METALLURGY OF RARE AND PRECIOUS METALS / МЕТАЛЛУРГИЯ РЕДКИХ И БЛАГОРОДНЫХ МЕТАЛЛОВ

UDC 66.081 (546.98 + 546.55 + 546.62)
https://doi.org/10.17073/0021-3438-2025-2-41-54

Research article
Научная статья

Selective sorption-based separation of palladium from process solutions using chemically modified silica

T.M. Buslaeva[1], **E.V. Volchkova**[1], **P.G. Mingalev**[2], **I.V. Boryagina**[3]

[1] **MIREA – Russian Technological University,**
Institute of Fine Chemical Technologies named after M.V. Lomonosov
86 Vernadskogo Prosp., Moscow 119571, Russia

[2] **Moscow State University**
1 Bld, 3 Leninskie Gory, Moscow 119991, Russia

[3] **JSC R&PC Supermetal**
2 Bld, 22/24 Ozerkovskaya nab., Moscow 115184, Russia

✉ Tat'yana M. Buslaeva (buslaevatm@mail.ru)

Abstract: This study focuses on investigating the possibility of selective separation of palladium (II) from solutions containing non-ferrous metals and iron by sorption onto chemically modified silica. The study used both individual (single-metal) and model multicomponent solutions. The sorbents included silicas functionalized with iminodiacetic acid (IDA-D), phosphonic acid (PA-D), and aminomethylphosphonic acid (AMPA-D) groups, as well as a well-known chemically modified silica bearing grafted γ-aminopropyltriethoxysilane (APTES) groups at a grafting density of 1.63 mmol/g. Under static conditions at room temperature, the time required to reach equilibrium sorption values for Cu(II), Ni(II), and Fe(III) ions – typically present in process solutions – was determined for the IDA-D, PA-D, and AMPA-D sorbents. Sorption dependencies on hydrochloric acid concentration were established for these metal ions. For IDA-D, the effect of halide ion concentration on sorption was also studied. It was shown that these ions are sorbed in weakly acidic media but not in 1–2 M HCl, and that sorption capacity decreases in the order: IDA-D > AMPA-D > PA-D. However, the conclusion that quantitative separation of Pd(II) from base metal ions could be achieved using these complexing sorbents (exemplified by IDA-D) under dynamic conditions was not confirmed. The sorption behavior of Pd(II), Cu(II), and Al(III) ions was also examined under static and dynamic conditions using the APTES-functionalized silica and chloride and chloride-bromide solutions, including model solutions simulating leach liquors generated from the treatment of spent catalysts for low-temperature carbon monoxide oxidation. These solutions contained 0.004–0.015 mol/L Pd, 0.014–0.049 mol/L Cu, and 0.015–0.060 mol/L Al. The results demonstrated the feasibility of selectively separating Pd(II) from leach solutions of spent catalysts using this sorbent. A processing scheme was proposed, comprising sorption from 0.1 M HCl, water rinsing of the loaded sorbent, and elution of Pd(II) with a 5 % thiourea solution in 0.1 M HCl. It was shown that separation of palladium from non-ferrous metals occurs already at the sorption and washing stages.

Keywords: sorption, chemically modified silicas, palladium, non-ferrous metals, desorption, thiourea.

For citation: Buslaeva T.M., Volchkova E.V., Mingalev P.G., Boryagina I.V. Selective sorption-based separation of palladium from process solutions using chemically modified silica. *Izvestiya. Non-Ferrous Metallurgy.* 2025;31(2):41–54.
https://doi.org/10.17073/0021-3438-2025-2-41-54

Выделение палладия из технологических растворов сорбцией на химически модифицированном кремнеземе

Т.М. Буслаева[1], **Е.В. Волчкова**[1], **П.Г. Мингалев**[2], **И.В. Борягина**[3]

[1] **МИРЭА – Российский технологический университет,**
Институт тонких химических технологий имени М.В. Ломоносова
Россия, 119571, г. Москва, пр-т Вернадского, 86

[2] **Московский государственный университет**
Россия, 119991, г. Москва, Ленинские горы, 1, стр. 3

[3] **АО «НПК «Суперметалл»**
Россия, 115184, г. Москва, Озерковская наб., 22/24, корп. 2

✉ Татьяна Максимовна Буслаева (buslaevatm@mail.ru)

Аннотация: Настоящая работа посвящена выявлению возможности селективного выделения сорбцией палладия на химически модифицированных кремнеземах из растворов, содержащих цветные металлы и железо. Объектами исследования являлись индивидуальные (содержащие соединения одного металла) и модельные многокомпонентные растворы. Сорбентами служили кремнеземы, модифицированные группами иминодиуксусной (IDA-D), фосфоновой (PA-D) и аминометилфосфоновой (AMPA-D) кислот, а также хорошо известный химически модифицированный кремнезем, содержащий привитые группы γ-аминопропилтриэтоксисилана (APTES) с плотностью прививки функциональных групп 1,63 ммоль/г. В статических условиях при комнатной температуре для сорбентов IDA-D, PA-D и AMPA-D установлено время достижения постоянных значений сорбции ионов меди (II), никеля (II) и железа (III), обычно присутствующих в технологических растворах различного состава. Построены зависимости сорбции ионов этих металлов от концентрации соляной кислоты. Для сорбента IDA-D изучена зависимость сорбции от концентрации галогенид-иона. Показано, что сорбция указанных ионов протекает в слабокислых средах и практически отсутствует в 1–2 М HCl, причем сорбционная способность сорбентов уменьшается в ряду: IDA-D > AMPA-D > PA-D. Сделанный из полученных результатов вывод о возможности количественного разделения ионов палладия (II) и неблагородных металлов на данных комплексообразующих сорбентах (на примере IDA-D) в динамических условиях не подтвердился. Изучена сорбция ионов Pd(II), Cu(II) и Al(III) в статических и динамических условиях на химически модифицированном кремнеземе, содержащем привитые группы γ-аминопропилтриэтоксисилана (APTES), из хлоридных и хлоридно-бромидных растворов, в том числе модельных, близких по составу к технологическим растворам, образующимся при вскрытии отработанных катализаторов низкотемпературного окисления монооксида углерода до его диоксида, содержащих палладий (0,004÷0,015 моль/л), медь (0,014÷0,049 моль/л) и алюминий (0,015÷0,060 моль/л). Выявлена возможность селективного выделения Pd(II) из растворов выщелачивания отработанных катализаторов указанным сорбентом. Предложена схема переработки отработанных катализаторов, включающая сорбцию из 0,1 М HCl, промывку насыщенной фазы сорбента водой, элюирование Pd(II) 5 %-ным раствором Thio в 0,1 М HCl. Показано, что разделение палладия и цветных металлов происходит уже на стадиях сорбции и промывки сорбента.

Ключевые слова: сорбция, химически модифицированные кремнеземы, палладий, цветные металлы, десорбция, тиомочевина.

Для цитирования: Буслаева Т.М., Волчкова Е.В., Мингалев П.Г., Борягина И.В. Выделение палладия из технологических растворов сорбцией на химически модифицированном кремнеземе. *Известия вузов. Цветная металлургия*. 2025;31(2):41–54.
https://doi.org/10.17073/0021-3438-2025-2-41-54

Introduction

Palladium is a unique platinum-group metal for which demand continues to grow year after year. According to market data [1], this demand cannot be met solely through the processing of primary raw materials: approximately one-third of palladium production over the past 2—3 years has been provided by the recycling of secondary raw materials, among which electronic scrap, jewelry scrap, and, most importantly, spent catalysts, are of particular significance.

Among the variety of palladium-based catalysts used for hydrogenation, dehydrogenation, oxidation, cross-coupling, and other reactions, a distinct group consists of catalysts also containing copper. Notable examples include the Moiseev reaction (oxidation of ethylene to vinyl acetate), the Sonogashira reaction, and several others [2—8]. Typically, these are heterogeneous catalysts supported on alumina, with metals, alloys, or salts deposited on the surface. This group includes catalysts for the low-temperature oxidation of carbon monoxide based on γ-Al_2O_3, containing palladium (II) chloride and copper (II) bromide [9—11].

The recycling of specific types of secondary raw materials is carried out by pyrometallurgical and hydrometallurgical methods, with hydrometallurgical processes clearly prevailing [12]. The leaching of spent catalysts results in the formation of complex process solutions containing a variety of cations and anions. This necessitates the use of tailored approaches suited to the processing of specific catalyst types to achieve selective separation and purification of palladium. It appears that the sorption method holds significant promise for recovering valuable components from such process solutions. This method enables the production of highly selective concentrates, is characterized by low energy consumption, high environmental friendliness, and simple equipment requirements. Implementing this technology requires a well-founded approach to selecting sorbents from the vast range available, comprising tens of thousands of options differing in chemical nature, structural characteristics, sorption capacity, and particle size.

