
PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Sorption Extraction of Palladium(II) with Modified Polysiloxane

L. K. Neudachina, A. Ya. Golub, and A. S. Kholmogorova

*Ural Federal University named after the first President of Russia B.N. Yeltsin,
ul. Mira 19, Yekaterinburg, 620002 Russia
e-mail: alexey.golub@urfu.ru*

Received May 27, 2014

Abstract—Sorption of palladium(II) from model solutions with polysiloxanes modified with amine and thiourea groups was studied and it was found that the maximum sorption on aminopropyl polysiloxane is shifted slightly to alkaline region compared with a sulfur-containing sorbent. First time an effect of a series of external factors on a sorption kinetics of palladium with polysiloxanes was researched, diffusion coefficients of sorbate ions were calculated, and evaluation of their dependence on an initial concentration of metal, a grain diameter of the sorbent, and a temperature of sorption environment was carried out. It is shown that quantitative desorption of palladium from thiocarbamoylated polysiloxane is achieved by double treating the sorbent with hydrochloric acid solution of thiourea at high temperature.

DOI: 10.1134/S1070427214070131

Extremely low concentrations of precious metals in the analyzed samples along with a multicomponent matrix of a sample containing macroquantities of elements, which accompany platinoids, stipulate an introduction into the analysis scheme of a stage of concentrating metals of platinum group.

Multi-component samples and the similarity of the chemical properties of the platinum metals require previous separation them from each other.

Organopolymeric ion exchange and complexing sorbents, which are of a low thermal stability, high chemical activity of the matrix, high swelling capacity, limited availability of functional groups, are often used for sorption concentrating of palladium [1–9].

There is a lot of work on sorption recovery of palladium with silica covalently modified with organic chelating groups [10, 11]. In this case all the functional groups are available on the surface of the sorbent matrix. Usually structural-adsorption characteristics of the original silica are kept.

Polysiloxanes obtained by a joint polycondensation of organosilicon compounds with tetraethoxysilane (sol-gel method) in the presence of precursors ensuring the formation of chelating groups of given composition

in the structure of the sorbent, are promising sorbents for the extraction of metals of the platinum groups. In [12, 13] conditions of platinum extraction with aminopropyl polysiloxane and also polysiloxane modified with thiourea were studied in detail. Conditions of separation of platinum from ions of base metals were found. Earlier sorption of palladium on such materials has not been studied.

The aim of the study was investigation of sorption of palladium(II) from model solutions with aminopropyl polysiloxane (APPS) and polysiloxane modified with thiourea groups (PSMT).

EXPERIMENTAL

Synthesis and identification of sorbents were described previously in [12]. (3-Aminopropyl)triethoxysilane (APTES, 98%, Sigma-Aldrich) and tetraethoxysilane (TEOS, 98%, Acrosorganics) were used as starting materials for the synthesis of adsorbents. The state standard (GSO 8432) was used to prepare the solution of palladium(II).

Sorption of palladium was studied under continuous stirring by an agitator PE-6410M (Ekros) equipped with the heated platform and a controller of the oscillation frequency in the static mode by a method of separate por-

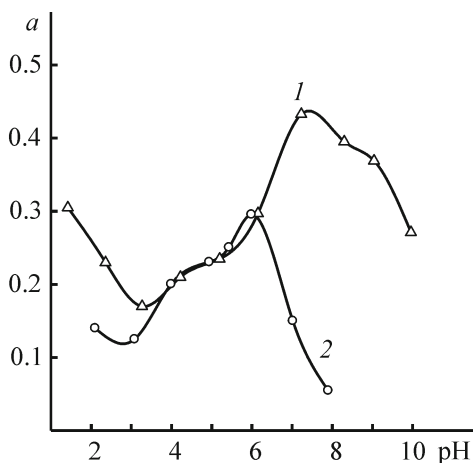


Fig. 1. Sorption a (mmol g^{-1}) of palladium(II) ions vs. pH of environmental for (1) APPS and (2) PSMT. The initial concentration of palladium(II) $0.148 \text{ mmol dm}^{-3}$, weighed portion of the sorbent 10 mg, $0.071 < d_{\text{grain}} < 0.100 \text{ mm}$, the process time 24 h.

