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Sorption Recovery of Palladium (II) and Platinum (IV) from Hydrochloric Acid Solutions

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The sorption preconcentration of Pd (II) and Pt (IV) from hydrochloric acid solutions on Purolite ion exchangers with different functional groups was investigated. The initial concentrations in contacting solutions were 0.025–0.25 mmol/L for palladium and 0.25 mmol/L for platinum at the HCl concentrations 0.01–4.0 mol/L. It was shown that the investigated resins have high sorption ability (more than 85–95 %) to chloride complexes of noble metals. We found out that the simultaneous elution of these complexes by hydrochloric acid thiourea solution (1 mol/L in 0.5 M HCl) is possible (to more than 80 %) from anion exchangers Purolite A 111 and Purogold™ A 193.

Keywords: ion exchange, palladium, platinum, hydrochloric acid solutions.

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Сорбционное извлечение палладия (II) и платины (IV) из солянокислых растворов

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Исследовано сорбционное концентрирование палладия (II) и платины (IV) из солянокислых растворов на анионитах марки Purolite с различными функциональными группами. Исходные концентрации палладия и платины составляли соответственно 0.025–0.25 ммоль/л и 0.25 ммоль/л при концентрации HCl в контактирующих растворах 0.01–4.0 моль/л. Показана высокая сорбционная способность исследуемых ионитов по отношению к хлоридным комплексам благородных металлов, проявляющаяся на уровне более 85–95 %. Установлено, что после извлечения этих комплексов возможно их совместное элюирование посредством солянокислого раствора тиомочевины (1 моль/л в 0.5 М HCl) на уровне более 80 % с анионитов Purolite A 111 и Purogold™ A 193.

Ключевые слова: ионный обмен, палладий, платина, солянокислые растворы.

Introduction

The worldwide consumption of platinum group metals (PGM) is steadily growing, and for years its application range continues to expand. Followed by that, the production of PGM became one of the most important branches in metallurgy [1, 2]. The low metal content ores as well as refractory ores are getting more involved in PGM processing, including the sulfide black-shale gold ores from the north-eastern regions of Russia [3, 4]. At the same time, the secondary PGM raw materials (such as spent automobile and chemical catalysts, electronic scrap, technological wastes) are more demanded as well [5, 6].

The recovery of noble metals from raw materials is normally carried out by precipitation or electrowinning [1, 7-10]. However, given the low concentrations of noble metals in initial industrial solutions after the breakdown, the above-mentioned methods do not result in significant recovery of PGM. Moreover, in this case the obtained solid products hinder the further processing [1, 7, 8, 11].

Fortunately, these problems can be avoided by using the sorption methods, known for their high efficiency, selectivity, environmental safety and good compatibility with PGM post-determination methods [1, 6, 7, 11-13]. In a variety of sorbents, the ion exchangers with different functional groups seem promising, as they possess high exchange capacity and good kinetic properties. This makes these sorbents usable even for the preconcentration of trace amounts of PGM in presence of accompanying components [1, 5-7, 11, 13, 14].

It should be noted that in most cases the ionic state of PGM industrial solutions is the chloride complexes with different stability and chemical inertness [1, 11, 15, 16]. As a rule, these complexes

are also subjected to hydrolysis and aquation – the factor that makes the system more complicated [1, 15, 16].

Since palladium and platinum are associated in primary and secondary raw materials, and also pass simultaneously into solution after the processing, the recovery of Pd and Pt on selective ion exchangers is a matter of academic and practical interest. In this case some researchers use strong base anion exchangers for recovery of chloride complexes of Pd and Pt because their sorption is carried out from strong acidic media (2–6 M HCl) [6, 11, 17]. However, when processing the secondary PGM sources, it often results in obtaining of hydrochloric acid solutions with lower acidity (0.01 mol/L and less). In turn, it requires using the weak base anion exchangers or chelating sorbents for the recovery of palladium and platinum from such kind of solutions. The sorption ability of these anion exchangers facilitates the extraction of complex ions of noble metals not only through ion exchange mechanism, but also by means of additional complex formation between the nitrogen atoms of functional groups and atoms of the recovered metals [18].