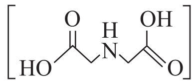
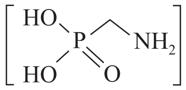
The volume of scientific research focused on the synthesis and investigation of sorbents for specific applications continues to grow [13; 14]. However, considering the need not only for selective recovery of valuable components but also for the repeated reuse of sorbents, porous silica-based materials bearing covalently bonded organic ligands appear particularly promising. These chemically modified silicas (CMSs) interact specifically with molecules of target substances. Notably, the rigid mineral framework of such materials prevents them from swelling (i.e., changing volume) in aqueous and organic media, which is especially important for column processes involving extraction and separation. Moreover, the use of mesoporous silicas with an average pore diameter slightly exceeding 10 nm for CMS synthesis provides superior mass transfer characteristics compared to organic polymer-based sorbents [14—19].

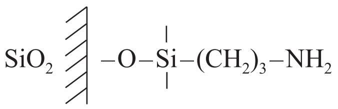
Nitrogen-containing CMSs are among the most versatile and, in principle, allow the separation of platinum-group metals from non-ferrous metals by varying the binding mechanism and the conditions of sorption and desorption. In earlier work, we studied the sorption of platinum (IV) and palladium (II) ions onto one of the best-known CMSs functionalized with monoamine groups, synthesized using the relatively inexpensive and industrially produced γ-aminopropyltriethoxysilane [20]. It was found that Pd(II), unlike Pt(IV), tends to form polynuclear complexes in the sorbent phase at high metal concentrations (tens of grams per liter), which leads to a substantial increase in sorption capacity but also causes difficulties in elution. Under these conditions, quantitative elution of Pd(II) could only be achieved using a 5 % thiourea (Thio) solution in 0.1 M HCl [21].

The aim of this study was to investigate the possibility of selective separation of palladium by sorption onto chemically modified silica from solutions containing base metal ions, including those formed during the processing of secondary raw materials such as spent catalysts used for the low-temperature oxidation of carbon monoxide to carbon dioxide.

Experimental procedure

The starting compounds for the sorption studies were palladium chloride ($PdCl_2$), synthesized according to the procedure described in [22], copper (II) chloride ($CuCl_2$), nickel (II) chloride ($NiCl_2$), iron (III) chloride ($FeCl_3$), copper (II) bromide ($CuBr_2$), γ-Al_2O_3, hydrochloric acid (HCl), sodium chloride (NaCl), sodium bromide (NaBr), and thiourea (Thio). All the listed reagents, produced by OOO TD KHIMMED (Russia), were of analytical grade. All organic reagents used for the synthesis of sorbents were supplied by Sigma-Aldrich. Sorption solutions were prepared by dissolving accurate weighed amounts of the respective compounds in HCl solutions of various concentrations.

The sorbents used in this study were chemically modified silica materials based on Davisil Grade 62 silica gel (W.R. Grace and Co., USA; particle size: 0.07—0.2 mm; specific surface area: 325 m^2/g; average pore diameter: 13.6 nm) containing grafted iminodiacetic acid  (IDA-D), phosphonic acid (PA-D), and aminomethylphosphonic acid  (AMPA-D) groups, as well as a well-known chemically modified silica based on Silochrom C-120, series VG-102/3A1 (specific surface area: 120 m^2/g; particle size: 0.1—0.2 mm; average pore diameter: 45 nm), containing grafted γ-aminopropyltriethoxysilane (APTES) groups with a grafting density of 1.63 mmol/g, having the following structure[1]:



$$SiO_2 \text{—O—Si—}(CH_2)_3\text{—}NH_2$$

---

[1] Sorbent produced by JSC Biokhimmak ST. https://bcmst.ru/

The synthesis of the complexing sorbents was carried out according to the following procedures.

1. Silica Gel Functionalized with Iminodiacetic Acid (IDA-D). Twenty grams of iminodiacetic acid were dissolved in 180 mL of 4 M NaOH under stirring with a magnetic stirrer at room temperature for 10 min (the pH value of the solution should be in the range of 12.3—12.5). Then, 3 mL of 3-glycidyloxypropyltrimethoxysilane were added, and the two-phase mixture was stirred until a clear solution was obtained. This solution was then added to a suspension of 65 g of Davisil silica gel in 600 mL of 5 % acetic acid (the pH value of the resulting mixture should be in the range of 5.4—5.8). The mixture was stirred using a mechanical stirrer at 80 °C for 2 h. The sorbent was filtered, washed four times (300 mL each) with distilled water, dried on the filter, and then held in a drying oven at 100 °C for 2 h.

2. Silica gel functionalized with diethylphosphonate (DEP-D)[1]. A mixture of 17.6 mL of 3-glycidyloxypropyltrimethoxysilane and 10.2 mL of diethyl phosphite in 100 mL of acetonitrile was prepared. Then, 20 g of Davisil silica gel were added, and the mixture was stirred with a mechanical stirrer at 70 °C for 11 h. The sorbent was filtered, washed three times with acetonitrile, three times with water, three times with acetonitrile, and dried on the filter.

3. Silica gel functionalized with phosphonic acid (PA-D). A mixture of 10 g of DEP-D sorbent and 50 mL of 20 % hydrochloric acid was stirred for 8 hours at 100 °C. The sorbent was then washed with water until neutral washings were obtained, washed three times with acetonitrile (25 mL each), and dried on the filter.

4. Silica gel functionalized with aminomethylphosphonic acid (AMPA-D). A mixture of 35 mL of 3-aminopropyltriethoxysilane, 25 g of phosphorous acid, and 186 mL of a 10 % formaldehyde solution was placed into a flask and stirred. Then, 660 mL of concentrated hydrochloric acid and 30 g of Davisil silica gel were added. The mixture was stirred for 12 h at room temperature, followed by 8 hours at 80 °C, and then stirred again for 12 h at room temperature. The silica gel was separated from the solution, washed three times with distilled water, evaporated at 100 °C under vacuum generated by a water-jet pump, washed with 100 mL of ethanol, and dried at 100 °C under vacuum generated by a water-jet pump.

The elemental analysis results for the sorbents are presented in Table 1. The amounts of grafted groups were: 0.35 mmol/g for IDA-D, 0.42—0.55 mmol/g for PA-D, and 0.85 mmol/g for AMPA-D.

The sorption of palladium (II), non-ferrous metals, and iron (III) ions under static conditions was carried out from individual hydrochloric acid solutions (0.1—4 M) and mixed chloride-bromide solutions at room temperature (three parallel experiments for each test). The solution volumes ranged from 10 to 15 mL, and the mass of sorbent (m_{sorb}) was 0.030 ± 0.001 g.

After sorption under static conditions, the sorbent was separated by filtration through a glass funnel with a paper filter, washed with water, and then subjected to desorption (elution). The eluents used were 2 M and 3 M HCl solutions and a 5 % Thio solution in 0.1 M HCl; the volume of eluent in each individual experiment was 15 mL.

Experiments under dynamic conditions were carried out in glass columns with an internal diameter of 0.4 cm. The masses of the sorbents were 0.6 g for IDA-D and 0.15 g for APTES. The solutions passed through the column under gravity flow. After sorption, the sorbent saturated with the extracted ions was washed with water until the washings became colorless, and the eluent solution was subsequently introduced.

The amount of sorbed metal (m'_{sorb}) was determined as the difference between its content in the solution before sorption (m_{in}) and after sorption (m_{out}). The metal efficiency onto the sorbent was calculated as follows:

$$E_{\text{sorb}} = \frac{m'_{\text{sorb}}}{m_{\text{in}}} \cdot 100\ \%.$$

The fraction of metal removed during washing was calculated as the ratio of the amount of metal in the wash water to the amount sorbed:

$$E_{\text{wash}} = \frac{m_{\text{wash}}}{m'_{\text{sorb}}} \cdot 100\ \%.$$

The amount of metal remaining on the sorbent after washing (m'_{wash}) was determined as the difference between the amount of sorbed metal and the amount of metal found in the wash water.

The overall recovery of metal into the solution after sorption and washing ($E_{\text{overall (solution)}}$) was calculated as the ratio of the sum of the amounts of metal in the solution after sorption (m_{out}) and in the wash water (m_{wash}) to the initial amount of metal in the solution (m_{in}):

$$E_{\text{overall solution}} = \frac{m_{\text{out}} + m_{\text{wash}}}{m_{\text{in}}} \cdot 100\ \%.$$

The elution efficiency was determined as the ratio of

---

[1] DEP-D can also serve as a sorbent for the extraction of transition metal ions; however, in this study, it was used only as an intermediate product in the synthesis of PA-D.