tions of the individual solutions of metal salts. A universal buffer mixture was used in order to maintain the acidity of sorption solutions. Exact values of pH of solutions were monitored using an ionomer I-130M. Potassium chloride (ionic strength of a solution 0.1 mol dm^{-3}) was used as a base electrolyte. Quantity of adsorbed metal was calculated by the difference of the initial and the equilibrium (after separation of the phases by filtration) concentrations. The equilibrium concentration after separation of the phases was determined spectrophotometrically (Helios- α) with thiocarbamide as an analytical reagent according to the known procedure [14]. The experimental kinetic data were mathematically treated in the software package OriginPro 8.1 in accordance with the equations of diffusion and kinetic models discussed in detail in [13].

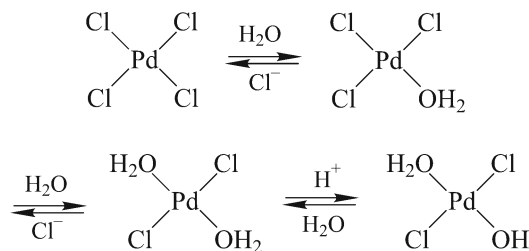
RESULTS AND DISCUSSION

Polysiloxanes grafted with thiourea and amine groups extract palladium(II) ions from weakly acidic and weakly alkaline solutions (Fig. 1).

Extraction of palladium(II) ions is maximum with PSMT at pH 5.0–6.5, and with APPS at pH 6.5–8.0. Under experimental conditions APPS is of the highest sorption capacity (0.43 mmol g^{-1}) as for PSMT a sorbability value is 0.30 mmol g^{-1} .

Despite the higher affinity of platinoids to a “soft” donor sulfur atom compared to nitrogen-containing groups, lower sorption capacity of thiocarbamoylated polysiloxane seems natural in view of the high kinetic

inertness of anionic aqua-chloro complexes and cationic hydroxocomplexes of palladium found in the solution. In [15] it was shown that in acidic environments palladium exists in the form of a complex ion $[\text{PdCl}_4]^{2-}$, and also the form of palladium complexes depending on the acidity of the environment are given. With increasing pH in solutions of palladium complexes hydrolysis occurs:



A dilution of the solution, an increase of pH from 1 to 3, and a decrease in the concentration of ions Cl^- contribute to development of this stage.

Then the polymerization occurs and at $\text{pH} > 4$ in the solution there exist polynuclear complexes of palladium(II). The concentration of palladium complexes, an increase in pH from 3 to 8, and reducing the concentration of chloride ions contribute to a growth of the polymer. At $\text{pH} > 7$ stable complexes $[\text{PdOH}]^+$ and $[\text{Pd}_4(\text{OH})_4]^{4+}$ are formed.

Aqua-chloro- and hydroxocomplexes of platinum metals are of a high degree of kinetic inertness in inner-ligand substitution reactions in the coordination sphere of the central ion. At the same time a possible anionic exchange on protonated amino groups enables proceeding of sorption on aminated polysiloxane by the ion-exchange mechanism with subsequent coordination of a metal by nitrogen atom of a grafted group.

An obvious way of increasing the lability of the palladium complexes is an increase in temperature. Indeed, heating of a sorption solution to $80\text{--}85^\circ\text{C}$ allows achievement of a 100% extraction of palladium with PSMT.

Noteworthy is the fact that platinum(IV) is extracted with PSMT at pH 2 quantitatively already at room temperature [12]. Under these conditions platinum(IV) is in solution in the form of chloride complexes and, therefore may be sorbed by the ion exchange with protonated amine groups. Thus, platinoids, which often accompany each other in the analyzed objects, can be divided by adjusting the temperature of the adsorption environment.

