kinetics, impregnation, macroporous polymeric carrier, trialkylamine, kinetic models.

АННОТАЦИЯ

Актуальность исследуемой проблемы обусловлена отсутствием данных по кинетике импрегнирования (пропитывания) экстрагентами полимерных носителей. Статья направлена на получение кинетических характеристик импрегнирования полимерного макропористого носителя – слабокислотного катионита с карбоксильными группами триалкиламином и его растворами в ацетоне. Методом ограниченного объема раствора получены интегральные кинетические кривые адсорбции экстрагента на носителе, позволяющие оценить время установления равновесия. Это время составило 25–30 ч, уменьшаясь при использовании разбавителя, а также повышении температуры. С помощью моделей псевдо-второго порядка, Еловича и внутренней диффузии рассчитаны кинетические характеристики процесса импрегнирования. Модель псевдо-второго порядка, по которой экспериментальные кинетические данные описываются с высокой степенью корреляции (R^2 0,995–0,997), указывает на то, что при адсорбции одной молекулы триалкиламина происходит, возможно, взаимодействие с двумя сорбционными центрами. Рассчитаны константы скорости импрегнирования экстрагентом при использовании всех кинетических моделей. Исходя из величины кажущейся энергии активации (37 ± 14 кДж/моль), можно предположить, что скорость-лимитирующей стадией процесса импрегнирования является диффузия. Материалы статьи могут быть полезными при создании импрегнатов, содержащих экстрагенты различных классов.

Ключевые слова: кинетика, импрегнирование, макропористый полимерный носитель, триалкиламин, кинетические модели.

INTRODUCTION

Sorption and extraction processes are widely used for the recovery and concentration of elements. Sorption of the elements, usually from dilute solutions, is carried out with the use of synthetic resins, activated carbons, inorganic sorbents, fibres and other materials (Dragan, 2015; Free, 2013; Kabay *et al.*, 2010; Kauckzor and Meyer, 1978; Kosandrovich and Soldatov, 2012; Laskorin, 1989; Meretukov, 1980; Mukhin *et al.*, 2000; Myasoedova and Nikashina, 2006; Warshawsky, 1981; Warshawsky and Cortina, 2002; Zagorodni, 2007). Extraction agents — often in the form of a solution in an organic diluent — are applied for the liquid-phase extraction.

Sorption materials used in hydrometallurgy should have good kinetic characteristics. The time of establishing the sorption equilibrium during metal extraction via granular synthetic ion exchangers usually exceeds 4–6 hours. The fibrous ion exchangers possess the best kinetic properties, but the problems of instrumentation to use them are not

completely solved at the moment.

Materials, whose properties are found between sorbents and extractants, are used for the extraction, separation, and concentration of elements. They are mainly obtained by means of impregnating the porous matrix with an extractant. Impregnated materials are called 'Solvent Impregnated Resins' (SIR). Polymeric carriers, ion exchangers, activated carbons, silica gel and other synthetic and natural materials are used as a porous matrix. The impregnates with the applied extractant are widely used in extraction chromatography.

In terms of density, bulk density, mechanical strength, the impregnates are similar to sorbents, and the mechanism of component extraction by the impregnates is similar to the extractive mechanism. The capacitive and kinetic characteristics of these materials are mainly determined by the porous structure, type, and state of the extraction agent in the matrix (Kabay *et al.*, 2010; Warshawsky and Cortina, 2002; Zagorodni, 2007).

The absence of a chemical bond between the extraction agent and the polymer matrix is a

characteristic feature of the impregnates. Due to the mobility of the liquid phase, these materials have improved kinetic characteristics.

The application of such materials makes it possible to exclude toxic and fire hazardous organic diluents provides means for carrying out the processes of extraction from non-clarified solutions and pulps and ensures the reduction of the contamination of raffinates and sewage waters with organic reagents in comparison with the liquid extraction.