Table 1. **Results of elemental analysis of the sorbents***

Таблица 1. Результаты элементного анализа сорбентов*

Sorbent	Content, wt.%			
	C	H	N	P
IDA-D	5.61	1.31	0.58	–
DEP-D	5.22	1.29	–	1.27
PA-D	5.33	1.27	–	1.69
AMPA-D	4.04	1.55	1.30	2.59

* Elemental analysis of the sorbents was performed at the Shared Research Facility of the Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia.

the amount of metal in the eluent (m_{el}) to the amount of metal remaining on the sorbent after washing:

$$E_{\text{el}} = \frac{m_{\text{el}}}{m'_{\text{wash}}} \cdot 100\ \%.$$

The initial metal concentrations used in the dynamic sorption experiments for model solutions simulating the composition of process solutions generated during the treatment of spent Pd—Cu catalysts for the low-temperature oxidation of carbon monoxide to carbon dioxide were varied based on their composition: 1.5 wt. % Pd and 3.5 wt. % Cu relative to the mass of the γ-Al_2O_3 carrier [9].

The analysis of aqueous solutions for palladium, copper, nickel, and iron was performed using a NOV AA 330 atomic absorption spectrometer with flame atomization (Analytik Jena, Germany), while the analysis of Al-containing solutions was carried out using a KVANT-Z atomic absorption spectrometer with electrothermal atomization (OOO “Kortek”, Russia). If dilution of the samples was necessary prior to analysis, three aliquots of equal volume were taken from each solution, transferred into volumetric flasks, and brought to the mark with a 1:5 HCl solution. The analytical error did not exceed 5 % relative for flame atomization analysis and 7 % relative for electrothermal atomization analysis.

The investigation of complex model solutions was carried out by inductively coupled plasma mass spectrometry (ICP-MS) either without preliminary sample preparation or after additional dilution with deionized water by factors of 50—10 000. Measurements were performed using an Agilent 7900 mass spectrometer (Agilent Technologies, USA) equipped with a double-pass glass spray chamber, a MicroMist glass nebulizer, and a quartz torch. The obtained data were processed using Agilent MassHunter software (Agilent Technologies, USA). The measurement error did not exceed 5 % relative.

Electronic absorption spectra (EAS) of the solutions were recorded over the wavelength range $\lambda = 200 \div 1000$ nm using a Helios Alpha Local Control System spectrophotometer (Thermo Spectronic, USA) in quartz cuvettes with a 1 cm optical path length at room temperature. The wavelength setting accuracy was within 0.05—0.1 nm.

X-ray photoelectron spectra (XPS) were recorded using a LAS instrument (Riber) with calibration based on the C1s binding energy line (285.0 eV) as an external standard.

Results and discussion

In our previous study [23], we investigated the sorption of Pd(II) ions from chloride solutions containing non-ferrous metal ions onto silicas functionalized with N- and S-containing organic molecules. The conditions for their separation from non-ferrous metal ions present in process solutions formed during the processing of various platinum metal concentrates were identified. It was shown that impurity ions pass through the entire technological process and eventually end up in the discharge stream. At the stages of sorption and desorption, it is necessary to monitor the completeness of Pd(II) ion separation from non-ferrous metal ions and to introduce an additional sorbent washing operation, if required [23]. In our opinion, the removal of impurities prior to the stage of palladium and/or other platinum-group metal recovery should positively influence the reduction of the valuable component regeneration/recycling time and the volume of washing solutions.

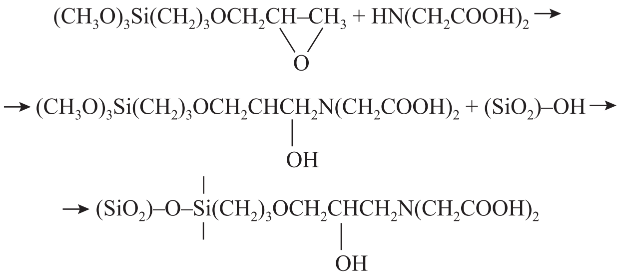
According to the literature data [24—31], the most promising types of sorbents for impurity metal ion removal are sorbents bearing grafted aminocarboxylic acid groups, particularly iminodiacetic acid (such as Dowex A-1 type sorbents), aminomethylphosphonic acid, and phosphonic acid groups[1]. Therefore, for the preliminary removal of base metal ions (Cu(II), Ni(II), and Fe(III)), we tested silica gels functionalized with iminodiacetic acid (IDA-D), aminomethylphosphonic acid (AMPA-D), and phosphonic acid (PA-D, derived from H_3PO_3.

Traditionally, the synthesis of sorbents with grafted aminocarboxylic acid groups, particularly iminodiacetic

---

[1] At this stage of the study, the sorption of Al(III) ions was not investigated.

acid groups, involves the treatment of amino-containing sorbents with halogenoacetic acids (XCH_2COOH, where X = Cl or Br). We proposed an alternative synthesis scheme using 3-glycidyloxypropyltrimethoxysilane and iminodiacetic acid (IDA-D):



$$(CH_3O)_3Si(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CH{-}CH_3} + HN(CH_2COOH)_2 \rightarrow$$

$$\rightarrow (CH_3O)_3Si(CH_2)_3OCH_2\underset{\overset{|}{OH}}{CH}CH_2N(CH_2COOH)_2 + (SiO_2){-}OH \rightarrow$$

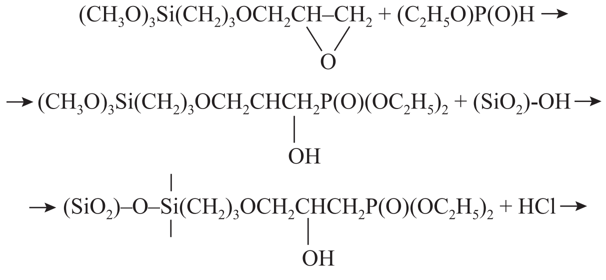
$$\rightarrow (SiO_2){-}O{-}\underset{|}{\overset{|}{Si}}(CH_2)_3OCH_2\underset{\overset{|}{OH}}{CH}CH_2N(CH_2COOH)_2$$

IDA-D

The synthesis of the modifier was carried out in an alkaline medium at pH = 12.3—12.5, while the deposition of the modifier onto the silica gel surface was performed at pH = 5.6—5.8. It should be noted that all stages of the process were conducted in aqueous solutions without the use of organic solvents.

It is important to emphasize that an attempt to apply a similar procedure to obtain silica gel functionalized with phosphonic acid was unsuccessful: during the reaction in an alkaline medium, a side process involving the oxidation of phosphorous acid by atmospheric oxygen occurred, which reduced the yield of the target product.

Therefore, an alternative method was used to synthesize the sorbent bearing diethylphosphonate groups (DEP-D), which consisted of the grafting of a phosphonic acid ester followed by its hydrolysis:

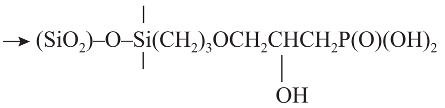


$$(CH_3O)_3Si(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} + (C_2H_5O)P(O)H \rightarrow$$

$$\rightarrow (CH_3O)_3Si(CH_2)_3OCH_2\underset{\overset{|}{OH}}{CH}CH_2P(O)(OC_2H_5)_2 + (SiO_2){-}OH \rightarrow$$

$$\rightarrow (SiO_2){-}O{-}\underset{|}{\overset{|}{Si}}(CH_2)_3OCH_2\underset{\overset{|}{OH}}{CH}CH_2P(O)(OC_2H_5)_2 + HCl \rightarrow$$

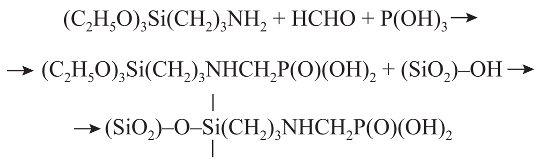
DEP-D



$$\rightarrow (SiO_2){-}O{-}\underset{|}{\overset{|}{Si}}(CH_2)_3OCH_2\underset{\overset{|}{OH}}{CH}CH_2P(O)(OH)_2$$

PA-D

For the grafting of aminomethylphosphonic acid groups onto the silica gel surface (AMPA-D), the following scheme was used:



$$(C_2H_5O)_3Si(CH_2)_3NH_2 + HCHO + P(OH)_3 \rightarrow$$

$$\rightarrow (C_2H_5O)_3Si(CH_2)_3NHCH_2P(O)(OH)_2 + (SiO_2){-}OH \rightarrow$$

$$\rightarrow (SiO_2){-}O{-}\underset{|}{\overset{|}{Si}}(CH_2)_3NHCH_2P(O)(OH)_2$$

AMPA-D

The elemental analysis data of the obtained sorbent (Table 1) showed a C : N : P ratio of 4 : 1 : 1, corresponding to the AMPA-D sorbent with grafted aminomethylphosphonic acid groups.

