

# Ion exchange recovery of palladium (II) from nitrate weak acidic solutions

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Received 12 August 2009; revised 2 September 2009; accepted 4 September 2009.

## ABSTRACT

**Sorption recovery of palladium (II) from nitrate weak acidic model solutions and solutions of spent catalysts on some ion exchangers with different physical and chemical structure has been investigated. The palladium concentration in contacting solutions was  $5.0 \cdot 10^{-5} - 1.0 \cdot 10^{-3}$  mol/L at nitric acid and potassium nitrate concentrations 0.01 and 1.0 mol/L, respectively. It was shown that anion exchangers AV-17-8 as well as Purolite S 985 and A 500 possess the best sorption and kinetic properties. These sorbents can be recommended for selective recovery of palladium from solutions of spent catalysts.**

**Keywords:** Palladium; Ion Exchange; Anion Exchangers; Nitrate Solutions

## 1. INTRODUCTION

As natural deposits of precious metals are being depleted, the technologies for precious metals recovery from different secondary raw materials are becoming more important. The hydrometallurgical methods are successfully used for these purposes [1-3]. One of the most promising methods for recovery of platinum group metals (in particular, of palladium) is sorption, characterized by high efficiency and selectivity [1,3-5]. However, the majority of investigations devoted to the sorption recovery of palladium, deal with chloride or sulfate solutions [6-14], and the studies of sorption of noble metals from nitric acidic media are rather limited [1,15-20]. At the same time, the recovery of palladium from some kinds of secondary sources (e.g. electronic scrap and exhausted nuclear fuel) requires its isolation from nitric acidic and nitrate solutions [1,21].

Our previous investigations were focused on sorption recovery of palladium from chloride model solutions and solutions of spent catalysts by various ion exchangers and carbon adsorbents [9,22,23]. Apart from

this, we started the research of sorption concentration of palladium on carbon adsorbents during its recovery from model nitric acidic solutions [24]. We have revealed high sorption abilities of some carbon adsorbents to palladium (II) ions depending on initial concentrations of nitric acid and *Pd(II)*.

The present paper is focused on sorption recovery of palladium from nitrate weak acidic solutions (model and of spent catalysts) by some ion exchangers with different physical and chemical structure.

## 2. MATERIALS AND METHODS

### 2.1. Characteristics of Ion Exchangers

Some ion exchangers from various manufacturers were taken for investigation. These sorbents possess different physical and chemical structure. Their physical-chemical characteristics are summarized in **Table 1**. It should be noted that ion exchangers produced by Purolite Company for the first time were used for recovery of platinum group metals. However, these ion exchangers were successfully applied in our previous investigations on sorption recovery of gold and silver [25].

Before sorption all the ion exchangers were prepared according to the standard procedures and then loaded with 1 M *NaCl* solution, in order to convert them to chloride form (anion exchangers) or to *Na<sup>+</sup>, Cl<sup>-</sup>*-form (amphoteric resin).

The acid-base properties of ion exchangers investigated were studied by a potentiometric titration with the glass electrode. Based on the experimental data obtained, we have calculated the average apparent ionization constants of functional groups of ion exchangers [5]. The calculation procedure is described below and the values of constants are presented in **Table 1**.

### 2.2. Preparation of Palladium Nitrate Solutions

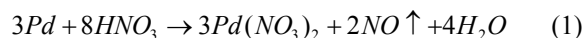
The initial model stock solution of palladium was prepared according to works [26,27]. The accurately

**Table 1.** Physical-chemical properties of ion exchangers investigated.

Trade name	Exchanger type	Copolymer	Physical structure	Functional groups	Exchange capacity to Cl <sup>-</sup> ion (mmol/g)	Swelling grade (%)	$p\overline{K}_a$	Manufacturer
Purolite A 500	Strong base anion exchanger	St – DVB	MP	QAB	1.2	15	2.31	Purolite, UK
Purolite A 530	Strong base anion exchanger	St – DVB	MP	QAB	0.60	12	1.15	Purolite, UK
Purolite S 985	Weak base anion exchanger	Ac – DVB	MP	PA	2.3	42	0.74	Purolite, UK
AV-17-8	Strong base anion exchanger	St – DVB	G	QAB	3.6	23	0.99	TOKEM, Russia
AN-251	Weak base anion exchanger	VP – DVB	MP	TAG, PN	5.3	10	1.78	Chercassy, Ukraine
ANKF-5	Amphoteric ion exchanger	VP – DVB	P	PAG, TAG, PN	3.8 (2.6 to Na <sup>+</sup> )	22	$\frac{1.42}{(p\overline{K}_b = 1.83)}$	Chercassy, Ukraine