The kinetics of the sorption process is determined by the time required to reach equilibrium between the concentrations of sorbed component in the solid and liquid

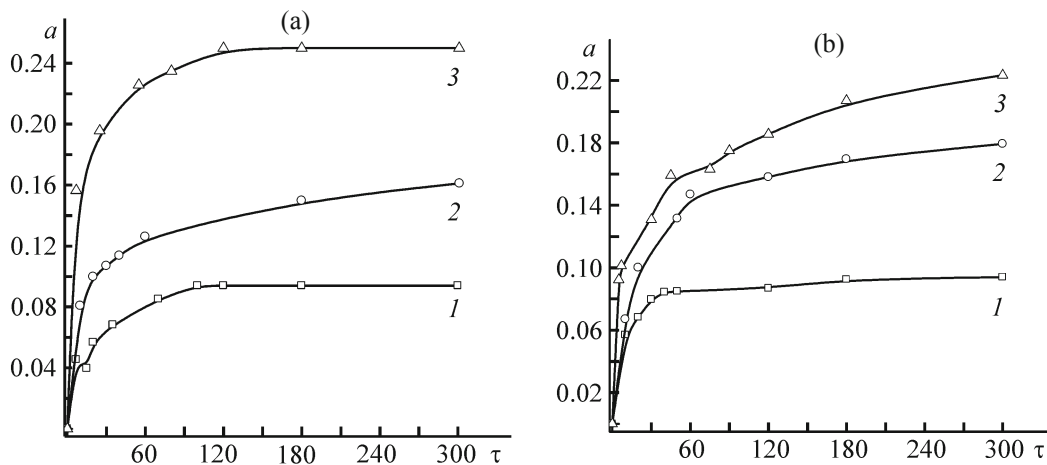


Fig. 2. Integral kinetic sorption curves of palladium(II) (a) to PSMT and (b) APPS at different initial concentrations of sorbate. (a) Sorption (mmol g^{-1}), (τ) time (min); the same for Figs. 3 and 5. The stirring speed 120 rpm, $0.071 < d_{\text{grain}} < 0.100$ mm, weighed portion of the sorbent 10 mg, pH 7.6, temperature 25°C . The initial concentration of palladium(II) (mmol dm^{-3}): (1) 0.018, (2) 0.037, (3) 0.079.

phases [16]. A rate of reaching equilibrium during sorption is an important characteristic of complexing sorbents and has both practical and theoretical importance. This parameter allows assessing the feasibility and usefulness of an applied absorbent to solve practical problems, as well as to make an assumption about the mechanism of the process.

In studying the mechanism of the sorption process determination of a limiting stage as well as stages that provide a relatively large contribution to the kinetics of the process plays a key role. An additional complexity consists in the possible imposition of stages at each other over time. Therefore, it is advisable to consider the relationship of kinetic dependences with various factors affecting the sorption process. It should be noted that studies, which systematically examine the impact of the various stages on the kinetics of extraction of palladium with polysiloxanes, could not be found.

The sorption of palladium with PSMT over time, first increases sharply and then grows gradually until it reaches its equilibrium value (Fig. 2), the contact time between phases is about 120 min. Further interaction of phases does not lead to a noticeable change in the degree of extraction of the metal.

With an increase in the initial concentration of a sorbate in a solution an increase in the metal sorbability is observed at a certain reduction of the phase contact time (Fig. 2). A higher rate of sorption at the initial time is due to the large number of free active sites that causes a significant concentration gradient between the sorbed ions in solution and in the sorbent phase. After some time

owing to the accumulation of the sorbate in the active sites the concentration gradient decreases and the rate of sorption is reduced. In the experiment the initial palladium concentrations correspond to the Henry adsorption isotherms that is an evidence of a proportional increase in the amount of adsorbed metal with increasing time.

Relations of the processing of the experimental data in the coordinates $F-\tau^{1/2}$, where F is a relative amount of ions in the sorbent, allow calculating the diffusion coefficients of ions (Table 1) therewith the coefficient of external diffusion (diffusion of solute from the solution to the surface of the sorbent through the film) determined by the slope of the first straight-line portion of the curve, and the coefficient of internal diffusion (diffusion in the sorbent grain), by the slope of the second portion of the curve [17, 18].

With increasing the initial concentration of the metal an increase in the coefficient of external diffusion in sorption to APPS and nonmonotonic variation of values D_1 in the case of PSMT were observed, a coefficient D_2 for both sorbents varies within a narrow range.

