

**Research Article**

## **Sorption of niobium from hydrochloric acid solutions by phosphine oxide impregnated resins**

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### **ABSTRACT**

This paper addresses the problems of low efficiency of the niobium extraction processes and loss of the extractant during niobium sorption. This study aims to eliminate these shortcomings by using the impregnated resins that combine the properties of sorbents and extractants. Sorption of niobium from concentrated hydrochloric acid solutions by impregnated macroporous polymers, containing phosphine oxide and trialkylamine, was studied. Equilibrium and kinetics of niobium sorption by impregnated resins of better capacity were obtained. It was observed that the distribution coefficient of niobium in the weak acid cation exchanger reached maximum during the sorption from hydrochloric acid solutions with a concentration of 10 mol/dm<sup>3</sup>. Niobium sorption isotherm was described by the Henry equation, where constant K is 473±4 ml/g. Integral kinetic curves of sorption were obtained by the method of limited solution volumes, and effective niobium diffusion coefficients for impregnated resins were calculated (5.5·10<sup>-11</sup> and 1.9·10<sup>-11</sup> m<sup>2</sup>/s). Kinetic curves with the highest correlation degree were described by the pseudo-second-order equation with the rate constants of 0.0549 g·(mmol·min)<sup>-1</sup> (for solid polymeric extractants containing phosphine oxide) and 0.0521 g·(mmol·min)<sup>-1</sup> (for weak-acid cation exchanger). This paper can be of use when organizing niobium sorption from concentrated hydrochloric acid solutions for industrial purposes.

**Keywords:** niobium, sorption, impregnated resins, phosphine oxide, trialkylamine, macroporous support, isotherm, diffusion coefficient, rate constant.

### **INTRODUCTION**

Niobium is a refractory metal that is widely used for production of vacuum tubes, electrolytic capacitors, chemical processing equipment, aerospace superalloys, and micro-alloyed steel. The hydrometallurgical methods, including extraction and sorption, are employed for the processing of minerals and technogenic waste that contain niobium [1, 2]. The sorption processes are based on strong base and medium base ion exchangers [2, 3], while the extraction processes, on neutral extractants (tributyl phosphate) or anion-exchangers (amine salts, for example, trialkylamine) [3, 4]. The disadvantages of these methods, such as low efficiency in the case of sorption and loss of

extractant in the case of extraction, can be partially eliminated by using materials that combine the properties of sorbents and extractants [5-12]. Such materials can be divided into two groups: solid polymeric extractants (TVEX) and impregnated resins, differing by the method of production. The impregnated resins are obtained by impregnating the support with the extractant [5-8], and the TVEX by introducing the extractant during the synthesis of the polymer matrix [9-12]. These materials appear to have better kinetic performance than conventional ion exchangers and do not swell in aqueous solutions [8, 11]. The objective of this research is to determine the sorption

characteristics of impregnated resins and TVEX that contain variously radical phosphine oxide and technical grade trialkylamine, for the purpose of extracting niobium from hydrochloric acid solutions.

## MATERIALS AND METHODS

Niobium pentachloride ( $\text{NbCl}_5$ , 98% pure, Technical Specifications TU 1763-030-00545484-2002) was used to prepare the hydrochloric acid solutions. Niobium pentoxide ( $\text{Nb}_2\text{O}_5$ , 99% chemically pure, Technical Specifications TU 1763-019-00545484-2000) was used to prepare the sulfuric acid solutions.

The impregnated resins were prepared by impregnating the support (stationary phase) with the technical grade trialkylamine (TAA) under static conditions [13].

The macroporous polymer supports were used as such stationary phase, namely, spherically granulated weak-acid cation exchanger (Technical Specifications TU 2227-019-72285630-2009-2009) and styrene-divinylbenzene copolymer *Porolas-T* (TU 24.1-30168850-048-2005) [14].

Their main physical and chemical characteristics are given in Table 1.