Preliminary static sorption experiments demonstrated that a 10-minute contact time between the phases was sufficient to achieve constant sorption values for base metal ions using the selected sorbents.

The dependencies of Cu(II), Ni(II), and Fe(III) ion sorption on the solution acidity for the IDA-D, AMPA-D, and PA-D sorbents are shown in Figs. 1 and 2. It can be seen that sorption occurs in weakly acidic media and is practically absent in 1—2 M HCl. The sorption capacity of the sorbents decreases in the order: IDA-D > > AMPA-D > PA-D.

The data on the effect of chloride ion concentration on the sorption of Cu(II), Ni(II), and Fe(III) ions on the IDA-D sorbent are presented in Table 2. It can be seen that, within the concentration range of 10 to 90 g/L, the effect is practically negligible.

Thus, the overall results indicate that IDA-D is the most promising sorbent for the removal of base metal ions from complex process solutions.

Experiments on the separation of Pd(II), non-ferrous metal, and iron ions using the IDA-D sorbent under dynamic conditions, with the results summarized in Table 3, showed that Cu(II) and Fe(III) ions predominantly transfer into the sorbent phase. Although Pd(II) ions are also sorbed by this complexing sorbent, their degree of extraction into the sorbent phase does not exceed 39 %. During the washing stage, Pd(II) ions are almost completely (99.3 %) transferred into the wash water (with an overall recovery into solutions reaching 99.7 %). Ni(II) ions are likely displaced by Cu(II) and Fe(III) ions, which have a higher affinity for the sorbent. This leads to the conclusion that the separation of Pd(II) ions from base metal ions, primarily Ni(II) and Cu(II), by sorption onto complexing sorbents is theoretically feasible; however, quantitative sorption of the metal ions accompanying palladium is not achieved. Therefore, we returned to the traditional approach aimed at providing the selective separation of Pd(II) from process solutions. For this purpose, a well-established chemically modified silica, APTES, was used to test the sorption extraction of Pd(II) from solutions generated during the regeneration of low-temperature carbon monoxide oxidation catalysts based on γ-Al_2O_3, which initially contained palladium (II) chloride and copper (II) bromide.

Given that the composition and structure of complexes significantly affect the sorption process, and that the processing of such catalysts yields solutions containing both chloride and bromide ions, determining the composition of the complexes is a critical task. The speciation of Cu(II) and Pd(II) ions in this system can be conveniently analyzed using electronic absorption spectroscopy (EAS), as the absorption bands of Pd(II) halide complexes appear in the visible region at wavelengths between $\lambda = 470 \div 505$ nm, while the absorption of Cu(II) ions occurs at longer wavelengths. Fig. 3 shows the EAS of a model solution corresponding to the composition of process solutions generated during the leaching of spent catalysts for low-temperature carbon monoxide oxida-

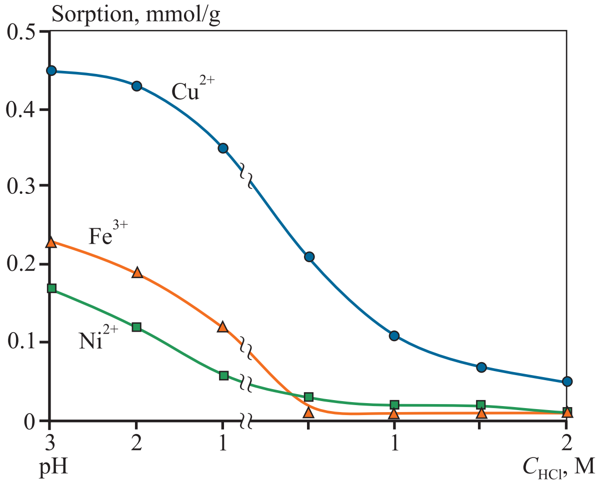


Fig. 1. Dependence of Cu(II), Ni(II), and Fe(III) sorption on HCl concentration on the IDA-D sorbent

$C_{met} = 5\cdot10^{-3}$ mol/L, $m_{sorb} = 0.03$ g, $V_{solution} = 10$ mL, contact time – 10 min

Рис. 1. Зависимость сорбции Cu(II), Ni(II) и Fe(III) от концентрации HCl на сорбенте IDA-D

$C_{мет} = 5\cdot10^{-3}$ моль/л, $m_{сорб} = 0{,}03$ г, $V_{р\text{-}р} = 10$ мл, время контакта фаз 10 мин

Table. 2. **Effect of chloride ion concentration on the sorption of Cu(II), Ni(II), and Fe(III) ions on the IDA-D sorbent**[*]

Таблица 2. Зависимость сорбции Cu(II), Ni(II), Fe(III) от концентрации хлорид-иона[*]

$[Cl^-]$, g/dm^3	Sorption, mmol/g		
	Cu^{2+}	Ni^{2+}	Fe^{3+}
10	0.36	0.07	0.13
30	0.33	0.07	0.16
50	0.33	0.07	0.11
70	0.38	0.05	0.11
90	0.38	0.05	0.12

[*] $C_{met} = 5\cdot10^{-3}$ mol/L, $m_{sorb} = 0.03$ g, $V_{solution} = 10$ mL, contact time = 10 min.

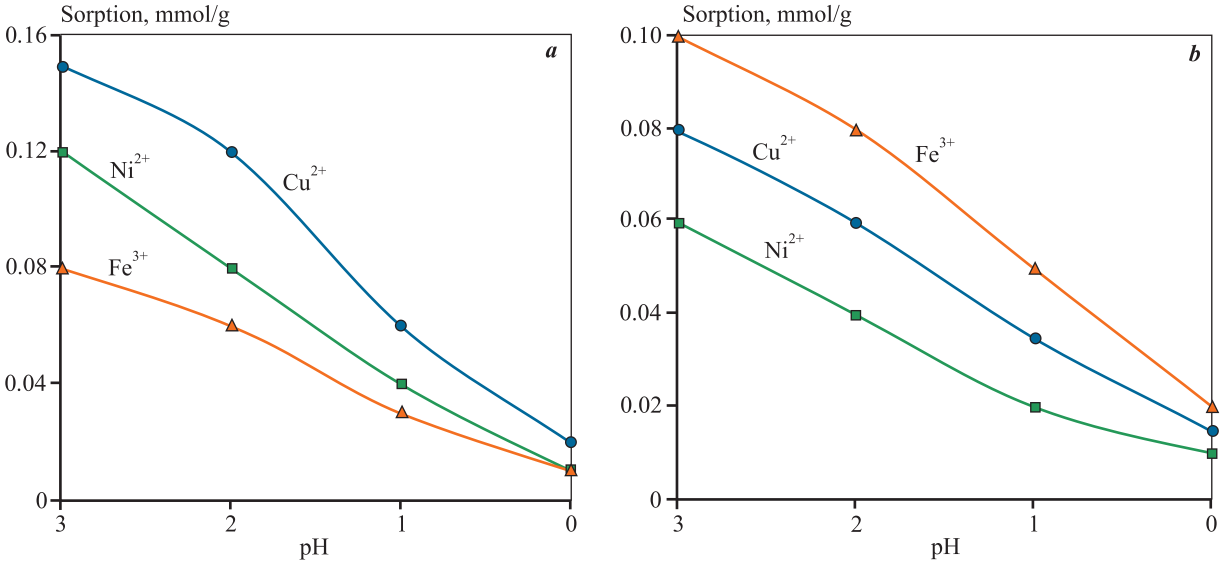


Fig. 2. Dependence of (II), Ni(II), and Fe(III) ion sorption on HCl concentration on the AMPA-D (***a***) and PA-D (***b***) sorbents

$C_{met} = 5\cdot10^{-3}$ mol/L, $m_{sorb} = 0.03$ g, $V_{solution} = 10$ mL, contact time – 10 min

Рис. 2. Зависимость сорбции ионов Cu(II), Ni(II) и Fe(III) от концентрации HCl на сорбентах AMPA-D (***a***) и PA-D (***b***)

$C_{мет} = 5\cdot10^{-3}$ моль/л, $m_{сорб} = 0{,}03$ г, $V_{р\text{-}р} = 10$ мл, время контакта фаз 10 мин

Table. 3. Results of separation of Pd(II), Cu(II), Ni(II), and Fe(III) ions during sorption on IDA-D sorbent under dynamic conditions (m_{sorb} = 0.6 g)

Таблица 3. Результаты разделения ионов Pd(II), Cu(II), Ni(II) и Fe(III) в процессе сорбции на сорбенте IDA-D в динамических условиях ($m_{сорб}$ = 0,6 г)

Paremeter	Pd(II)	Cu(II)	Ni(II)	Fe(III)
Sorption ($V_{in} = V_{out}$ = 7 mL)				
m_{in}, μg	3720	2220	2050	1960
m_{out}, μg	2280	77	1645	350
m'_{sorb}, μg	1440	2143	405	1610
E_{sorb}, %	38.7	96.5	19.8	82.1
Washing with water (V_{wash} = 5.4 mL)				
m_{wash}, μg	1430	130	405	162
m'_{wash}, μg	10	2013	0	1448
E_{wash}, %	99.3	6.1	>99.9	10.1
$E_{overall\ (solution)}$, %	99.7	9.3	>99.9	26.1
Elution with 2 M HCl (V_{el} = 7 mL)				
m_{el}, μg	0.7	1995	0	1295
E_{el}, %	7	99.1	0	89.4

tion [9]. The figure also presents the absorption spectra of $PdCl_2$ and $CuBr_2$ solutions in 1 M HCl.