Considering the data obtained in the processing of kinetic dependences $F-\tau^{1/2}$ and $-\ln(1-F)-\tau$ it can be concluded that the sorption process is in a mixed diffusion mode and both stages (the external and internal diffusion) contribute significantly to the overall rate of the process.

Since the functional groups of polysiloxanes under study can form coordination bonds with the metal ion, i.e., are complexing, a treatment of kinetic relations in accordance with the equations of chemical kinetics models also seems advisable. These models describe the process, the

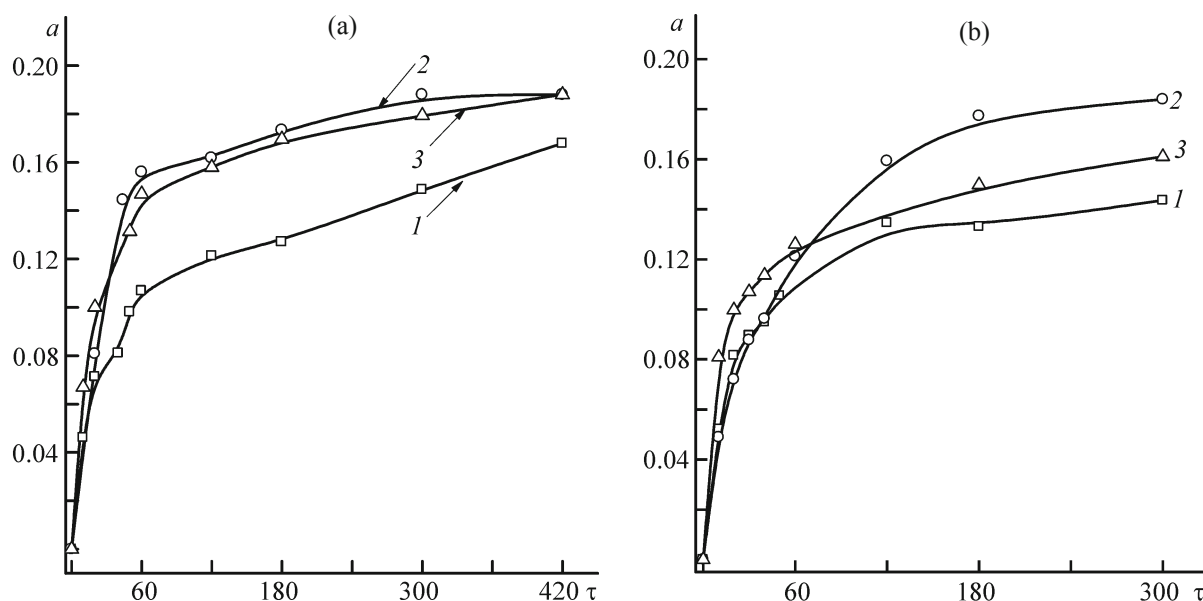


Fig. 3. Integral kinetic sorption curves of palladium(II) to (a) PSMT and (b) APPS at different grain sizes of the sorbent. The stirring speed 120 rpm, weighed portion of the sorbent 10 mg, pH 6.7, temperature 25°C. The grain size of the sorbent (mm): (1) 0.100–0.125, (2) 0.071–0.100, (3) less than 0.071; the same for Fig. 4.

rate-limiting stage of which is the interaction of sorbate with the functional groups of the sorbent.

Correlation coefficients obtained in the processing of the experimental curves in accordance with the model equations of chemical kinetics are presented in Table 2. The data of Table 2 shows that a pseudo-second order model most adequately describes the sorption process in the whole timeslot. The rate-limiting stage is the chemical reaction between sorbed ions and the functional groups

of the sorbent. At small values of the time processes of diffusion of sorbate ions are superimposed on the stage of the chemical interaction.