Moreover, it should be noted that platinum and palladium complexes in real industrial hydrochloric acid solutions are often accompanied by iron and non-ferrous metal ions that complicate the isolation of noble metals. These real industrial solutions differ from each other by the composition and concentrations of components, stipulated by the differences in the breakdown methods for primary or secondary sources of mineral materials. Consequently, this requires various approaches to the recovery of noble metals, adjusted to the specific types of real solutions. Previously we have investigated the recovery of platinum and palladium from refractory sulfide black-shale ores [4], when the metals were successfully recovered with selective ion exchangers after the breakdown of ores. The similar problems were successfully solved by the authors [6-8].

The present work is devoted to the sorption recovery of palladium and platinum on various ions exchangers from model hydrochloric acid solutions. We intend to develop this investigation further by studying the effect of accompanying ions on the recovery of these noble metals.

Materials and methods

In the present work we investigate some anion exchangers synthesized by Purolite Int. Ltd. The resins are based on styrene and divinylbenzene (DVB), except the sorbent Purolite S 985, which is based on polyacrylate and DVB. Their physical-chemical characteristics are presented in Table 1. As

Table 1. Physical-chemical properties of the anion exchangers investigated

Trade name	Exchanger type	Functional groups*	Exchange capacity in the chloride form, mmol/g	Swelling grade, %
Purolite A 500	Strong base	QAB	1.2	20
Purogold™ S 992	Complexing resin	Mixed amines	4.4	20
Purolite S 985	Complexing resin	Polyamines	2.3	20
Purolite A 111	Weak base	TAG	1.7	40
Purogold™ A 193	Intermediate base	TAG, QAB	3.8	22

*QAB – quaternary ammonia base; TAG – tertiary amino-groups.

follows from this Table, the studied resins possess various functional groups and, therefore, different basicity. Their physical structure belongs to the macroporous type. Prior to the experiment, the ion exchangers were prepared according to the conventional methods and converted into the initial chloride form [19].

The initial working palladium solution with concentration 5.55 mmol/L and platinum solution with concentration 102.6 mmol/L were prepared by dissolution of accurately weighed quantities of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in low volume of concentrated HCl. Then the solutions were placed into a graduated flask (50 mL) and brought to the flask's mark with distilled water [15, 20].

We have used in the present work the freshly prepared solutions of palladium with concentrations 0.025 and 0.25 mmol/L and of platinum with concentration 0.25 mmol/L. The HCl concentrations in the contacting solutions were 0.01, 2.0 and 4.0 mol/L. The concentrations and acidity of the investigated solutions were chosen with an intention to make the experimental conditions closer to real industrial conditions.

The concentrations of palladium and platinum in solutions were determined by spectrophotometrical method with nitroso-R-salt and tin (II) chloride, respectively [15, 20, 21]. The ionic state of noble metals in the solutions was confirmed by absorption spectra at 190–700 nm.

The sorption of noble metals was studied under batch experiment conditions: resin mass – 0.1 g; volume of contacting solution – 10.0 mL. The equilibrium time determined by special test was 24 h.

The sorption ability of the anion exchangers investigated was estimated by means of the recovery degree (R, %), distribution coefficient (D) and separation coefficient (S), calculated as follows:

$$R = \frac{C_0 - C_{eq}}{C_0} \cdot 100\%, \quad (1)$$

$$D = \frac{WEC}{C_{eq}}, \quad (2)$$

$$S = \frac{D_{Pd}}{D_{Pt}}, \quad (3)$$

where C_0 and C_{eq} are the initial and equilibrium molar concentrations of palladium and platinum solutions, respectively; WEC (mmol/g) is working exchange capacity of the resins towards the recovered ions. The latter was calculated from the equation:

$$WEC = \frac{(C_0 - C_{eq}) \cdot V}{q}, \quad (4)$$

where V (L) is volume of the contacting solution and q (g) is the resin quantity.