**Table 1.** Characteristics of the polymer supports

Polymer support	Functional group	Matrix	Granular size (mm)	BET surface area ( $\text{m}^2/\text{g}$ )
Weak-acid cation exchanger	-COOH	Acrylic-divinylbenzene	0.63÷1.6	-
Copolymer <i>Porolas-T</i>	-	Styrene-divinylbenzene	0.63÷1.6	700-900

The properties of the technical grade trialkylamine  $\text{R}_3\text{N}$ , where  $\text{R} = \text{C}_n\text{H}_{(2n+1)}$ ,  $n = 8-10$ , complied with Technical Specifications TU 2413-003-48590531-2009. Impregnation of the polymer supports was carried out in excess of the extractant. After the specified time of impregnation, the saturated supports were transferred to a vacuum filter and washed with ethyl alcohol to remove the excess extractant. Then the impregnated resins were dried at  $50^\circ\text{C}$  for 5 hours in a drying cabinet. The extractant content in the impregnated resin was determined by the difference in weight of the initial polymer support and the impregnated resins, according to Formula 1:

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

where  $\omega$  is the extractant mass percentage (%),  $m_{\text{imp}}$  is the impregnated resin mass (g), and  $m_{\text{ini}}$  is the initial polymer support mass (g). The extractant mass percentages in the impregnated resins based on weak-acid cation exchanger (IPHOR-TAA) and copolymer *Porolas-T* (IPHOR-TAA) were 42 и 48 %, respectively. The solid polymeric extractants containing variously radical phosphine oxide (TVEX-PHOR) and tributyl phosphate (TVEX-TBP), taken for reference, were used in the investigation. Both extractants were produced by Leading Research Institute of Chemical Technology (VNIHT) AO. The characteristics

of these materials are can be found in [15]. The sorption of niobium by the impregnated resins and TVEX from the test solutions, which contained up to 300 mg/l of niobium, was studied under static conditions at different ratios of sorbent weight (g) to solution volume (ml). After contacting the phases with intensive stirring (120 rpm) in laboratory shaker LAB-PU-02 and their decantation, the concentration of niobium in the solution ( $C$ , mg/l) was determined by the photometric method [16]. Sorption capacity of the ion-exchangers (CE, mg/g) was calculated according to Formula 2:

$$CE = (C_{\text{ini}} - C_{\text{fin}}) \cdot V_{\text{sol}} / g \quad (2)$$

where CE is the sorption capacity (mg/g),  $C_{\text{ini}}$  is the niobium concentration in the initial solution (mg/l),  $C_{\text{fin}}$  is the niobium concentration after sorption (mg/l),  $V_{\text{sol}}$  is the solution volume (l), and  $g$  is the sorbent weight (g). The distribution coefficient of niobium in the impregnated resin or TVEX ( $K_d$ , ml/g) was determined as the ratio of the sorption capacity (CE, mg/g) to the solution concentration after sorption ( $C_{\text{fin}}$ , mg/l). The equilibrium characteristic of sorption — the isotherm — was determined by the method of weighed portions: the impregnated resin sample (0.1 g) was saturated with niobium from the sulfuric acid solutions at various values of the impregnated resin (g) to solution (ml) ratio. The niobium concentration in the initial solution was

300 mg/l. The niobium content in the sorbents was determined from the balance ratio, taking into account the analysis data on niobium concentration in the solutions and the ratio of the contacting phase volumes. The kinetics of niobium sorption was investigated by the method of limited solution volume [17] at the sorbent to solution ratio of 1:600 (g:ml) for 4 hours. The niobium content in the hydrochloric acid 10 mol/l solution was 300 mg/l.

## RESULTS AND DISCUSSION

To select a sorption material with the mobile extractant phase under static conditions, sorption

of niobium from hydrochloric acid solutions was studied using the following sorbents: TVEX-TBP, TVEX-PHOR, impregnated resins I-PHOR-TAA and IP-PHOR-TAA. The analysis of the data on niobium sorption by TVEX-TBP, given in [18], showed that the concentration of hydrochloric acid should be high ( $> 9$  mol/l); hence niobium was sorbed from the concentrated 10 mol/l solutions.