With decreasing a diameter of the grains the rate of absorption of the ions must increase due to the fact that in the sorption process uneven distribution of the ion with the concentration gradient along the radius of the grain is observed in the mass and volume of the grain. More complete ion exchange occurs upon the grain size

Table 1. The diffusion coefficients of palladium (II) ions

Influence factor		A model of the diffusion, D_1		Model of internal diffusion, D_2	
		$\text{cm}^2 \text{ s}^{-1}$			
		APPS	PSMT	APPS	PSMT
$c_{\text{Pd}}^0 \times 10^5, \text{ mol dm}^{-3}$	1.8	5.51×10^{-9}	9.88×10^{-9}	1.84×10^{-8}	2.44×10^{-8}
	3.7	6.44×10^{-9}	2.94×10^{-9}	1.84×10^{-8}	1.71×10^{-8}
	7.9	9.17×10^{-9}	1.86×10^{-8}	2.64×10^{-8}	1.73×10^{-8}
$d_{\text{grain}}, \text{ mm}$	0.100–0.125	6.12×10^{-9}	2.52×10^{-9}	1.89×10^{-8}	2.63×10^{-9}
	0.071–0.100	4.21×10^{-9}	5.29×10^{-9}	1.89×10^{-9}	3.56×10^{-9}
	< 0.071	6.44×10^{-9}	3.22×10^{-9}	2.38×10^{-9}	2.61×10^{-9}
$T, \text{ K}$	293	6.44×10^{-9}	2.52×10^{-9}	2.38×10^{-9}	2.63×10^{-9}
	323	3.31×10^{-8}	2.45×10^{-8}	1.99×10^{-8}	3.64×10^{-9}
	358	2.70×10^{-8}	2.92×10^{-8}	1.07×10^{-8}	7.61×10^{-8}

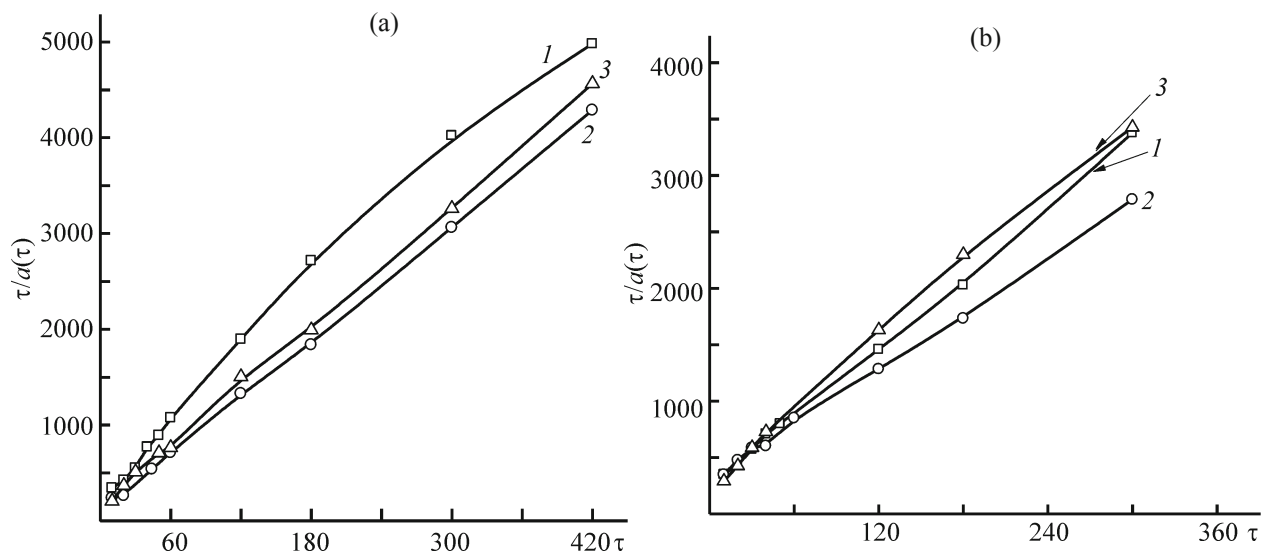


Fig. 4. Treatment of integral equations of the model kinetic curves of pseudo second order with different diameter of sorbent particles of (a) PSMT and (b) APPS. (τ) time (min).

reduction. However, the experimental curves (Fig. 3) do not exhibit monotonic dependence of the sorption rate on the grain size of the sorbent.