The production method associated with the use of extractant solutions in an organic diluent, whose role consists in swelling and loosening the polymer base, has become the most widespread among the known methods of creating such materials.

The organic phase can either completely fill the carrier pores or be distributed over its surface in the form of a film, depending on the application technique and the amount of injected extractant (Meretukov, 1980).

The purpose of a carrier is the ability to tightly hold the mobile phase. In this respect, it must meet the following requirements: to be well wetted by mobile phase; to be chemically inert, not to react with the mobile phase, not to absorb the components being extracted; to have the particles of the same size and shape, better spherical, which contributes to the most uniform and reproducible column filling; to have a sufficient surface for the mobile phase, to be evenly distributed in the form of a thin film; to have sufficient mechanical strength.

The carriers may be divided into two main large groups.

The carriers, whose surface is covered with hydroxyl groups, belong to the first group. Such substances have high surface energy and can be well wetted by such strongly polar liquids as water only. This group includes mainly inorganic materials, such as silicates, silica gels, glass, aluminum oxide, cellulose. Their general disadvantage lies in the fact that the hydroxyl groups themselves are capable of ion exchange. Besides, these carriers can retain a limited number of extractants only.

Various polymer materials that have low surface energy and are well wetted with various organic solvents may be referred to the second group.

The composition of various carriers and

extractants is rather well studied, and the rationale for their choice is usually available. However, there is almost no information on the kinetics of carrier impregnation by an extractor determining and conditions of the impregnation the process. This paper aims to fill this gap.

The objective of this research is to define the kinetic impregnation characteristics of a polymeric macroporous carrier in case of impregnation with trialkylamine extractant (TAA).

MATERIALS AND METHODS

Reagents. Technical TAA (R_3N) was used as an extractant, where $R = C_nH_{2n+1}$, $n = 8-10$, whose properties corresponded to those stated in TU 2413-003-48590531-2009. Acetone of chemically pure grade was used to prepare the TAA solution.

Spherically granulated, macroporous, weak-acid cation resin on an acryl-divinylbenzene base containing carboxyl groups (TU 2227-019-72285630-2009-2009) was used as a polymeric carrier. The size of its granules was (0.63 ± 1.6) mm.

Methodology. Impregnation of a polymer carrier was fulfilled by the limited solution volume method (Kokotov and Pasechnik, 1979) in excess of extractant or its solution in acetone under the static conditions. For that, a sample of the air-dried carrier (1 g) was put in contact with 2 ml of TAA or 4 ml of its solution in acetone (the ratio of TAA and acetone volumes was 1:1) with gentle mixing on the LAB-PU-01 shaking apparatus (30 rpm) for a certain time period. The impregnation time was from 10 to 1440 min. The carrier, saturated with the extractant, was transferred to the vacuum filter and washed with 10-15 cm³ of distilled water upon the expiration of adsorption time. The drying of impregnating washed free of the excess of the extractant, was accomplished in a drying chamber at a temperature of 50 °C for 5 hours.

When studying the influence of temperature on the impregnation process, the carrier samples were in contact with TAA in a thermostated cell at a temperature of 50 °C (calibration error: ± 0.1 °C).

The TAA content in the impregnate was evaluated based on the difference in weight of the initial polymer and the obtained impregnate

(under equilibrium conditions) according to the following formula:

$$\omega = (m_{imp} - m_{ini}) / m_{imp} \cdot 100 \%, \quad (\text{Eq.1})$$

where ω is the extractant mass fraction in the impregnate (%), m_{imp} is the impregnate weight (g); m_{ini} is the primary carrier mass (g).

The impregnation rate was estimated based on the behaviour of the impregnate sorption capacity in time. The process behaviour can be examined with the help of a metal. Rhenium was chosen for this purpose since TAA is widely used for its extraction, and the isotherm of sorption by the rhenium-based impregnate is linear in a wide range of the equilibrium concentrations of rhenium (Palant, 2015, p. 151).