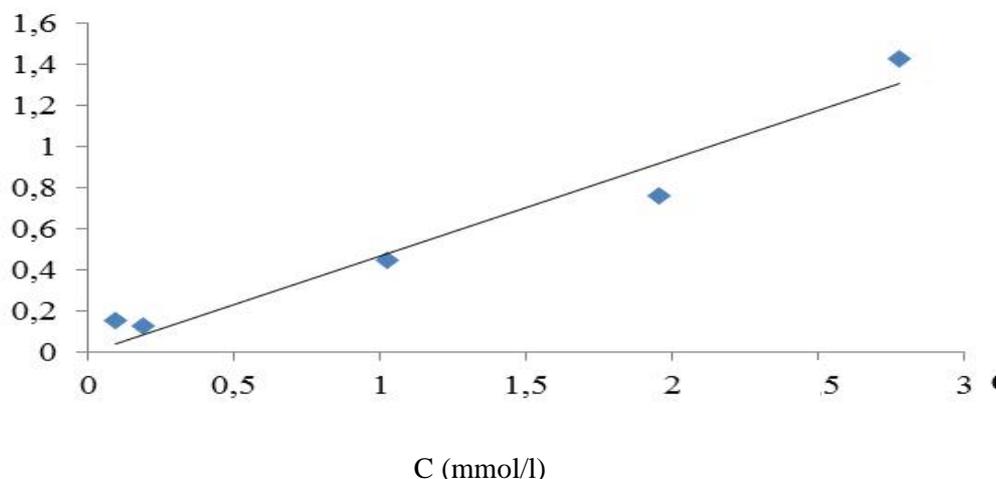
The capacity properties of the impregnated resins and TVEX in the extraction of niobium from hydrochloric acid solutions are given in Table 2.

**Table 2.** Niobium sorption by the impregnated resins and TVEX from hydrochloric acid solutions under the specified conditions: [Nb] – 100 mg/l; [HCl] – 10 mol/l, the sorbent to solution ratio – 1:100 (0.1 g : 10 ml)

Sorbent	Niobium sorption capacity (CE, mg/g)	Niobium distribution coefficient in the sorbent (Kd, mg/l)	Degree of extraction (%)
TVEX-TBP	10.8	386	79.4
TVEX-PHOR	11.8	659	86.9
I-PHOR-TAA	11.7	603	85.7
IP-PHOR-TAA	11.6	583	85.4

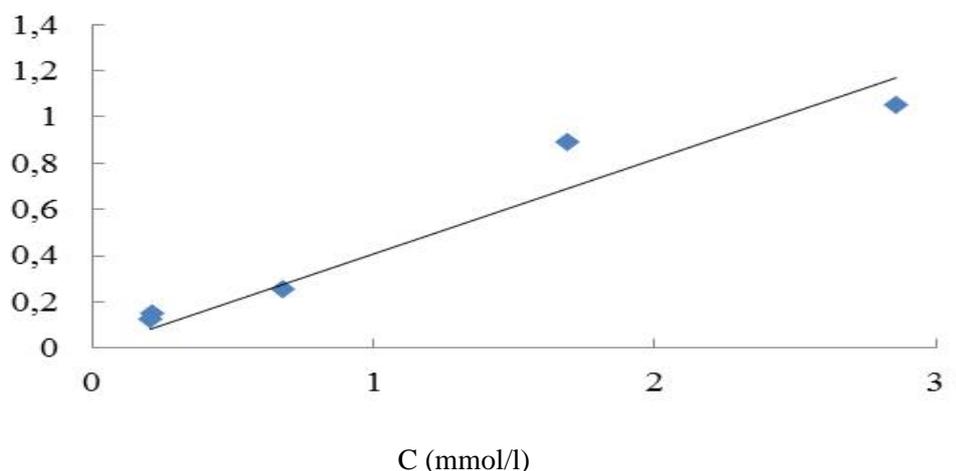
Analysis of the capacity properties of sorbents in the extraction of niobium (ref. Table 2) showed that the sorption capacity of TVEX-PHOR and the impregnated resin based on the macroporous cation exchanger I-PHOR-TAA, and the niobium distribution coefficient ( $> 603$  ml/g) have the highest values. The degree of niobium extraction in one contact at the specified sorption conditions exceeded 85.7%. Therefore, the study was continued with these sorbents. The isotherm is one of the most important equilibrium characteristics of the sorption process. The isotherms of niobium sorption by TVEX-PHOR and I-PHOR-TAA from hydrochloric acid 10 mol/l solutions are shown in Figures 1 and 2.