The calculated internal diffusion coefficients (Table 1) for all sorbents do not depend linearly on the the grain diameter that, according to [19], does not allow determining the gel kinetics as a limiting stage of the process. Sorption at all polysiloxanes investigated is adequately described by the pseudo-second order model (Table 2) that is evidenced by the linear character of the corresponding curves (Fig. 4).

Kinetic curves obtained for PSMT at different temperatures are shown in Fig. 5. The diffusion coefficients

D_1 and D_2 vary non-monotonically (Table 1), the change in values of the coefficients occurs within a single order. This fact indicates that the diffusion can not be considered as a limiting stage of sorption of palladium on polysiloxanes under study, although it is important in the early stages of interaction. This conclusion is also confirmed by the relatively low values of the corresponding diffusion coefficients (Table 1).

Mathematical analysis of sorption isotherms of palladium(II) on thiocarbamoylated polysiloxane based on the use of well-known formal models, shows that in the concentration range of palladium(II) up to 6 mmol dm^{-3}

Table 2. Fitment of kinetic models for describing the sorption of palladium(II)

Influence factor		Pseudo-first order model		Pseudo-second order model	
		APPS	PSMT	APPS	PSMT
$c_{\text{Pd}}^0 \times 10^5, \text{ mol dm}^{-3}$	1.8	0.979	0.998	0.996	0.999
	3.7	0.989	0.984	0.994	0.997
	7.9	0.987	0.896	0.999	0.998
$d_{\text{grain}}, \text{ mm}$	0.100–0.125	0.997	0.986	0.998	0.988
	0.071–0.100	0.955	0.991	0.998	0.999
	< 0.071	0.986	0.852	0.996	0.999
$T, \text{ K}$	293	0.986	0.986	0.996	0.988
	323	0.984	0.983	0.999	0.997
	358	0.966	0.992	0.966	0.999

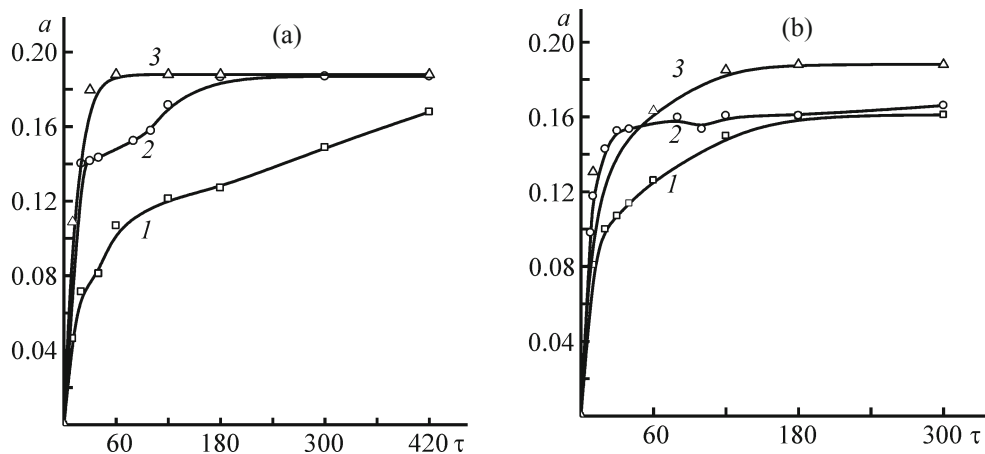


Fig. 5. Integral kinetic sorption curves of palladium(II) to (a) PSMT and (b) APPS at different temperatures of the reaction medium. The stirring speed 120 rpm, $0.071 < d_{\text{grain}} < 0.100$ mm, weighed portion of the sorbent 10 mg. The temperature of the reaction mixture (K): (1) 293, (2) 323, (3) 358.

sorption isotherm is most adequately described by the Redlich–Peterson and Langmuir–Freundlich equations. This demonstrates the chemical heterogeneity of the surface containing various functional groups in nature. This conclusion is supported by the calculated values of the parameters of the inhomogeneity.