As shown in Fig. 3, two absorption bands are observed in the visible region of the model solution spectrum, with maxima at λ = 480 nm and 830 nm. It is well established that in solutions containing both chloride and bromide ions, Pd(II) tends to form mixed halide complexes, $[PdCl_{4-n}Br_n]^{2-}$, with the complex composition determined by the halide ion ratio [32]. The EAS of solutions dominated by the $[PdCl_4]^{2-}$ complex is characterized by absorption bands at λ = = 473 nm (ε = 161 L·mol^{-1}·cm^{-1}) and λ = 606 nm (ε = = 10 L·mol^{-1}·cm^{-1}) [33]. In the visible region, the EAS of solutions containing $[PdBr_4]^{2-}$ anions exhibit a charge transfer band at λ = 417 nm (ε = 790 L·mol^{-1}·cm^{-1}) and a broad absorption band at λ = 495—505 nm (ε = = 360 L·mol^{-1}·cm^{-1}) corresponding to *d—d* transitions [32—34].

Preliminary experiments demonstrated that the addition of bromide ions to a hydrochloric Pd-containing solution causes the absorption band at λ = = 473 nm to shift toward longer wavelengths, reflecting the substitution of chloride ions in the inner coordination sphere by bromide ions. In 0.1 M HCl, complete substitution was observed at a $[PdCl_4]^{2-}$ to Br^- ratio of 1:100 (with the band shifting to λ = = 505 nm), whereas in 1 M HCl, even at a $[PdCl_4]^{2-}$ to Br^- ratio of 1:500, the formation of the $[PdBr_4]^{2-}$ complex did not occur.

Thus, the presence of an absorption band at λ = = 480 nm in the model solution spectrum indicates that, in the process solution obtained by leaching the catalyst in 1 M HCl, palladium remains predominantly in the form of $[PdCl_4]^{2-}$. However, as the solution acidity decreases, for example through dilution with water, the likelihood of forming mixed $[PdCl_{4-n}Br_n]^{2-}$ complexes increases significantly.

The state of Cu(II) ions in this solution is discussed below. The EAS of an individual solution obtained by dissolving a weighed sample of $CuBr_2$ in 1 M HBr is characterized by a broad absorption band in the range of λ = 810÷815 nm (Fig. 3). According to the literature [35], in chloride media, depending on the chloride ion concentration, Cu(II) may exist as a mixture of aquated complexes with the compositions $[Cu(H_2O)_4]^{2+}$, $[Cu(H_2O)_2Cl_2]$, $[Cu(H_2O)_3Cl]^+$ and $[Cu(H_2O)Cl_3]^-$. In the visible region, the $[Cu(H_2O)_3Cl]^+$ complex, which dominates at chloride ion concentrations of 0.1— 1.0 mol/L, exhibits an absorption band at λ = 870 nm (ε = 80 L·mol^{-1}·cm^{-1}). A slight shift of its maximum to 830 nm in the leaching solution indicates the presence of mixed aquated and halide forms of Cu(II) in the solution.

Static sorption studies of Pd(II), Cu(II), and Al(III) ions on the APTES sorbent from individual hydrochloric solutions showed that equilibrium sorption values for Pd(II) were achieved after 5—10 min of phase

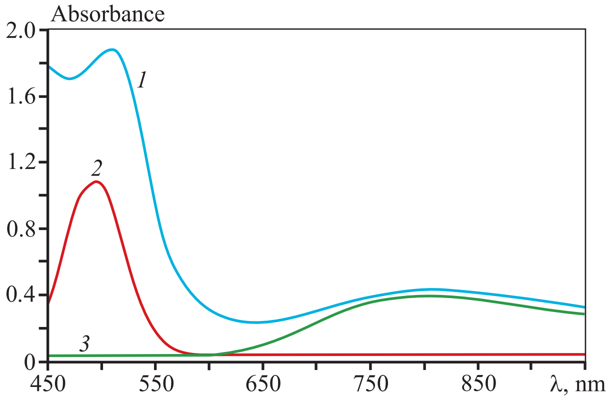


Fig. 3. Electronic absorption spectra (EAS) of the model solution in 1 M HCl (*1*), the $PdCl_2$ solution in 1 M HCl (*2*), and the $CuBr_2$ solution in 1 M HBr (*3*)
$C_{Pd} = 2\cdot10^{-3}$ mol/L, $C_{Cu} = 1\cdot10^{-2}$ mol/L

Рис. 3. ЭСП модельного раствора в 1 М HCl (*1*), раствора $PdCl_2$ в 1 М HCl (*2*) и раствора $CuBr_2$ в 1 М HBr (*3*)
$C_{Pd} = 2\cdot10^{-3}$ моль/л, $C_{Cu} = 1\cdot10^{-2}$ моль/л

mixing (0.156 mmol/g), for Cu(II) after 20—30 min (0.084 mmol/g for $CuCl_2$ and 0.060 mmol/g for $CuBr_2$ solution in 1 M HCl), whereas the equilibrium sorption time for Al(III) ions was 45 min (0.319 mmol/g). It should be noted that the sorption of Pd(II) by the selected sorbent, as well as complex formation during the sorption process, have been discussed in detail in our earlier work [20].

An increase in HCl concentration in the solution leads to a decrease in the sorption of Pd(II) and Cu(II) (Table 4). For example, in 0.1 M HCl, the sorption capacities for Pd(II) and Cu(II) are 1.43 and 0.97 mmol/g, respectively, whereas in 4 M HCl they decrease to 0.4 and 0.6 mmol/g, respectively.

A decrease in the sorption of palladium and copper ions on the APTES sorbent with increasing hydrochloric acid concentration is generally attributed to the competitive sorption of halide ions [20; 36; 37]. In contrast, Al(III) ions are sorbed only at HCl concentrations above 1 M, and their sorption capacity remains nearly constant at approximately 2.8 mmol/g of sorbent. This behavior is likely due to the involvement of silanol groups on the sorbent matrix in cation exchange, whereby protons are replaced by Al(III) cations [38]. It should also be noted that the formation of a certain proportion of anionic Al(III) chlorocomplexes at higher acid concentrations, as reported in several studies [39; 40], cannot be excluded.

Based on the static sorption data obtained, the possibility of separating Pd(II) ions from Cu(II) and Al(III) ions under dynamic conditions was evaluated. To achieve better separation of these elements, sorption was carried out from a solution with an HCl concentration of 0.1 M.

Solutions of 2 M and 3 M HCl (at room temperature and at 60—65 °C) were initially tested as eluents. However, the desorption results proved unsatisfactory under both static and dynamic conditions. Therefore, a 5 % thiourea (Thio) solution in 0.1 M HCl was subsequently used as the eluent [21].

The separation of non-ferrous metal ions from palladium was studied under dynamic conditions using a model solution simulating the leaching solution of the catalyst, diluted to 0.1 M HCl. Three sorption—washing—desorption cycles were carried out using the same portion of the sorbent. The initial volumes of solution used in the sorption stage were 2.4, 1.7, and 1.2 mL for the first, second, and third cycles, respectively. After sorption, the sorbent was washed with distilled water until the washings became colorless (the volume of wash water was approximately 50 mL), followed by elution of palladium ions using a 5 % Thio solution in 0.1 M HCl (8.5—11.4 mL). The data presented in Table 5 show that during sorption, more than 99.9 % of Pd(II) ions were transferred to the sorbent phase, while the sorption of Cu(II) ions ranged from 15.1 % to 18.3 %, and that of Al ions from 1.3 % to 17.2 %. Washing the sorbent with distilled water allowed for the almost complete removal of non-ferrous metal ions from the sorbent phase (E^{Σ}_{Cu} = 95.4÷97.0 %, E^{Σ}_{Al} = 95.2÷99.0 %).