St-styrene; DVB-divinylbenzene; Ac-acryl; VP-vinylpyridine; MP-macroporous; G-gel; P-porous; QAB-quaternary ammonium base; PA-polyamine; TAG-tertiary aminogroups; PAG-phosphorylic acid groups; PN-pyridine nitrogen.

weighed metallic palladium (0.50 g) was dissolved under heating in concentrated  $HNO_3$  (analytical grade) according to the following reaction:



The palladium concentration in initial stock solution was 0.01 mol/L. The working solutions with palladium concentrations  $5.0 \cdot 10^{-5} - 1.0 \cdot 10^{-3}$  mol/L were prepared from the stock solution. The nitric acid concentration in these solutions was 0.01 mol/L and the constant ionic strengths was made by means of 1.0 M  $KNO_3$ . Before the preparation of working solutions, the palladium concentration in initial stock solution was controlled by gravimetric method with dimethylglyoxime as a reagent [26]. The palladium (II) concentration in working solutions and in solutions after sorption was determined by spectrophotometrical with nitroso-R-salt [27,28].

We chose the range of palladium and nitric acid concentrations for our experiment, aiming to make it closer to real industrial conditions.

Apart from the model nitrate solutions of palladium, we also used the solutions of spent palladium-containing catalysts. These solutions were prepared as follows: the catalyst quantities (0.20 g) were dissolved under heating in concentrated nitric acid, similar to preparation of model solution. The working solutions of spent catalysts with palladium concentrations  $5.0 \cdot 10^{-5} - 5.0 \cdot 10^{-4}$  mol/L were prepared from the initial solution. Before dissolution of spent catalysts samples in nitric acid, we have determined their average composition by X-ray-fluorescence method. The results are represented in **Table 2**.

### 2.3. Batch Studies

The sorption of palladium was studied under batch experimental conditions: resin mass–0.20 g, volume of contacting solution–20.0 mL, stirring in a thermostat at  $(20 \pm 1)$  °C. The equilibrium time determined by special tests was about 24 h.

Sorption ability of ion exchangers investigated was estimated by means of the recovery degree ( $R, \%$ ) and distribution coefficient ( $D, L/g$ ), which were calculated from:

$$R = \frac{(C_0 - C_{eq})}{C_0} \cdot 100\% \quad (2)$$

$$D = \frac{EC}{C_{eq}} \quad (3)$$

where  $C_0$  and  $C_{eq}$  are the initial and equilibrium molar concentrations of palladium solution;  $EC$  is the exchange capacity of the resin for palladium, mmol/g.

The kinetics of sorption of palladium from weak acidic nitrate solutions on ion exchangers investigated was studied by the “limited bath” method [29,30] and diffusion coefficients of  $Pd(II)$  ( $\overline{D}_s, cm^2/s$ ) were calculated. The kinetic experiment procedure is described below.

The desorption of palladium was carried out by 1 M thiourea solution in 0.01 M  $HNO_3$  or in 1 M  $NaOH$ . The mechanism of palladium sorption recovery by ion exchangers from nitrate systems was studied by means of IR-spectroscopy and diffuse reflectance spectroscopy. The preparation procedures of samples are present below.

**Table 2.** Average composition of initial sample of palladium-containing spent catalyst.

Component	Content (%)
Palladium	0.79
Sodium	0.41
Aluminum oxide	~ 84
Silicon	0.03
Sulfur	0.12
Chlorine	0.80
Iron	0.19
Nickel	< 0.02
Zinc	< 0.02
Gallium	< 0.02

All the results were statistically processed by standard methods [31,32]. The average experimental error for 3-4 parallel runs was below 6 %.

## 2.4. Calculation of Apparent Constants of Acid-Base Ionization of Ion Exchangers

The constants values were calculated using potentiometric titration data. For each point of the titration curve, the functional groups content was determined and the apparent ionization degree ( $\alpha$ ) of the resin was calculated:

$$\alpha = \frac{[H^+]}{C_0} \quad (4)$$

where  $[H^+]$  is the equilibrium concentration of  $H^+$  ions in the ion exchanger phase, mmol/mL;  $C_0$  is the initial concentration of the titrant solution (0.1 M HCl).