The sorption isotherms were plotted by varying the molar ratio of resins to the amount of Pd and Pt in contacting solution [22, 23]. Then, using the obtained curves, the apparent constants of ion exchange equilibrium were calculated according to the law of mass action [22, 23].

The elution of palladium and platinum after their simultaneous sorption was carried out under dynamic conditions in glass columns (~1 cm diameter and ~20 cm height). First, the air-dried resin quantities were placed into hydrochloric acid solution (2.0 or 4.0 mol/L) and left for 30 min for swelling. Then the swelled resins were placed into the column (bed height was 1.5 cm) and 100.0 mL of palladium and platinum solutions were passed through the column. The flow rate was 1 mL/min.

The separate solution portions of the filtrate (5.0–10.0 mL) were collected. After that the contents of palladium and platinum were determined in each portion. After the saturation of resin with the sorbed ions, the column was washed with a low volume (~10 mL) of 0.5 M HCl and then the eluent was passed through the column, to achieve Pd and Pt recovery. The hydrochloric acid thiourea solution (1 M in 0.5 M HCl) was taken as an elution agent. The separate filtrate portions (5.0 mL) were collected and the concentrations of Pd and Pt were determined by a spectrophotometrical method according to intrinsic colors of the metal complexes with thiourea [20, 21]. All the reagents used were of analytical purification grade.

The results obtained were subjected to statistical processing according to conventional procedures [24, 25]. The average experimental error for 3 parallel runs and at confidence level of 0.95 was less than 6 %.

Results and discussion

The complexation of palladium and platinum in chloride and hydrochloric acid solutions is investigated in detail [1, 15, 16, 26]. It was found out that the ionic state of PGM in such solutions depends on their acidity as well as on concentration of chloride ions. Depending on these factors, the various aqua and hydroxo-chloride complexes with different stability and kinetic inertness can be formed in aqueous solutions.

Palladium (II) complexes $[\text{PdCl}_4]^{2-}$ predominate in solutions where HCl concentration exceeds 1 mol/L. With the decrease in acidity, these complexes are subjected to aquation under the formation of forms $[\text{Pd}(\text{H}_2\text{O})_n\text{Cl}_{n-4}]^{n-2}$, where n changes from 0 to 3 [1, 20, 26]. The cumulative stability constant of $[\text{PdCl}_4]^{2-}$ ions is estimated as $\log \beta_4 = 11.12\text{--}12.24$ [1, 20]. It should be noted that the chloride complexes of palladium (IV) are stable only in presence of oxidants. That is why solely palladium (II) complexes exist in hydrochloric acid solutions [1, 20].

$[\text{PtCl}_6]^{2-}$ predominate in solutions with HCl concentration 3 mol/L and more. The dilution of these solutions and increase in their pH value leads to the formation of aqua and hydroxo-complexes in the system, which co-exist in different proportions [1, 15, 20, 26]. The chloride complexes of platinum (IV) are very stable and kinetically inert. The cumulative stability constant of $[\text{PtCl}_6]^{2-}$ ions is $\log \beta_6 = 33.9$ [1, 20].

As it was mentioned above, in the present work we have investigated the sorption recovery of noble metals from strong acidic solutions (with hydrochloric acid concentrations 4.0 and 2.0 mol/L) and from weak acidic solutions (with HCl concentration 0.01 mol/L) as well. We have recorded the absorption spectra of freshly prepared palladium solutions in 2 M and 0.01 M HCl and revealed that both spectra had absorption maximum at 325 nm. These indicates the presence of $[\text{PdCl}_4]^{2-}$ ions, in full compliance with the literature data [1, 20, 26].

The spectrum of freshly prepared platinum solution in 2 M HCl had absorption maximum at 251 nm, which corresponds to $[\text{PtCl}_6]^{2-}$. The spectrum of freshly prepared platinum solution in 0.01 M HCl had two absorption maxima, at 251 nm and 355 nm, pointing out to the presence of complexes $[\text{PtCl}_6]^{2-}$ and $[\text{Pt}(\text{OH})\text{Cl}_5]^{2-}$, respectively. Again, all these results are in full compliance with the literature [1, 20, 26].