Rhenium sorption by the impregnated samples, saturated during the above-mentioned period of time, was carried out from the sulfuric acid solutions (pH 2), containing 100 mg/dm³ of rhenium, under static conditions. Prior to sorption, each impregnate sample was put in contact with a solution having the same pH value as the initial solution, prepared for the sorption. The time of contact was 30 min. The solution pH value was determined using SevenEasypH pH meter (Mettler Toledo). Then, the impregnate was separated from the solution and put in contact with the solution containing rhenium with a ratio of impregnate phases to solution of 1:1000 (0.1 g of sorbent: 100 cm³ of solution) on the LAB-PU-01 shaking apparatus (120 rpm) for 4 hours, or for 12 hours without shaking. The phase separation was performed, and the liquid phase was filtered through a 'white tape' filter after the contact. The resulting solution was analyzed for rhenium content by the photometric method with rhodanate complexes (Borisova and Ermakov, 1974) using the KFK-03-01 concentration photoelectric photometer (Experimental Optomechanical Plant, Russia). The impregnate sorption capacity (CE, mg/g) was calculated according to the balance ratio:

$$CE = (C_{ini} - C_{con}) \cdot V_{sol} / g, \quad (\text{Eq.2})$$

where CE is the sorption capacity (mg/g); C_{ini} is the concentration in the initial solution (mg/l); C_{con} is the concentration in the solution after sorption

(mg/l); V_{sol} is the solution volume (dm³); g is the sorbent sample weight (g).

To process the kinetic data on TAA impregnation, the data on impregnate capacity of rhenium was used. These data were recalculated through the saturation degree F (%), which was determined by the following equation:

$$F = CE / C_{equal} \cdot 100, \quad (\text{Eq.3})$$

where CE_{equal} is the capacity of the rhenium impregnate being observed when the equilibrium is reached during the impregnation.

RESULTS AND DISCUSSION

Integral kinetic curves in the CE – t coordinates, where t is the impregnation time (Fig. 1), were obtained to determine the optimal impregnation time of the polymer carrier with TAA and its solution in acetone.

The data analysis in Fig. 1 shows that the equilibrium in the carrier/extractant system occurs after 25-35 hours. The presence of a diluent (acetone) contributes to an increase in the impregnation rate. In this case, the process of TAA diffusion into the carrier is accompanied by the process of polymer carrier swelling in the presence of acetone, which promotes the adsorption of its larger amount per unit time as compared with the original extractant diffusion.

The increase in the impregnation temperature (Fig. 2) also contributes to the increase in its rate.

Apparently, a decrease in the extractant viscosity also contributes to this.

Mathematical processing of the experimental kinetic data was performed in accordance with the models of sorption kinetics that describe the diffusion and the mechanism of interaction of various numbers of molecules in the process by means of linearizing them according to the following equations (Azizian, 2004; Foo and Hameed, 2010; Helfferich, 1962; Ho, 2006; Tran, *et al.*, 2017):

1. Pseudo-first-order model

$$\lg(Q_e - Qt) = \lg Q_e - (k_1 / (2.303t)) \quad (\text{Eq.4})$$

2. Pseudo-second-order model

$$t/Q_t = 1/(k_2 \cdot Q_e^2) + 1/Q_e t \quad (\text{Eq.5})$$

3. Internal diffusion model

$$Q_t = k_{id} \cdot t^{0.5} + C \quad (\text{Eq.6})$$

4. Elovich model

$$Q_t = 1/\beta \cdot \ln(\alpha \beta) + 1/\beta \cdot \ln(t), \quad (\text{Eq.7})$$

where Q_e is the equilibrium sorption capacity (mg/g); Q_t is the sorption capacity at time t (mg/g); $k_1(k_2)$ is the rate constant of the pseudo-first (pseudo-second) order ($\text{min}^{-1}(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$); k_{id} is the internal diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$); α is the sorption process initial rate ($\text{r} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); β is the Elovich rate constant ($\text{r} \cdot \text{mg}^{-1}$).