Then a curve was plotted on the coordinates  $pH = f(\log \frac{\alpha}{1-\alpha})$  and at  $\alpha = 0.5$ , the apparent acid-base ionization constants of functional groups of the ion exchangers ( $p\overline{K}_a$ ) were calculated from Henderson's equation:

$$p\overline{K}_a = pH - m \log\left(\frac{\alpha}{1-\alpha}\right) \quad (5)$$

where  $m$  is the slope angle tangent of the curve.

## 2.5. "Limited Bath" Method for Sorption Kinetics of Palladium (II)

The quantities of preswollen resin (0.10 g) were stirred with 25.0 mL of palladium nitrate solutions at  $(20 \pm 1)^\circ\text{C}$  over a period of 30 s to 24 h. The suspensions were in-

tensively stirred (more than 800 rev/min). After a certain time period, the resins and solutions were quickly separated and the concentration of  $Pd(II)$  was determined in the solutions. Then the exchange degree ( $F$ ) was calculated from

$$F = \frac{Q_t}{Q_\infty} \quad (6)$$

where  $Q_t$  and  $Q_\infty$  are the amounts (in mmol) of the palladium sorbed to the time  $t$  (s) and to the equilibrium time.

According to the Boyd's method [29,30,33], the kinetic coefficient  $B$  was calculated from

$$B = \frac{(1.08)^2 \cdot F^2}{t} \quad (7)$$

The data obtained were plotted as a function  $Bt = f(t)$ . If the process is controlled by gel diffusion [29,30,33], this function should be linear. After that, the diffusion coefficients ( $\overline{D}_s$ ) were calculated according to the equation:

$$\overline{D}_s = \frac{Br^2}{\pi^2} \quad (8)$$

where  $r$  is the radius of the resin grain (cm).

The half-exchange time of the kinetic process ( $t_{1/2}$ ) was calculated as follows:

$$t_{1/2} = \frac{r^2}{4\pi^2 \overline{D}_s} \quad (9)$$

## 2.6. Preparation of Sample for FT-IR-Spectroscopy

IR-spectra of ion exchangers investigated were recorded by means of FT-IR- spectrometer Vector 22 (Bruker). Before that, ion exchanger samples were dried during 4 h at  $40^\circ\text{C}$  in convection drier. Then the samples were held in a vacuum-desiccator over freshly calcinated calcium chloride. The specimens were ground in a mechanical mill without air access and after that were pressed with spectrally pure  $KBr$  to discs. The quantities of resin samples and potassium bromide were constant (200 mg each of resin and  $KBr$ ).

## 2.7. Preparation of Samples for Diffuse Reflectance Spectroscopy

The diffuse reflectance spectra were recorded by means of spectrometer PULSAR (Russia). The resin quantities (0.20 g) were preliminary saturated with palladium (II) ions with concentration  $5.0 \cdot 10^{-4}$  mol/L during 24 h. After that, the resins were filtered and wet samples were placed into cell. Then the diffuse reflectance spectra

were recorded.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Ionic State of Palladium in Contacting Solutions

It is known from [26,27,34,35] that the ionic state of platinum group metals in solutions depends on acidity of contacting solution as well as on concentration of chloride or nitrate ions (for chloride and nitrate systems, respectively). It is determined at present that  $Pd(NO_3)_2 \cdot (H_2O)_2$  is formed after the dissolution of metallic palladium in concentrated nitric acid according to reaction (1) and subsequent diluting of the solution obtained [36,37]. It is also determined [38] that the hydrated palladium (II) ions  $[Pd(H_2O)_4]^{2+}$  and their mononitrate complexes  $[PdNO_3]^+$  are present in solution at  $C_{HNO_3} \geq 1$  mol/L.

With the increase in nitric acid concentration, the amount of different nitrate cationic and anionic complexes as well as of neutral species is growing [19,20]:  $[Pd(H_2O)_3NO_3]^+$ ,  $[Pd(H_2O)_2(NO_3)_2]$ ,  $[Pd(H_2O)(NO_3)_3]^-$ ,  $[Pd(NO_3)_4]^{2-}$ . When the nitric acid concentration diminishes from 1 mol/L to 0.01 – 0.001 mol/L, the formation of hydroxocomplexes with the general formula  $[Pd(OH)_n]_{aq}^{(2-n)+}$  is observed in solution [36,38]. That occurs due to the so-called “aging” of solutions, which takes place in weak acidic media, and especially after keeping of such solutions for longer than 24 h. This phenomenon is typical for solutions of platinum group metals [27,34,38]. At  $C_{HNO_3} \leq 0.001$  mol/L, the solution does not contain aquatic  $Pd(II)$  ions and its nitrate complexes, and only hydroxocomplexes of different composition exist in this media [38].