Therefore, the composition of contacting palladium solutions is the same in strong and weak acidic media, whereas platinum solutions have different composition depending on acidity of solution.

Our further studies were devoted to the sorption properties of the ion exchangers during the recovery of chloride complexes of Pd (II) and Pt (IV) from individual solutions in dependence of HCl concentration. The results are presented in Tables 2 and 3.

It can be seen from these data that all the investigated anion exchangers reveal high sorption ability to the recovered chloride complexes of noble metals, regardless of their functional groups. With the decrease in HCl concentration in contacting solution, a slight increase in sorption parameters takes place because of reduction of competing effect of chloride ions.

After that we have investigated the sorption preconcentration of noble metals at their simultaneous presence in HCl solutions. The results are presented in Tables 4 and 5.

These data also demonstrate high sorption ability of the investigated resins, although there is a slight decrease in recovery degree of palladium (II) in the presence of platinum (IV) – in comparison with its sorption from individual solutions (Table 2). This can be explained by several

Table 2. Sorption of Pd (II) from individual hydrochloric acid solutions ($C_0(\text{Pd})=0.025$ mmol/L)

Trade name	Parameter	$C_0(\text{HCl})$, mol/L		
		4.0	2.0	0.01
Purolite A 500	lg D	3.66 ± 0.22	3.51 ± 0.21	3.67 ± 0.18
	R, %	93 ± 5	94 ± 5	95 ± 5
Purogold™ S 992	lg D	2.03 ± 0.11	2.61 ± 0.16	2.68 ± 0.16
	R, %	92 ± 5	95 ± 5	95 ± 5
Purolite S 985	lg D	2.29 ± 0.12	2.59 ± 0.13	2.58 ± 0.13
	R, %	95 ± 5	95 ± 5	95 ± 5
Purolite A 111	lg D	2.18 ± 0.13	2.42 ± 0.15	2.44 ± 0.15
	R, %	93 ± 5	94 ± 5	95 ± 5
Purogold™ A 193	lg D	1.81 ± 0.11	2.03 ± 0.12	2.56 ± 0.15
	R, %	86 ± 4	91 ± 5	95 ± 5

Table 3. Sorption of Pt (IV) from individual hydrochloric acid solutions ($C_0(\text{Pt})=0.25$ mmol/L)

Trade name	Parameter	$C_0(\text{HCl})$, mol/L		
		4.0	2.0	0.01
Purolite A 500	lg D	2.37 ± 0.12	2.59 ± 0.16	2.59 ± 0.16
	R, %	92 ± 5	94 ± 5	94 ± 5
Purogold™ S 992	lg D	2.01 ± 0.12	2.71 ± 0.14	2.84 ± 0.14
	R, %	92 ± 5	95 ± 5	95 ± 5
Purolite S 985	lg D	1.88 ± 0.11	2.18 ± 0.13	3.02 ± 0.15
	R, %	88 ± 5	94 ± 5	95 ± 5
Purolite A 111	lg D	1.97 ± 0.12	3.05 ± 0.18	3.09 ± 0.19
	R, %	93 ± 5	94 ± 5	95 ± 5
Purogold™ A 193	lg D	2.48 ± 0.15	2.53 ± 0.15	2.55 ± 0.15
	R, %	94 ± 5	95 ± 5	95 ± 5

Table 4. Sorption of Pd (II) in presence of Pt (IV) in hydrochloric acid solutions ($C_0(\text{Pd})=0.025$ mmol/L; $C_0(\text{Pt})=0.25$ mmol/L)