CE (mmol/g)



**Figure 1.** Isotherm of niobium sorption by TVEX-PHOR from HCl 10 mol/l solution.

CE (mmol/g)

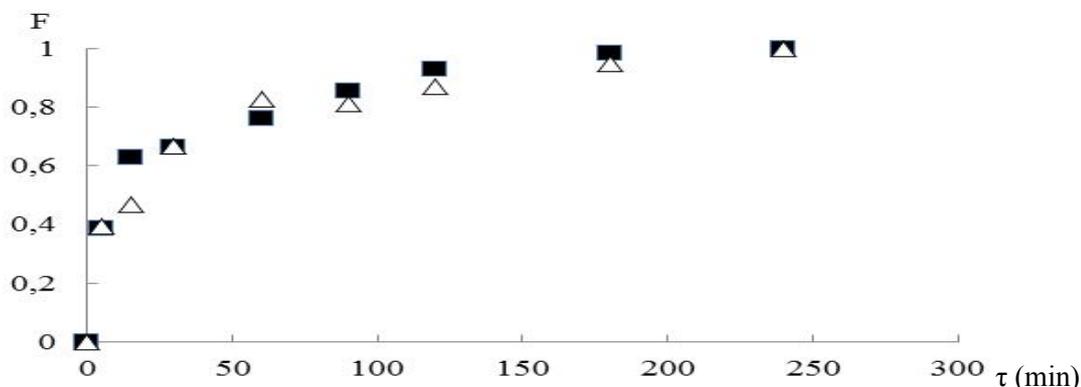


**Figure 2.** Isotherm of niobium sorption by I-PHOR-TAA from HCl 10 mol/l solution.

The dependences in the specified niobium concentration range are linear and can be described by the Henry equation (Formula 3):

$$CE = KC \quad (3)$$

where CE is the sorption capacity (mg/g), K is the Henry constant (ml/g), and C is the equilibrium metal concentration after sorption (mg/l). The calculated Henry constant values for the niobium sorption isotherms were  $473 \pm 4$  ml/g for TVEX-PHOR and  $410 \pm 8$  ml/g for I-PHOR-TAA. The integral kinetic curves of the niobium sorption by TVEX-PHOR and I-PHOR-TAA were obtained by the method of limited solution volume [17]. Based on this, the dependence of the saturation degree F on time was drawn (ref. Figure 3). It shows that the equilibrium in niobium sorption by the selected materials was reached in about 5 hours.



**Figure 3.** Dependence of the saturation degree F on time in the course of niobium sorption by TVEX-PHOR (■) and I-PHOR-TAA (Δ). The half-life period  $\tau_{0.5}$  was graphically determined from Figure 3; refer to Table 3.