The graphical representation of the mathematical data processing results according to these models is presented in Fig. 3-6.

According to the correlation coefficient values, the kinetic impregnation curves can be best described with the pseudo-second-order model, the Elovich model, and the internal diffusion model.

Apparently, interaction with two sorption centres takes place during the adsorption of a single TAA molecule in accordance with the pseudo-second order model.

The Elovich model is used for the description of adsorption processes, so it can be assumed that the physical adsorption of the extractant on the carrier's inner and outer surfaces is a limiting stage while impregnating. The internal diffusion model suggests that the internal diffusion of TAA in the pores of the polymeric matrix can be one of the process limiting stages.

The velocity constants and the correlation factors of the linearized lines, describing the impregnation process for the selected models are presented in Table 1.

According to the constants values (Table

1) obtained while describing the integral kinetic curves according to the pseudo-second-order model equation, the impregnation rate increase is observed at a temperature effect. On the contrary, the injection of a diluent (acetone), reduces the TAA layer formation rate of the polymer carrier surface despite the fact that the extractant solution is less viscous in the diluent.

The value of apparent energy (E_{app} , kJ/mol) of the sorption activation was calculated from the dependence $\ln k = f(T^{-1})$, which follows from the Arrhenius equation. The calculation was based on the formula below, using the rate constants obtained when employing the pseudo-second-order equation:

$$E_{app} = (R \cdot \ln(k_1/k_2) \cdot T_1 \cdot T_2)/(T_2 - T_1) \quad (\text{Eq.8})$$

where R is the universal gas constant ($\text{J}/(\text{mol} \cdot \text{K})$); k_1 and k_2 are the rate constants at a temperature T_1 and T_2 , ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); T_1 is the temperature (295 K); T_2 is the temperature (323K).

Based on the obtained value of the apparent activation energy (37 ± 4 kJ/mol), it can be assumed that the diffusion is a rate-limiting stage of an impregnation process. The pseudo-second-order model, by which the experimental kinetic data is described with a high correlation degree (R^2 0.995-0.997), points out that the interaction with two sorption centres possibly takes place while the adsorption of a single TAA molecule is in progress.

CONCLUSIONS:

The kinetic data obtained by the limited solution volume method made it possible to determine the optimal impregnation time of a macroporous polymeric carrier with technical TAA, that is 25-35 h. The presence of a highly volatile diluent (acetone) contributes to the reduction of the extractant layer formation rate on the carrier surface, thereby decreasing the sorption characteristics over time. On the contrary, the temperature increase leads to the increase in the impregnation rate, since the extractant viscosity reduces without the injection of additional components of the organic phase (diluent). This can be confirmed by the rate

constants, calculated according to the data of linearized integral kinetic curves with the aid of a pseudo-second-order model.

The impregnation process takes place in the diffusion region since the apparent activation energy of the process is relatively low (37 ± 4 kJ/mol). However, the kinetic data, described with a high degree of correlation by means of the pseudo-second order and Elovich models, is indicative of the contribution of TAA physical adsorption on the carrier and the possible interaction of the extractant molecule with two sorption centres of the carrier.

To shorten the impregnation time, it is reasonable to carry out the process of obtaining impregnates at an elevated temperature.

ACKNOWLEDGEMENTS:

This research was partially funded by the Ministry of Education and Science of the Russian Federation under the Subsidy Agreement No. 14.580.21.0004 of 19.08.2015 (project identification number RFMEFI58015X0004).