Sorption capacity of PSMT with respect to the ions of palladium(II) determined by the horizontal part of the isotherm (Fig. 6) is 0.65 mmol g^{-1} . The number of functional groups of the sorbent reaches 1.49 mmol g^{-1} [12], i.e., the molar ratio of Pd : TM is equal to 1 : 2 that corresponds to the binding of the complex ion of a palladium with two thiourea groups.

The structure of complex compounds of palladium(II) with loose thiourea of $\text{Pd}(\text{Thio})_2\text{Cl}_2$ and $\text{Pd}(\text{Thio})_4\text{Cl}_2$

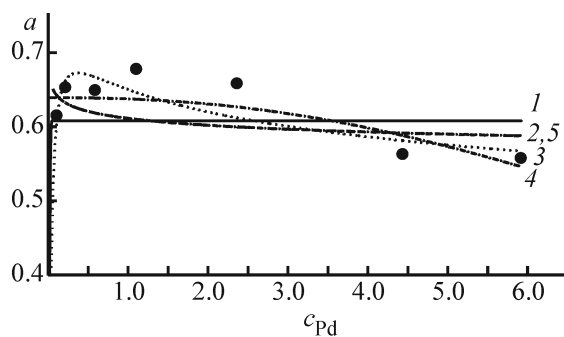


Fig. 6. Sorption isotherms of palladium(II) to PSMT. Weighed portion of the sorbent 10 mg, $d_{\text{grain}} < 0.071$ mm, pH 6, temperature 25°C , process time 24 h. (a) Sorption (mmol g^{-1}), (c_{Pd}) palladium(II) concentration (mmol dm^{-3}). Model: (1) Langmuir, (2) Freundlich, (3) Redlich–Peterson, (4) Langmuir–Freundlich, (5) Thoth.

composition is considered in detail in [20]. Based on the data of instrumental methods of analysis it is confirmed in [21] that thiourea is coordinated by metal through sulfur atom. By IR, XPS spectroscopy, ESR, elemental, and derivatographic analysis it was found that recovery of palladium(II) is associated with reactions of complexation with functional groups of sorbents. IR spectra of a Mtilon-T fiber containing thiourea fragments before and after sorption indicate the possibility of association between the metal ions and nitrogen and sulfur atoms of thioamide group [22].

Practical implementation of sorption implies the possibility of desorption of the sorbate from the sorbent surface. High stability of thiourea complexes of palladium significantly hinders a selection of a way of sorbent regeneration. In particular, widespread acid desorption with respect to PSMT regeneration after sorption of palladium is ineffective, as evidenced by the acid-base dependencies (Fig. 1).

Sorption of palladium(II) with thiocarbamoylated polysiloxane is reversible. It was shown (Table 3) that

Table 3. Degree of palladium(II) desorption vs. eluent type

Eluent	Desorption degree D , %			
	Sage I	Sage II	Sage III	Σ
$\text{NH}_3(\text{conc.}), 25^\circ\text{C}$	10.3	17.7	2.8	30.8
10% TM + 0.5 mol dm^{-3} HCl:				
25°C	54.4	10.9	0.9	66.2
85°C	87.5	12.07	–	99.6

with the concentrated solution of ammonia no more than 30% of palladium can be desorbed (phase contact time 24 h at 20°C), but a quantitative desorption of palladium is achieved by double treating of the sorbent with acidic thiourea solution at 85°C.

These results agree with those of other authors that demonstrate that with thiourea solution palladium is quantitatively extracted from silica [23], chitosan [9], anion exchangers [4] and fibrous sorbents [3].

CONCLUSIONS

(1) It is shown that with aminated and thiocarbamoylated polysiloxanes by pH adjustment a group separation of palladium from accompanying base metals may be performed. The maximum pH of the sorption of palladium(II) (pH 6.5–8.0) is substantially spaced from the highest sorption of platinum (pH 2) that enables separation of palladium and platinum ions with the aminated sorbent by the selection of optimal parameters of sorption or transition to the dynamic conditions. Separation of platinum with PSMT can be performed by changing the temperature regime of sorption.