Trade name	Parameter	$C_0(\text{HCl})$, mol/L		
		4.0	2.0	0.01
Purolite A 500	lg D	1.91 ± 0.11	1.89 ± 0.11	1.98 ± 0.12
	R, %	89 ± 5	91 ± 5	95 ± 5
Purogold™ S 992	lg D	1.68 ± 0.11	1.81 ± 0.11	1.82 ± 0.11
	R, %	83 ± 4	87 ± 5	89 ± 5
Purolite S 985	lg D	1.76 ± 0.11	1.64 ± 0.10	1.68 ± 0.11
	R, %	85 ± 5	82 ± 4	83 ± 4
Purolite A 111	lg D	1.82 ± 0.11	1.56 ± 0.10	1.85 ± 0.11
	R, %	87 ± 5	78 ± 5	88 ± 5
Purogold™ A 193	lg D	1.92 ± 0.12	1.54 ± 0.10	1.64 ± 0.10
	R, %	89 ± 5	88 ± 5	90 ± 5

Table 5. Sorption of Pt (IV) in presence of Pd (II) in hydrochloric acid solutions ($C_0(\text{Pt})=0.25$ mmol/L; $C_0(\text{Pd})=0.025$ mmol/L)

Trade name	Parameter	$C_0(\text{HCl})$, mol/L		
		4.0	2.0	0.01
Purolite A 500	lg D	2.60 ± 0.16	2.81 ± 0.17	2.77 ± 0.17
	R, %	95 ± 5	95 ± 5	95 ± 5
Purogold™ S 992	lg D	2.27 ± 0.14	2.40 ± 0.14	2.62 ± 0.16
	R, %	95 ± 5	95 ± 5	95 ± 5
Purolite S 985	lg D	2.15 ± 0.13	2.24 ± 0.13	2.95 ± 0.18
	R, %	93 ± 5	95 ± 5	95 ± 5
Purolite A 111	lg D	2.37 ± 0.14	2.50 ± 0.15	2.80 ± 0.17
	R, %	95 ± 5	95 ± 5	95 ± 5
Purogold™ A 193	lg D	2.29 ± 0.14	2.58 ± 0.15	2.89 ± 0.17
	R, %	95 ± 5	95 ± 5	95 ± 5

reasons. First, this is the result of the reciprocal influence of chloride complexes of the recovered noble metals. Second, it is explained by higher selectivity of the anion exchangers towards platinum (IV) complexes, that are more stable compared to palladium (II) complexes [1, 20]. The general theory of selectivity of ion exchange states that an ion exchanger usually is more selective to the complex ion with higher stability [22, 27, 28]. Noteworthy, the acidity of contacting solutions is practically not important for sorption preconcentration of the recovered complexes at their simultaneous presence.

We have calculated the separation coefficients for palladium (II) and platinum (IV), which are represented in Table 6. It can be seen from this Table that these values point out to the difficulties for the separation of chloride complexes of palladium and platinum due to the high selectivity of investigated resins.

We have studied the ion exchange equilibria for the recovery of chloride complexes of Pd (II) and Pt (IV) by obtaining sorption isotherms. These curves are shown in Figures 1 and 2 for anion exchangers Purolite™ A 193 and Purolite A 111. It can be seen that the curves are convex in general, i.e. the anion exchangers are selective towards the recovered noble metals [18, 22, 23]. The isotherms were used to calculate the apparent constants of ion exchange equilibrium. The values are presented in Table 7.

Table 6. Separation coefficients of Pd (II) and Pt (IV) during their sorption from hydrochloric acid solutions ($C_0(\text{Pd}) = C_0(\text{Pt}) = 0.25 \text{ mmol/L}$)

Trade name	$C_0(\text{HCl}), \text{ mol/L}$		
	4.0	2.0	0.01
Purolite A 500	0.20	0.06	0.11
Purogold™ S 992	0.35	0.19	0.11
Purolite S 985	0.31	0.26	0.05
Purolite A 111	0.27	0.11	0.12
Purogold™ A 193	0.41	0.09	0.06