Table 4. **Dependence of Pd(II), Cu(II), and Al(III) sorption under static conditions on HCl concentration**

Таблица 4. Зависимость сорбции Pd(II), Cu(II) и Al(III) в статических условиях от концентрации HCl

Metal*	Sorption, mmol/g, at C_{HCl}, M				
	0.1	0.5	1	2	4
Pd	1.43	1.07	0.77	0.43	0.4
Cu	0.97	**	0.67	0.65	0.6
Al	–	**	2.87	2.81	2.69

* C^{in}_{Pd} = 14 mmol/L, C^{in}_{Cu} = 55 mmol/L, C^{in}_{Al} = 56 mmol/L.
** No experiment was conducted.

Thus, nearly complete separation of Pd(II) from accompanying non-ferrous metals was achieved during the sorption and washing stages. The degree of Pd(II) recovery into the eluate was 85—90 %. It was demonstrated that the proposed sorbent remains stable over at least three sorption cycles.

Based on the results of the present study, we propose a process scheme for the recycling of spent low-temperature carbon monoxide oxidation catalysts containing $PdCl_2$ and $CuBr_2$, which includes the following stages:

1) leaching of the spent catalysts with 1 M HCl;
2) adjustment of the acidity of the resulting solution to pH 1;
3) sorption onto the APTES sorbent;
4) washing of the sorbent with water;
5) desorption of palladium using a hydrochloric acid solution of Thio;
6) recovery of palladium from the resulting eluate.

During the sorption stage, selective sorption of palladium onto the APTES sorbent occurs, while non-ferrous metals are concentrated in the solution combined with the wash water after sorption [21].

It should be noted that during the desorption stage, a tetrathiourea complex of the composition $[Pd(Thio)_4]^{2+}$ of orange color is formed in the eluate [20], from which an *X*-ray amorphous precipitate of metallic palladium can be obtained by treatment with a 5 M NaOH solu-

Table. 5. **Results of the experiment on the separation of Pd(II), Cu(II), and Al(III) using the APTES sorbent**
Таблица 5. Результаты эксперимента по разделению Pd(II), Cu(II) и Al(III) на сорбенте APTES

Experiment	Sorption stage E_{sorb}, %			Washing stage (combined solutions after sorption and washing), E_{wash}, %			Elution stage (solution after elution with 5 % Thio in 0.1 M HCl)		
	Pd	Cu	Al	Pd	Cu	Al	$V_{solution}$, mL	C_{Pd}, µg/mL	E_{el}^{Pd}, %
1st cycle	>99.9	15.1	1.3	**	95.2	99.0	8.5	406	90.1
2st cycle	>99.9	17.0	4.6	**	98.0	97.1	11.4	212	89.1
3st cycle	>99.9	18.3	17.2	**	97.0	95.2	9.9	164	84.8

* $C_{Pd} = 15$ mmol/L, $C_{Cu} = 49$ mmol/L, $C_{Al} = 60$ mmol/L, $C_{HCl} = 0.1$ M, $m_{sorb} = 0.15$ g.
** Pd(II) ions were not detected in the solutions.

tion. Indeed, according to *X*-ray photoelectron spectroscopy data, the binding energies of the Pd $3d_{3/2}$ and $3d_{5/2}$ electrons in the investigated sample are 341.1 and 335.8 eV, respectively, which correspond to metallic palladium (Pd^0) [41]. In this process, thiourea, which is oxidized to formamidinodisulfide (Fds), acts as a reducing agent for palladium ($E^0_{Pd^{2+}/Pd} = 0.92$ V); the standard redox potential of the Fds/2Thio system is 0.42—0.48 V [42].

The recovery of palladium into the solid product is practically quantitative.

Conclusions

1. Under static conditions, the sorption behaviors of Cu(II), Ni(II), and Fe(III) ions on IDA-D, AMPA-D, and PA-D sorbents as a function of solution acidity were investigated. For the IDA-D sorbent, the effect of chloride ion concentration was additionally studied. Based on the obtained results, IDA-D can be recommended for the removal of base metals.

2. Based on the sorption data for Pd(II), Cu(II), Ni(II), and Fe(III) ions onto the specified sorbent under dynamic conditions, it was established that the preliminary recovery of base metal ions from process solutions formed during the processing of various types of noble metal-bearing raw materials (in this study, palladium) by sorption onto complexing chemically modified silicas does not ensure the selective separation of Pd(II).

3. Using model solutions simulating those formed during the regeneration of low-temperature carbon monoxide oxidation catalysts and containing chloride and bromide anions, the possibility of separating palladium from non-ferrous metals by sorption onto chemically modified silica bearing grafted γ-aminopropyltriethoxysilane (APTES) groups was demonstrated.Considering the chemical states of the sorbed ions, the equilibrium times for Pd(II), Cu(II), and Al(III) sorption were determined under static conditions, and the dependencies of their sorption on solution acidity were established. It was shown that the sorption capacities for Pd(II) and Cu(II) decrease with increasing HCl concentration from 0.1 M to 4 M, while Al(III) begins to sorb at HCl concentrations above 1 M, with its sorption capacity remaining practically constant.

4. The optimal conditions for the separation of Pd(II), Cu(II), and Al(III) ions on the APTES sorbent under dynamic conditions were determined: sorption from 0.1 M HCl, washing the sorbent with water, and desorption of Pd(II) with a 5 % Thio solution in 0.1 M HCl. It was found that under these conditions, the separation of palladium from non-ferrous metals is achieved already during the sorption and washing stage.

5. Metallic palladium is obtained by reducing the thiourea eluate with 5 M NaOH solution.

References

1. PGM Market Report, May 2024. London: Johnson Matthey, 2024. P. 48. https://matthey.com/documents/161599/509428/PGM-Market-Report-24.pdf/4d557d3b-47d1-d975-c4af-5df1c81000f0?t=1715228936090
2. Chorkendorf I., Naimantsvedrait Kh. Modern catalysis and chemical kinetics. Dolgoprudny: Publishing House “Intellect”, 2010. 599 p. (In Russ.).
Чоркендорф И., Наймантсведрайт Х. Современный катализ и химическая кинетика. Долгопрудный: ИД «Интеллект», 2010. 599 с.
3. Valishina E.A., Guedes da Silva M.F.C., Kinzhalov M.A., Timofeeva S.A., Buslaeva T.M., Haukka M., Pombeiro A.J.L., Boyarskiy V.P, Kukushkin V.Yu., Luzyanin K.V. Palladium — ADC complexes as effective catalysts in copperfree and room temperature Sonogashi-

ra coupling. *Journal of Molecular Catalysis A: Chemical.* 2014;395:162—171.
https://doi.org/10.1016/j.molcata.2014.08.018