**Table 3.** Kinetic properties of niobium sorption by TVEX-PHOR and I-PHOR-TAA from hydrochloric acid solutions.

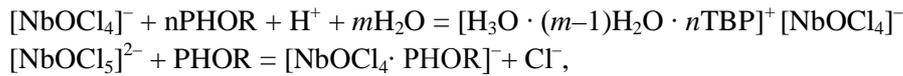
Sorbent	Half-life period $\tau_{0.5}$ (sec)	Effective diffusion factor D ( $m^2/sec$ )
TVEX-PHOR	110	$5.5 \cdot 10^{-11}$
I-PHOR-TAA	370	$1.9 \cdot 10^{-11}$

The effective diffusion factor was calculated according to the Formula 4 [17] given the half-life period ( $\tau_{0.5}$ ):

$$D = 0.03 \cdot R^2 / \tau_{0.5} \quad (4)$$

where D is the effective diffusion factor ( $m^2/sec$ ),  $\tau_{0.5}$  is the half-life period (sec), and R is the sorbent radius (m), which is equal to 0.45 mm for TVEX-PHOR granules and 0.48 mm for I-PHOR-TAA

granules on the average. The calculated diffusion factor values, given in Table 3, are typical of the processes occurring in the diffusion region. Niobium is extracted by TVEX-PHOR in the way similar to sorption by TVEX-TBP [18], probably, in accordance with the solvation mechanism:



while the FOR and TAA impregnated resins can extract niobium if the chloride ion (salt form of the amine) is introduced into these reactions to balance the anions  $[\text{NbOCl}_4]^-$  and  $[\text{NbOCl}_5]^{2-}$  according to the formal anion exchange mechanism. Therefore, the pseudo-first-order model, the pseudo-second-order model and the Elovich model [19-25] were used to process the kinetic data. Such models allow identifying the impact of the chemical interaction stage on the sorption process.

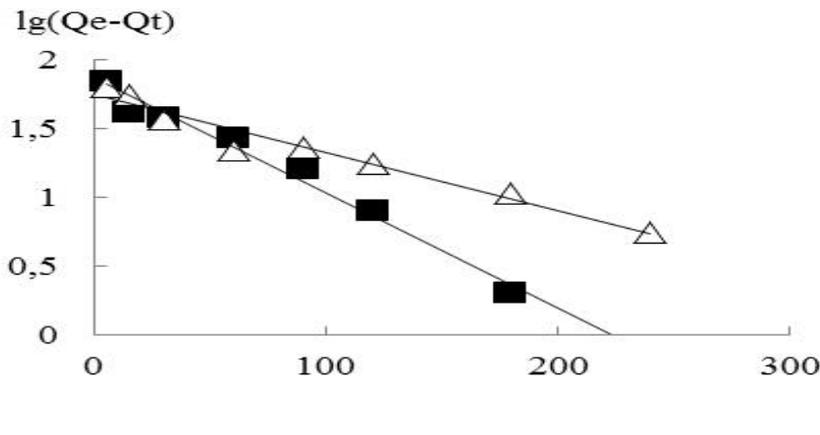
The kinetic equations of the pseudo-first-order and pseudo-second-order models, and the kinetic equation of the Elovich model in linear form, can be presented as:

$$\lg(Q_e - Q_t) = \lg Q_e - (k_1/2.303)\tau \tag{5}$$

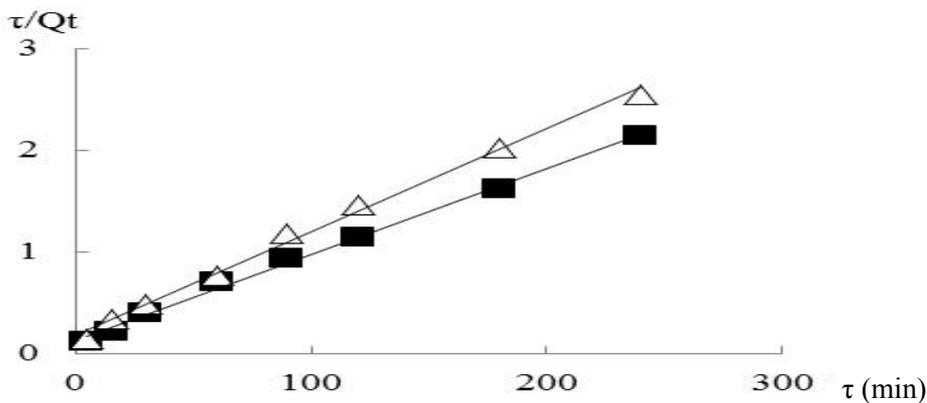
$$\tau/Q_t = 1/k_2 Q_e^2 + (1/Q_e)\tau \tag{6}$$