REFERENCES:

1. Azizian, S.; *Journal of Colloid and Interface Science* **2004**, 276, 47.
2. Borisova, L. V.; Ermakov, A. N.; *Analytical chemistry of rhenium*, Khimiya: Moscow, 1974.
3. Dragan, E. S., ed.; *Advanced separations by specialized sorbents*, CRC Press: Boca Raton, 2015.
4. Foo, K. Y.; Hameed, B. H.; *Chemical Engineering Journal* **2010**, 156, 2.
5. Free, M. L.; *Hydrometallurgy. Fundamentals and applications*, John Wiley & Sons: Hoboken, 2013.
6. Helfferich, F.; *Ionites. Fundamentals of ion exchange*, Inostrannaya literatura: Moscow, 1962.
7. Ho, Y. S.; Review of second-order models for adsorption systems, *J. of Hazardous Materials* **2006**, B136, 681.
8. Kabay, N.; Cortina, J. L.; Trochimczuk, A.; Streat, M.; *React. Funct. Polym.* **2010**, 70(8), 484.
9. Kauckzor, H. W.; Meyer, A.; *Hydrometallurgy* **1978**, 3, 65.
10. Kokotov, Yu.A.; Pasechnik, V. A.; *Ion exchange equilibrium and kinetics*, Khimiya: Leningrad, 1979.
11. Kosandrovich, E. G.; Soldatov, V. S.; Fibrous Ion Exchangers; Inamuddin; Luqman, M., eds.; *Ion Exchange Technology I: Theory and Materials*, Springer Science+Business Media B.V., 2012, 299.
12. Laskorin, B. N., ed.; *Ion-exchange materials for hydrometallurgy, waste-water treatment and water conditioning processes*, All-Russian Scientific Research Institute of Chemical Technology: Moscow, 1989.
13. Meretukov, M. A.; Application of impregnated materials for extraction and separation of non-ferrous metals, *Review. Inform. TsNIEITsM* **1980**, 3.
14. Mukhin, V. M.; Tarasov, A. V.; Klushin, V. N.; *Active coals of Russia*, Metallurgy: Moscow, 2000.
15. Myasoedova, G. V.; Nikashina, V. A.; *Russian Chemistry Journal* **2006**, 50(5), 55.
16. Palant, A. A.; Troshkina, I. D.; Chekmarev, A. M.; Kostylev, A. I.; *Rhenium technology*, Galleya-Print: Moscow, 2015.
17. Tran, H. N.; You, S.-J.; Hosseini-Bandegharai, A.; Chao, H.-P.; *Water Research* **2017**, 120, 88.
18. Warshawsky, A.; Cortina, J. L.; *Proc. of the Intern. solvent extract. conf.: ISEC* **2002**.
19. Warshawsky, A.; *Ion Exchange and Solvent Extraction* **1981**, 8(3), 229.
20. Zagorodni, A. A.; *Ion Exchange Materials*, Elsevier: Amsterdam, London, 2007.

Table 1. Rate constant values of the TAA carrier impregnation

Pseudo-first-order model		Pseudo-second-order model		Internal diffusion model		Elovich model	
k_1, min^{-1}	R^2	$k_2, \text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$	R^2	$k_p, \text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$	R^2	$\beta, \text{g} \cdot \text{mg}^{-1}$	R^2
Trialkylamine (295K)							
0.0011	0.862	0.00025	0.994	2.79	0.829	0.085	0.967
Solution of trialkylamine in acetone (295K)							
0.0019	0.592	0.00017	0.986	2.12	0.796	0.059	0.937
Trialkylamine (323K)							
0.0037	0.573	0.00091	0.998	1.37	0.745	0.133	0.902

Figure 1. Kinetic curves of the cation exchanger impregnation with the TAA solution in acetone (□) and pure TAA (▲)

Figure 2. Kinetics of the cation exchanger impregnation with TAA at the temperatures of 295 (▲) and 323 (□) K

Figure 3. Dependence of $\lg(Q_e - Q_t)$ on time t for the experimental data on TAA carrier impregnation

Figure 4. Dependence of t/Q_t on time t for the experimental data on TAA carrier impregnation

Figure 5. Dependence of Q_t on $t^{0.5}$ for the experimental data on TAA carrier impregnation

Figure 6. Dependence of Q_t on $\ln(t)$ for the experimental data on TAA carrier impregnation