4. Goulas K.A., Sreekumar S., Song Y., Kharidehal P., Gunbas G., Dietrich P.J., Johnson G.R., Wang Y.C., Grippo A.M., Grabow L.C., Gokhale A.A., Toste F.D. Synergistic effects in bimetallic palladium—copper catalysts improve selectivity in oxygenate coupling reactions. *Journal of the American Chemical Society.* 2016;138(21): 6805—6812.
https://doi.org/10.1021/jacs.6b02247
5. Yang H., Qin S., Yue Y., Liu L., Wang H., Lu J. Entrapment of a pyridine derivative within a copper—palladium alloy: a bifunctional catalyst for electrochemical reduction of CO_2 to alcohols with excellent selectivity and reusability. *Catalysis Science and Technology.* 2016;6: 6490—6494.
https://doi.org/10.1039/ C6CY00971A
6. Kanwal I., Mujahid A., Rasool N., Rizwan K., Malik A., Ahmad G., Shah S.A.A., Rashid U., Nasir N.M. Palladium and copper catalyzed Sonogashira cross coupling an excellent methodology for C—C bond formation over 17 years: A review. *Catalysts.* 2020;10(4):443.
https://doi.org/10.3390/catal10040443
7. Obradović M.D., Lačnjevac U.Č., Radmilović V.V., Gavrilović-Wohlmuther A., Kovač J., Rogan J.R., Radmilović V.R., Gojković S.Lj. Palladium-copper bimetallic surfaces as electrocatalysts for the ethanol oxidation in an alkaline medium. Available at SSRN 4455250.2023.
https://dx.doi.org/10.2139/ssrn.4455250
8. Lesiak M., Binczarski M., Karski S., Maniukiewicz W., Rogowski J., Szubiakiewicz E., Berlowska J., Dziugan P., Witońska I. Hydrogenation of furfural over Pd—Cu/Al_2O_3 catalysts. The role interaction between palladium and copper on determining catalytic properties. *Journal of Molecular Catalysis A: Chemical.* 2014;395: 337—348.
https://doi.org/10.1016/j.molcata.2014.08.41
9. Bruk L., Titov D., Ustyugov A., Zubavichus Ya., Chernikova V., Tkachenko O., Kustov L., Murzin V., Oshanina I., Temkin O. The mechanism of low-temperature oxidation of carbon monoxide by oxygen over the $PdCl_2—CuCl_2/\gamma\text{-}Al_2O_3$ nanocatalyst. *Nanomaterials.* 2018;8(4):217.
https://doi.org/10.3390/nano8040217
10. Bruk L. G., Ustyugov A. V., Katsman E. A., Iskhakova L.D., Oshanina I.V., Tkachenko O.P., Kustov L.M., Temkin O.N. Kinetics and mechanism of the low-temperature oxidation of carbon monoxide with oxygen on a $PdCl_2—CuCl_2/\gamma\text{-}Al_2O_3$ catalyst. *Kinetics and Catalysis.* 2017;58 (2):179—190.
https://doi.org/10.1134/S0023158417020033
11. Feng Ya., Wang Li, Zhang Ya., Guo Yu. Deactivation mechanism of $PdCl_2—CuCl_2/Al_2O_3$ catalysts for CO oxidation at low temperatures. *Chinese Journal of Catalysis.* 2013;34(5):923—931.
https://doi.org/10.1016/S1872-2067(12)60556-7
12. Giovanna N., Goosey E., Yildiz D.S., Loving E., Nguyen V.T., Riaño S., Yakoumis I., Martinez A.M., Siriwardana A., Unzurrunzaga A., Spooren J., Atia T.A., Michielsen B., Dominguez-Benetton X., Lanaridi O. Platinum group metals recovery using secondary raw materials (PLATIRUS): Project overview with a focus on processing spent autocatalyst. *Johnson Matthey Technology Review.* 2021;65(1)127—147.
https://doi.org/10.1595/205651321X16057842276133
13. Ehrlich G.V., Buslaeva T.M., Maryutina T.A. Trends in sorption recovery of platinum metals: A critical survey. *Russian Journal of Inorganic Chemistry.* 2017;62(14): 1797—1818.
https://doi.org/10.1134/S0036023617140030
14. Lisichkin G.V., Olenin A.Y. Chemically modified silica in sorption-instrumental analytical methods. *Russian Journal of General Chemistry.* 2021;91(5):870—889.
https://doi.org/10.1134/S1070363221050182
15. Radi Smaail, El-Abiad Chahrazad, Moura Nuno M.M., Faustino Maria A.F., Neves M. Graça P.M.S. New hybrid adsorbent based on porphyrin functionalized silica for heavy metals removal: synthesis, characterization, isotherms, kinetics and thermodynamics studies. *Journal of Hazardous Materials.* 2019;370:80—90.
https://doi.org/10.1016/j.jhazmat.2017.10.058
16. Giannakoudakis D.A., Anastopoulos I., Barczak M., Antoniou E., Terpiłowski K., Mohammadi E., Shams M., Coy E., Bakandritsos A., Katsoyiannis I.A., Colmenares J.C., Pashalidis I. Enhanced uranium removal from acidic wastewater by phosphonate-functionalized ordered mesoporous silica: Surface chemistry matters the most. *Journal of Hazardous Materials.* 2021;413:125279.
https://doi.org/10.1016/j.jhazmat.2021.125279
17. Abdelrahman E.A., Khalil M.M.H., Khairy M., El-Reash Ya.G.A., Gad H.M., Katouah H.A., Saad F.A., Rayes S.M.E., Rehman Kh.U. Modification of hydroxysodalite nanoparticles by (3-aminopropyl)trimethoxysilane and isatoic anhydride as a novel composite for efficient sorption of Cu(II) ions from aqueous media. *Silicon.* 2024;16:1083—1096.
https://doi.org/10.1007/s12633-023-02743-6

18. Losev V.N., Volkova G.V., Maznyak N.V., Trofimchuk A.K., Yanovskaya E. Ya. Sorption of palladium by silica chemically modified with N-allyl-N'-propyltylthiourea, followed by spectrometric determination. *Zhurnal analiticheskoi khimii*. 1999;54(12):1254—1258. (In Russ.).
Лосев В.Н., Волкова Г.В., Мазняк Н.В., Трофимчук А.К., Яновская Э.Я. Сорбция палладия кремнеземом, химически модифицированном N-аллил-N'-пропилтилтиомочевиной с последующим спектрометрическим определением. *Журнал аналитической химии*. 1999; 54 (12): 1254—1258.
19. Losev V.N., Kudrina U.V., Trofimchuk A.K. Features of the interaction of chloride and tin chloride complexes of rhodium and iridium with N-(2,6-dimethyl-4-methylenetriphenylphosphonium chloride)—N'-propylthiourea groups covalently attached to the silica surface. *Zhurnal neorganicheskoi khimii*. 2005;50(6): 961—966. (In Russ.).
Лосев В.Н., Кудрина Ю.В., Трофимчук А.К. Особенности взаимодействия хлоридных и оловохлоридных комплексов родия и иридия с N-(2,6-диметил-4-метилентрифенилфосфоний-хлорид)—N'-пропилтиомочевинными группами, ковалентно закрепленными на поверхности кремнезема. *Журнал неорганической химии*. 2005;50(6):961—966.
20. Boryagina I.V., Volchkova E.V., Buslaeva T.M., Vasileva M.V., Erlich G.V. Sorption of chloride complexes of palladium and platinum by chemically modified silicas. *Tsvetnye metally*. 2012;(5):59—64. (In Russ.).
Борягина И.В., Волчкова Е.В., Буслаева Т.М., Васильева М.В., Эрлих Г.В. Сорбция хлоридных комплексов палладия и платины химически модифицированными кремнеземами. *Цветные металлы*. 2012;(5):59—64.
21. Volchkova E. V., Boryagina I. V., Mishikhina E. A., Buslaeva T. M., Erlich G.V., Lisichkin G. A. Method for extracting palladium (II) from spent catalysts: Patent 2442833 (RF). 2010. (In Russ.).
Волчкова Е.В., Борягина И.В., Мищихина Е.А., Буслаева Т.М., Эрлих Г.В., Лисичкин Г.А. Способ извлечения палладия (II) из отработанных катализаторов: Патент 2442833 (РФ). 2010.
22. Brauer G. Manual of inorganic synthesis. Vol. 5. Moscow: Mir, 1985. 360 p. (In Russ.).
Брауэр Г. Руководство по неорганическому синтезу. Т. 5. М.: Мир, 1985. 360 с.
23. Buslaeva T.M., Volchkova E.V., Boryagina I.V. Application of nitrogen- and sulfur-containing chemically modified silica for the selective sorption of Palladium. *Tsvetnye metally*. 2024;(1):24—32. (In Russ.).
https://doi.org/ 10.17580/tsm.2024.01.03
Буслаева Т.М., Волчкова Е.В., Борягина И.В. Применение азот- и серосодержащих химически модифицированных кремнеземов для селективной сорбции палладия. *Цветные металлы*. 2024;(1):24—32.
https://doi.org/ 10.17580/tsm.2024.01.03
24. Bruening R.L., Tarbet B.J., Krakowiak K.E., Bradshaw J.S., Izatt R.M. Support bonded polyalkylene-polyamine-poly(carboxylic acid) and extraction of metal ions therewith: Application WO9217403. (USA) 1992.
25. Bruening R.L., Tarbet B.J., Bradshaw J.S., Izatt R.M., Krakowiak K.E. Aminoalkylphosphonic acid containing ligands attached to solid supports for removal of metal ions: Patent 5182251 (USA). 1993.
26. Rosenberg E., Pang D.C. System for extracting soluble heavy metals from liquid solitions: Patent 5695882 (USA). 1997.
27. Fischer R.J., Pang D., Beatty S.T., Rosenberg E. Silica—polyamine composite materials for heavy metal ion removal, recovery, and recycling. II. Metal ion separations from mine wastewater and soft metal ion extraction efficiency. *Separation Science and Technology*. 1999;34(16):3125—3137.
https://doi.org/10.1081/ss-100100826
28. Hughes M.A., Wood J., Rosenberg E. Polymer structure and metal ion selectivity in silica polyamine composites modified with sodium chloroacetate and nitriloacetic acid (NTA) anhydride. *Industrial & Engineering Chemistry Research*. 2008;47(17):6765—6774.
https://doi.org/10.1021/ie800359k
29. Mingalev P.G., Lisichkin G.V. Chemical modification of oxide materials with organic acids of phosphorus (V) and their esters. *Uspekhi khimii*. 2006;75(6):604—624. (In Russ.).
https://doi.org/10.1070/RC2006v075n06ABEH002478
Мингалев П.Г., Лисичкин Г.В. Химическое модифицирование оксидных материалов органическими кислотами фосфора (V) и их эфирами. *Успехи химии*. 2006;75(6):604—624.
https://doi.org/10.1070/RC2006v075n06ABEH002478
30. Ehrlich G.V., Lisichkin G.V. Sorption in the chemistry of rare earth elements. *Russian Journal of General Chemistry*. 2017;87(6):1220—1245.
https://doi.org/10.1134/S1070363217060196
31. Tihomirova T.I., Nesterenko P.N. Features of complexation reactions on the surface of modified silica sorbents: sorption and complexation chromatography of metals. *Koordinatsionnaya khimiya*. 2022;48(10): 615—624. (In Russ.).
https://doi.org/10.31857/S0132344X22100085