(2) Sorption of palladium occurs in the kinetic mode with significant influence of the diffusion of ions in the film and grain of the sorbent. It was established that the experimental results are most adequately described by the pseudo-second order model.

(3) Mixed chloride-thiourea complexes of palladium(II) with a ratio of Pd : thiourea 1 : 2 is formed on the surface of the polysiloxane modified with thiourea groups.

REFERENCES

- Zolotov, Yu.A., Tsizin, G.I., Morosanova, E.I., et al., *Russ. Chem. Rev.*, 2005, vol. 74, no. 1, pp. 37–60.
- Bondareva, V.V., Troshkina, I.D., Bryskin, D.A., et al., *Sorbts. Khromatogr. Protsessy*, 2007, vol. 7, no. 3, pp. 469–472.
- Simanova, S.A., Burmistrova, N.M., Kazakevich, Yu.E., et al., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 5, pp. 772–777.
- Kopylova, V.D., Pogodina, T.B., and Klyuev, N.V., *Zh. Fiz. Khim.*, 1990, vol. 64, no. 3, pp. 724–728.
- Hubicki, Z., Wawrzkiwicz, M., and Wołowicz, A., *Chem. Anal.*, 2008, vol. 53, no. 6, pp. 759–784.
- Myasoedova, G.V. and Komozin, P.N., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 2, pp. 280–288.
- Dakshinamoorthy, A., Kumar, T., Nandy, K.K., et al., *J. Radioanalyt. a. Nuclear Chem.*, 2000, vol. 245, no. 3, pp. 595–598.
- Bratskaya, S.Yu., Ustinov, A.Yu., Azarova, Y.A., et al., *Carbohydrate Polym.*, 2011, vol. 85, pp. 854–861.
- Guibala, E., Von Offenbergsweeneyb, N., Vincenta, T., et al., *Reactive a. Functional Polym.*, 2002, vol. 50, no. 2, pp. 149–163.
- Mironov, Yu.I. and Anpilogova, G.R., *ARKIVOC.*, 2002, vol. 2001, no. 9, pp. 166–186, <http://www.arkat-usa.org>.
- RF Patent 2354448, 2013.
- Neudachina, L.K., Golub, A.Ya., Yatluk, Yu.G., et al., *Inorg. Mat.* 2011, vol. 47, no. 4, pp. 435–441.
- Neudachina, L.K., Golub, A.Ya., and Yatluk, Yu.G., *Butlerovskie Soobshcheniya*, 2011, vol. 27, no. 14, pp. 55–68.
- Niensch, W., *Mikrochim. Acta*, 1954, vol. 42, no. 5, pp. 532–538.
- Semikolenov, V.A., *Russ. Chem. Rev.*, 1992, vol. 61, no. 2, pp. 168–174.
- Venitsianov, E.V., *Molekulyar. Tekhnologii*, 2010, vol. 4, pp. 9–26.
- Wang, S. and Li, H., *Dyes Pigments*, 2007, vol. 72, no. 3, pp. 308–314.
- Guibal, E., Milot, C., and Tobin, J., *Ind. Eng. Chem. Res.* 1998, vol. 37, no. 4, pp. 1454–1463.
- Tszacar, M. and Şengil, I.A., *Coll a. Surf. A: Physicochem. Eng. Aspects*, 2004, vol. 242, pp. 105–113.
- Sibirskaya, V.V. and Kukushkin, Yu.N., *Koord. Khim.*, 1978, vol. 4, no. 7, pp. 963–991.
- Vorob'ev-Desyatovskii, N.V., Kukushkin, Yu.N., and Sibirskaya, V.V., *Koord. Khim.*, 1985, vol. 11, no. 10, pp. 1299–1328.
- Shcherbinina, N.I., Myasoedova, G.V., and Savvin, S.B., *Zh. Anal. Khim.*, 1988, vol. 43, no. 12, pp. 2117–2131.
- Boryagina, I.V., Volchkova, E.V., Buslaeva, T.M., et al., *Non-Ferrous Metals*, 2012, no. 2, pp. 59–64.