$$Q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta)\tau \tag{7}$$

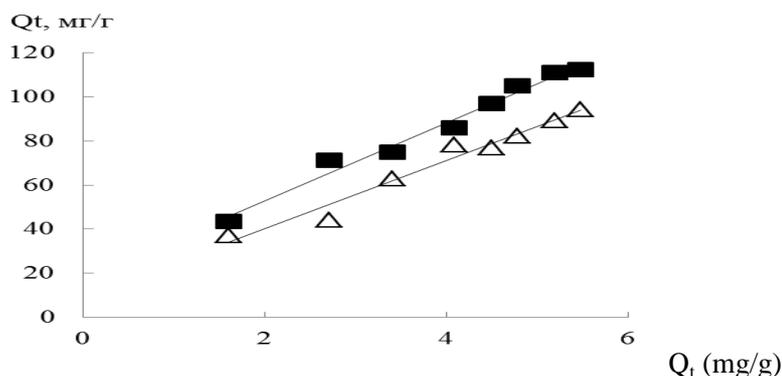
where  $Q_e$  and  $Q_t$  are the sorption capacity at the moment of equilibrium and at a given time  $\tau$  (mmol/g),  $k_1$  and  $k_2$  are the rate constants of the pseudo-first order ( $\text{min}^{-1}$ ) and the pseudo-second order ( $\text{g} \cdot (\text{mmol} \cdot \text{min})^{-1}$ ),  $\alpha$  is the initial sorption rate ( $\text{g}/(\text{mmol} \cdot \text{min})$ ), and  $\beta$  is the Elovich constant ( $\text{g} \cdot \text{mmol}^{-1}$ ). Dependences of the processed kinetic data in the linearized coordinates  $\lg(Q_e - Q_t) - \tau$ ,  $\tau/Q_t - \tau$  and  $Q_t - \ln\tau$  for these models are given in Figures 5-7.



**Figure 5.** Dependence  $\lg(Q_e - Q_t) = f(\tau)$  for niobium sorption by TVEX-PHOR(■) and I-PHOR-TAA ( $\Delta$ ) from hydrochloric acid solutions.



**Figure 6.** Dependence  $\tau/Q_t = f(\tau)$  for niobium sorption by TVEX-PHOR(■) and I-PHOR-TAA ( $\Delta$ ) from hydrochloric acid solutions.



**Figure 7.** Dependence  $Q_t = f(\ln t)$  for niobium sorption by TVEX-PHOR(■) and I-PHOR-TAA (Δ) from hydrochloric acid solutions.

The rate constants and correlation coefficients, calculated by the kinetic equations of the models used, are given in Table 4.

**Table 4.** The rate constants of niobium sorption by TVEX-PHOR and I-PHOR-TAA, calculated using the pseudo-first-order, pseudo-second-order and Elovich models.

Pseudo-first-order model		Pseudo-first-order model		Elovich model	
$k_1$ (min <sup>-1</sup> )	$R^2$	$k_2$ (g·(mmol·min) <sup>-1</sup> ),	$R^2$	B (g·mmol <sup>-1</sup> )	$R^2$
I-PHOR-TAA					
0.0101	0.958	0.0521	0.995	5.86	0.968
TVEX-PHOR					
0.0083	0.990	0.0549	0.997	5.12	0.981

Proceeding from the correlation coefficient values, the obtained kinetic data on niobium sorption by the studied materials appear to be more adequately described by the pseudo-second-order equation ( $R^2 \geq 0.995$ ). This fact may indicate that one of the limiting factors of the studied process is the chemical reaction. The rate constant of niobium sorption by TVEX-PHOR and I-PHOR-TAA is  $0.0549 \text{ g} \cdot (\text{mmol} \cdot \text{min})^{-1}$  and  $0.0521 \text{ g} \cdot (\text{mmol} \cdot \text{min})^{-1}$ , respectively.