Тихомирова Т.И. Нестеренко П.Н. Особенности реакций комплексообразования на поверхности модифицированных кремнеземных сорбентов: сорбция и комплексообразующая хроматография металлов. *Координационная химия*. 2022;48(10):615—624. https://doi.org/10.31857/S0132344X22100085

32. Biryukov A.A., Shelenskaya V.I., Alimarin I.I. Mixed halide and thiocyanate complex compounds of palladium (II) in aqueous solutions. *Izvestiya Akademii nauk SSSR. Ser. Khimicheskaya, neorganicheskaya i analiticheskaya khimiya*. 1966;(1):3—8. (In Russ.).
Бирюков А.А., Шленская В.И., Алимарин И.И. Смешанные галогенидные и роданидные комплексные соединения палладия (II) в водных растворах. *Известия Академии наук СССР. Сер. Химическая, неорганическая и аналитическая химия*. 1966;(1):3—8.
33. Buslaeva T. M., Simanova S.A. The state of platinum metals in hydrochloric acid and chloride aqueous solutions. Palladium, platinum, rhodium, iridium. *Koordinatsionnaya khimiya*. 1999;25(3):165—176. (In Russ.).
Буслаева Т.М., Симанова С.А. Состояние платиновых металлов в солянокислых и хлоридных водных растворах. Палладий, платина, родий, иридий. *Координационная химия.* 1999;25(3):165—176.
34. Gmelin L., Griffith W. P. Gmelin handbook of inorganic chemistry. Palladium. Berlin, Heidelberg, New York, London, Paris: Springer-Verlag, 1989. 354 p.
35. Kovalchukova O.V. Features of structure, geometrical, and spectral characteristics of the $(HL)_2[CuX_4]$ and $(HL)_2[Cu_2X_6]$ (X — Cl, Br) complexes. In book: Current trends in *X*-Ray Crystallography. 2011:450. https://doi.org/10.5772/27969
36. Ivanov V.M., Gorbunova G.N., Kudryavtsev G.V., Lisichkin G.V., Shurupova T.I. Sorption of palladium, iridium and platinum by chemically modified silicas. *Zhurnal analiticheskoi khimii*. 1984;39(11):504—509. (In Russ.).
Иванов В.М., Горбунова Г.Н., Кудрявцев Г.В., Лисичкин Г.В., Шурупова Т.И. Сорбция палладия, иридия и платины химически модифицированными кремнеземами. *Журнал аналитической химии*. 1984;39(11):504—509.
37. Tikhomirova T.I., Fadeeva V.I., Kudryavtsev G.V., Nesterenko P.N., Ivanov V.M., Savitchev A.T., Smirnovay N.S. Sorption of noble-metal ions on silica with chemically bonded nitrogen-containing ligands. *Talanta*. 1991;38(3):267—274.
https://doi.org/10.1016/0039-9140(91)80046-3
38. Onizhuk M., Ivanov V., Kholin Y., Panteleimonov A. Quantum chemical evaluation of dissociation constants. Test calculations. *National University Bulletin. Chemical Series*. 2016;26(49):65—72.
https://doi.org/10.26565/2220-637X-2016-26-07
39. Branzoi V., Golgovici F., Brânzoi F. Aluminium corrosion in hydrochloric acid solutions and the effect of some organic inhibitors. *Materials Chemistry and Physics*. 2003;78(1):122—131.
https://doi.org/10.1016/S0254-0584(02)00222-5
40. Abd El Aal Emad El Din, Wanees S., Farouk A., Abd El Haleem S. Factors affecting the corrosion behaviour of aluminium in acid solutions. II. Inorganic additives as corrosion inhibitors for Al in HCl solutions. *Corrosion Science*. 2013;68:14—24.
https://doi.org/10.1016/j.corsci.2012.09.038
41. Nefedov V.I. X-ray electron spectroscopy of inorganic compounds: Handbook. Moskow: Khimiya, 1984. 255 p. (In Russ.).
Нефедов В.И. Рентгеноэлектронная спектроскопия неорганических соединений: Справочник. М.: Химия, 1984. 255 с.
42. Buslaeva T.M., Buslaev A.V., Kopylova E.V. Sorption of iridium chlorocomplexes with chemically modified silica. *Izvestiya. Non-Ferrous Metallurgy*. 2000;(3):59—62. (In Russ.)
Буслаева Т.М., Буслаев А.В., Копылова Е.В. Сорбция хлорокомплексов иридия химически модифицированными кремнеземами. *Известия вузов. Цветная металлургия*. 2000;(3):59—62.

Information about the authors

Tat'yana M. Buslaeva – Dr. Sci. (Chem.), Professor of the Departments of Chemistry and Technology of Rare Elements, MIREA – Russian Technological University.
https://orcid.org/0000-0003-2043-8919
E-mail: buslaevatm@mail.ru

Elena V. Volchkova – Cand. Sci. (Chem.), Associate Professor of the Departments of Chemistry and Technology of Rare Elements, MIREA – Russian Technological University.
https://orcid.org/0000-0001-5737-6816
E-mail: volchkovaev@bk.ru

Pavel G. Mingalev – Cand. Sci. (Chem.), Leading Researcher of the Department of Chemistry of Petroleum and Organic Catalysis, Moscow State University named after M.V. Lomonosov.
https://orcid.org/0000-0002-8050-2216
E-mail: uuk2@mail.ru

Irina V. Boryagina – Deputy Head of the Testing laboratory, JSC R&PC Supermetal.
https://orcid.org/0009-0000-5320-8401
E-mail: irinaboryagina@mail.ru

Информация об авторах

Татьяна Максимовна Буслаева – д.х.н., профессор кафедры химии и технологии редких элементов, МИРЭА – Российский технологический университет.
https://orcid.org/0000-0003-2043-8919
E-mail: buslaevatm@mail.ru

Елена Владимировна Волчкова – к.х.н., доцент кафедры химии и технологии редких элементов, МИРЭА – Российский технологический университет.
https://orcid.org/0000-0001-5737-6816
E-mail: volchkovaev@bk.ru

Павел Германович Мингалев – к.х.н., вед. науч. сотрудник кафедры химии нефти и органического катализа, Московский государственный университет им. М.В. Ломоносова.
https://orcid.org/0000-0002-8050-2216
E-mail: uuk2@mail.ru

Ирина Валентиновна Борягина – зам. начальника испытательной лаборатории, АО «НПК «Суперметалл».
https://orcid.org/0009-0000-5320-8401
E-mail: irinaboryagina@mail.ru

Contribution of the authors

T.M. Buslaeva – defined the research objectives, investigated the speciation of sorbed metal ions in solutions, and wrote the manuscript.

E.V. Volchkova – conducted experiments on model solutions and participated in the discussion of the results.

P.G. Mingalev – synthesized the sorbents and participated in the discussion of the results.

I.V. Boryagina – conducted experiments on process solutions and participated in the discussion of the results.

Вклад авторов

Т.М. Буслаева – определение цели работы, изучение состояния ионов сорбируемых металлов в растворах, написание текста статьи.

Е.В. Волчкова – проведение экспериментов на модельных растворах, участие в обсуждении результатов.

П.Г. Мингалев – осуществление синтеза сорбентов, участие в обсуждении результатов.

И.В. Борягина – проведение экспериментов на технологических растворах, участие в обсуждении результатов.

The article was submitted 06.09.2024, revised 22.11.2024, accepted for publication 28.11.2024

Статья поступила в редакцию 06.09.2024, доработана 22.11.2024, подписана в печать 28.11.2024