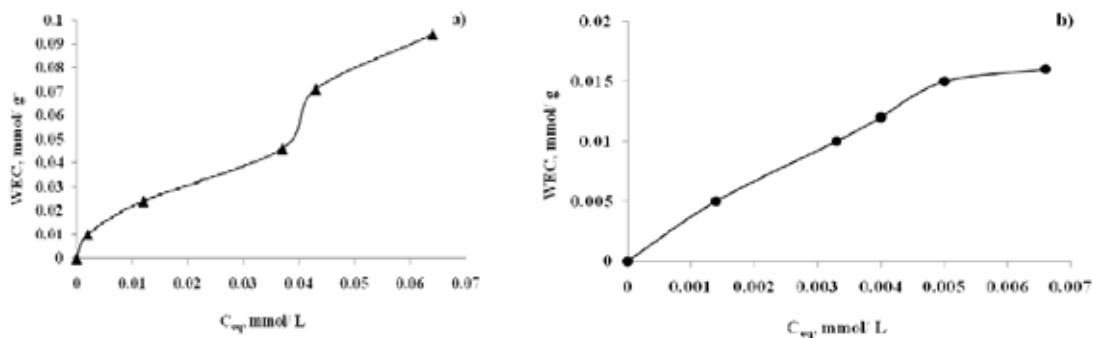


Fig. 1. Sorption isotherms of chloride complexes of Pd (II) (a) and Pt (IV) (b) from individual solutions on anion exchanger Purolite™ A 193 ($C_0(\text{HCl}) = 2.0 \text{ mol/L}$)

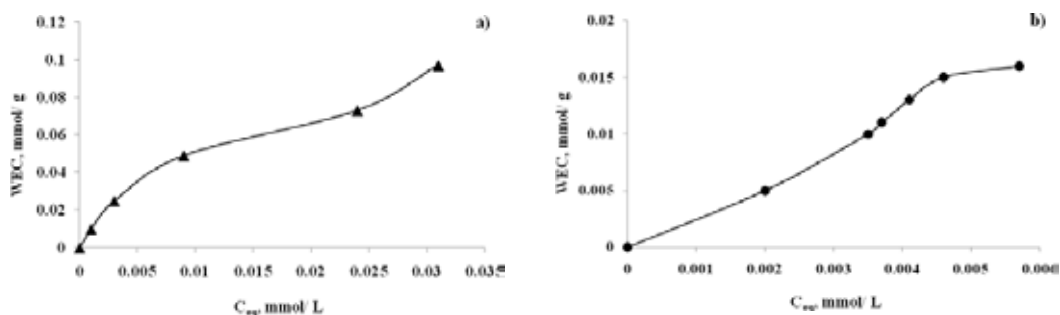


Fig. 2. Sorption isotherms of chloride complexes of Pd (II) in presence of Pt (IV) (a) and of Pt (IV) in presence of Pd (II) (b) on anion exchanger Purolite A 111 ($C_0(\text{HCl}) = 2.0 \text{ mol/L}$)

Table 7. Apparent constants of sorption equilibrium during recovery of Pd (II) and Pt (IV) from individual solutions and at simultaneous presence (C_0 (HCl) = 2.0 mol/L)

Trade name	Sorption from individual solutions		Sorption at simultaneous presence	
	Pd (II)	Pt (IV)	Pd (II)	Pt (IV)
Purolite A 500	0.54	0.31	0.47	0.47
Purogold™ S 992	0.33	0.12	0.48	0.35
Purolite S 985	0.65	0.28	0.58	0.22
Purolite A 111	0.16	0.14	0.86	0.42
Purogold™ A 193	0.35	0.18	0.43	0.21

It is known that these constants are quantitative characteristics of the ion exchangers affinity to the recovered ions [22, 23]. Therefore, the obtained data prove the selectivity of ion exchangers. This conclusion is consistent with the data on sorption of Pd (II) and Pt (IV) from individual hydrochloric acid solutions as well as at their simultaneous presence in these solutions (Tables 2–4).

Since we have revealed the high selectivity of the ion exchangers investigated towards the recovered chloride complexes of Pd (II) and Pt (IV), it was a matter of practical interest to study of the desorption of these ions under the dynamic conditions. It is known that high selectivity of ion exchangers to the recovered components means that desorption of these components would be more problematic [18, 22, 23, 27].