## CONCLUSION

Based on the equilibrium properties of niobium (V) sorption determined by this study, it can be said that the solid polymeric extractant TVEX-PHOR and the impregnated resin I-PHOR-TAA can both be used to extract niobium from concentrated hydrochloric solutions. At that, TVEX-PHOR gave the highest values of distribution coefficient and sorption capacity. The sorption of niobium by the selected sorbents occurs in the diffusion region. However, the kinetic data, described by the pseudo-second-order model with a high degree of correlation, indicate certain impact of the chemical reaction that proceeds in accordance with the solvation

mechanism or — in the presence of a tertiary amine — the anion exchange mechanism.

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## REFERENCES

1. Korovin S.S., Drobot D.V., Fedorov P.I. Redkiye i rasseyannyye elementy. Uchebnik dlya vuzov [Rare and trace elements. Textbook for universities], in 3 volumes. Moscow, MISiS, 1999-2003. (in Russian).
2. Lebedev K.B. (Ed.) Ionity v tsvetnoy metallurgii [Ionites in non-ferrous metallurgy]. Moscow, Metallurgiya, 1975. (in Russian).
3. Zelikman A.M., Korshunov B.G., Elyutin A.V., Zakharov A.M. Niobiy i tantal [Niobium and tantalum]. Moscow: Metallurgiya, 1990. (in Russian).
4. Maslov A.A., Ostvald R.V., Shagalov V.V., Maslova E.S., Gorenjuk Yu.S.