It was mentioned above that we used hydrochloric acid thiourea solution as a desorption agent. The advantage of this eluent is in its ability to form the positively charged complexes $[\text{Pd}(\text{SCN}_2\text{H}_4)_4]^{2+}$ and $[\text{Pt}(\text{SCN}_2\text{H}_4)_4]^{2+}$, the stability of which is much higher than that one of the chloride complexes of palladium and platinum ($\log \beta_4 > 40-43$) [20].

The elution curves for anion exchanger Purogold™ A 193 are represented in Fig. 3. According to these data, the practically complete elution of palladium and platinum is achieved after passing of 50–60 mL of thiourea solution.

Table 8 contains the data on palladium and platinum desorption from the anion exchangers investigated after the simultaneous sorption of noble metals from HCl solutions with concentrations

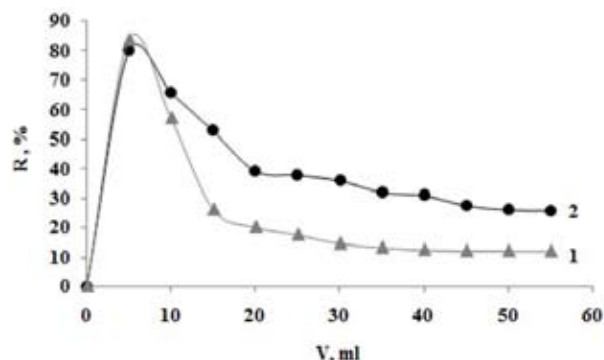


Fig. 3. Elution curves for desorption of Pd (1) and Pt (2) from anion exchanger Purogold™ A 193 by hydrochloric acid thiourea solution. Sorption conditions: C_0 (HCl) = 2.0 mol/L; C_0 (Pd) = C_0 (Pt) = 0.25 mmol/L

Table 8. Elution of Pd and Pt by thiourea solution (1 mol/L in 0.5 M HCl). Sorption conditions: $C_0(\text{Pd}) = C_0(\text{Pt}) = 0.25$ mmol/L

Trade name	Desorption degree, % for			
	Pd recovery from		Pt recovery from	
	2 M HCl	4 M HCl	2 M HCl	4 M HCl
Purolite A 500	69	66	84	85
Purogold™ S 992	54	54	77	83
Purolite A 111	87	86	98	98
Purogold™ A 193	84	87	80	88

4.0 and 2.0 mol/L. It can be seen from these results that desorption of noble metals from the resins proceeds in different way. Moreover, the recovery degree of platinum is greater than that of palladium. The best results were obtained for weak base anion exchanger Purolite A 111. It should be noted that after 24 h, desorption of palladium and platinum complexes is on the level of 95–100 % for all the ion exchangers investigated.

We have pointed above to the probable difficulties in palladium and platinum separation, originating from the low values of their separation coefficients (Table 6) and high selectivity of the sorbents investigated. This fact is confirmed by the desorption data, in the case of simultaneous elution of both noble metals. However, the positively charged Pd and Pt thiourea complexes can be successfully separated after their simultaneous isolation by electrolysis – an industrial method [1, 20, 29]. Therefore, the anion exchangers Purolite A 111 and Purogold™ A 193 can be recommended for use in technological schemes for palladium and platinum recovery from hydrochloric acid solutions.

Conclusions

The investigation revealed the high sorption ability of studied ion exchangers during their recovery of chloride complexes of palladium (II) and platinum (IV). The high selectivity of the resins makes it impossible to separate the investigated noble metals – neither during sorption, nor during elution. However, the simultaneous desorption of Pd and Pt by hydrochloric acid thiourea solution does not reduce the practical significance of the present work, as the separation of noble metals from thiourea complexes can be achieved by electrolysis – the widespread procedure for the plant conditions. That is why we recommend anion exchangers Purolite A 111 and Purogold™ A 193 for technological schemes for the recovery of palladium and platinum from various in HCl concentration solutions.

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