- Khimicheskaya tekhnologiya niobiya i tantala: uchebnoye posobiye [Chemical technology of niobium and tantalum: a learning aid]. Tomsk, Tomsk Polytechnic University, 2010. (in Russian).
5. Meretukov M.A. Ispolzovaniye impregnirovannykh materialov dlya izvlecheniya i razdeleniya tsvetnykh metallov: Obzor. Inform. [Use of impregnated materials for extraction and separation of non-ferrous metals: a review]. Moscow, TsNIIEMTs, 1980, Issue 3. (in Russian).
  6. Warshawsky A. (1981). Extraction with solvent-impregnated resins. In: Ion Exchange and Solvent Extraction, Vol. 8. pp. 229-310. Marinsky J.A., Marcus Y. (Eds.) Marcel-Dekker, New York, NY, U.S.A.
  7. Warshawsky A., Cortina J.L. Solvent impregnated resins: performance and environmental applications in metal extraction. In: Proc. of the Intern. Solvent Extract. Conf.: ISEC, 2002. Johannesburg, 2002. P. 493–499.
  8. Kabay N., Cortina J.L., Trochimczuk A., Streat M. Solvent-impregnated resins (SIRs) – Methods of preparation and their applications. *React. Funct. Polym.* 2010. V. 70, N. 8. P. 484–496.
  9. Yagodin G.A., Savelyeva V.I., Kireeva G.N., Pokidysheva I.D., Korovin Yu.F. Tverdye ekstragenty i primeneniye ikh dlya izvlecheniya metallov [Solid extractants and their use in metal extraction]. *Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya* [Proceedings of Universities. Chemistry and Chemical Technology]. 1984. V. 27, No. 10. P. 1179–1184. (in Russian).
  10. Korovin V.Yu., Randarevich S.B. Sintez, svoystva i primeneniye tverdykh ekstragentov (obzor) [Synthesis, properties and application of solid extractants (review)]. *Khimicheskaya tekhnologiya* [Chemical Technology]. 1991. V. 5. P. 3-13. (in Russian).
  11. Korovin V., Shestak Yu., Pogorelov Yu., Cortina J.L. Solid Polymeric Extractants (TVEX): Synthesis, Extraction Characterization and Application for Metal Extraction Processes. In: Aguilar M., Cortina J.L. (Eds.) *Solvent Extraction and Liquid Membranes. Fundamentals and Applications in New Materials*. CRC Press Taylor & Francis, Boca Raton, Florida (USA), 2008. P. 261–301.
  12. Pokidysheva (Troshkina) I.D., Savelyeva V.I., Kireeva G.N. et al. Osobennosti TVEKSov pri izvlechenii aktinoidnich elementov iz azotnokislichykh rastvorov. *Radiokhimiya* [Features of TVEX in the extraction of actinide elements from nitric acid solutions]. *Radiokhimiya*. 1986. Vol. 28, No. 1. P. 110-112. (in Russian).
  13. Brown T., Gersini G.M. (Eds.) *Extraction chromatography*. Translation from English into Russian. Moscow, Mir, 1978. (in Russian).
  14. Laskorin B.N. (Ed.) *Ionoobmennyye materialy dlya protsessov gidrometallurgii, ochistki stochnykh vod i vodopodgotovki: Spravochnik* [Ion-exchange materials for processes of hydrometallurgy, waste water purification and water treatment: Handbook]. Moscow, Stroiizdat, 1984. (in Russian).
  15. Laskorin B.N. (Ed.) *Ionoobmennyye materialy dlya protsessov gidrometallurgii, ochistki stochnykh vod i vodopodgotovki: Spravochnik* [Ion-exchange materials for processes of hydrometallurgy, waste water purification and water treatment: Handbook]. Moscow, VNIHT, 1989. (in Russian).
  16. Malyutina T.M., Konkova O.V. *Analiticheskiy kontrol v metallurgii tsvetnykh i redkikh metallov* [Analytical control in the metallurgy of non-ferrous and rare metals]. Moscow, Metallurgiya, 1988. (in Russian).
  17. Kokotov Yu.A., Pasechnik V.A. *Ravnovesiye i kinetika ionnogo obmena* [Equilibrium and kinetics of ion exchange]. Leningrad, Khimiya, 1979. (in Russian).
  18. Korovin V., Shestak Yu. Niobium extraction by TVEX-polymer resin containing tributylphosphate. *React. Funct. Polym.* 1999. V. 40 (2). P. 107–113.
  19. Ho Y.S. Review of second-order models for adsorption systems. *J. Haz. Materials*. 2006. V. B136. P. 681-689.

<http://dx.doi.org/10.1016/j.jhazmat.2005.12.043>.

20. Lagergren S. About the theory so-called adsorption of soluble substances. *Kung Sven Vetén Hand.* 1898. V. 24. N.1. P. 1-39.
21. El-Khaiary M.I., Malash G.F., Ho Y.-S. On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems. *Desalination.* 2010. V. 257 P. 93–101. doi:[10.1016/j.desal.2010.02.041](https://doi.org/10.1016/j.desal.2010.02.041)
22. Azizian S. Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science.* 2004. V. 276. P. 47–52. doi:[10.1016/j.jcis.2004.03.048](https://doi.org/10.1016/j.jcis.2004.03.048)
23. Foo K.Y., Hameed B.H. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal.* 2010. V. 156. P. 2–10. doi:[10.1016/j.cej.2009.09.013](https://doi.org/10.1016/j.cej.2009.09.013)
24. Limousin G., Gaudet J.-P., Charlet L., Szenknect S., Barthe`s V., Krimissa M. Sorption isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry.* 2007. V. 22. P. 249–275. doi:[10.1016/j.apgeochem.2006.09.010](https://doi.org/10.1016/j.apgeochem.2006.09.010)
25. Tran H.N., You S.-J., Hosseini-Bandegharai A., Chao H.-P. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Research,* 2017. V. 120. P. 88-116. doi:[10.1016/j.watres.2017.04.014](https://doi.org/10.1016/j.watres.2017.04.014).