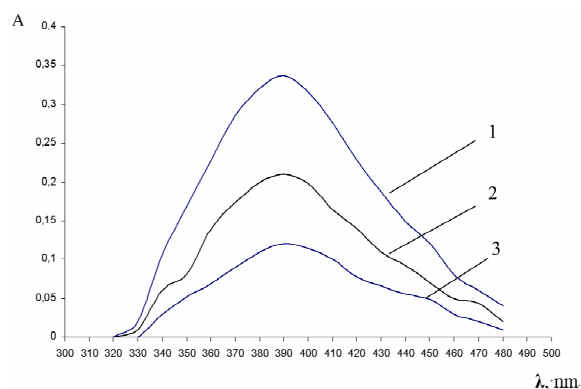
The above discussion concerns only the  $Pd(II) - HNO_3$  systems, i.e. without adding background electrolytes. Our previous investigation [24] was focused on palladium (II) recovery from strong acidic solutions ( $C_{HNO_3}$  was 1, 2 and 5 mol/L) in the system sorbent –  $Pd(II) - HNO_3$ . However, the sorption of palladium from weak acidic solutions in the presence of salt background is also of practical interest, since such media are formed in number of technological schemes [1,3]. Therefore, we have also studied the following system: ion exchanger –  $Pd(II) - 0.01$  M  $HNO_3 - 1$  M  $KNO_3$ . It should be noted that data on ionic state of palladium in such systems are not available at present and this problem requires a special study. However, we have attempted to make some conclusions on this matter in the present paper, as discussed below.

Before studying the palladium sorption recovery, we have obtained electron absorption spectra of freshly

prepared palladium solutions in 1 M  $HNO_3$  and at pH=2, presented in **Figure 1**. It should be noted that palladium sorption was carried out from freshly prepared solutions to minimize their “aging”. It can be seen from Figure 1 that absorption maximum in spectrum 1 ( $Pd$  in 1 M  $HNO_3$ ) is located at 390 nm and indicates the presence of complexes  $[Pd(H_2O)(NO_3)_3]^-$  as a prevailing form [36-38]. However, the absorption maxima in spectra 2 and 3 ( $Pd$  in 0.01 M  $HNO_3$  in the presence of 1 M  $KNO_3$ ) are also located at 390 nm and show presence of the same  $Pd(II)$  complexes in solution. Probably, the formation of anionic nitrate complexes of palladium (II) is promoted by the high concentration of nitrate ions, despite the weak acidity of solution (pH=2). Later, during our experiments on  $Pd(II)$  sorption, we have not observed any precipitation of metal specimens on a surface of resins, unlike authors [20]. It means that there was no hydrolysis in the investigated systems under chosen conditions (fresh prepared weak acidic solutions and presence of 1 M  $KNO_3$ ). However, the precipitation effect was clearly observed when palladium sorption was carried out from solutions kept more than 8 h or from freshly prepared solutions with pH=4. This proves the formation of different hydroxocomplexes. Therefore, we can conclude from the absorption spectra that complexes  $[Pd(H_2O)(NO_3)_3]^-$  prevail in contacting freshly prepared solutions under the chosen conditions.

#### 3.2. Sorption Recovery of Palladium from Model Nitrate Solutions

The sorption properties of ion exchangers investigated to palladium (II) are presented in **Table 3**. It can be seen from these data that in general all the resins reveal high sorption ability, since they recover  $Pd$  on the level ~70



**Figure 1.** Absorption spectra of palladium (II) working solutions in 1 M  $HNO_3$  (1) and in the system 0.01 M  $KNO_3 + 1.0$  M  $KNO_3$  (2,3),  $C_0(Pd) = 2.0 \times 10^{-3}$  mol/L (1,2) and  $1.0 \times 10^{-3}$  mol/L (3).



% (ANKF-5) and more than 90 % (Purolite S 985). The studied sorbents can be arranged by their affinity grade to palladium in the following order: Purolite S 985 > Purolite A 530 > Purolite A 500 ~ AV-17-8 > AN-251 > ANKF-5.

It is interesting to note, that all ion exchangers except Purolite S 985 possess approximately equal affinity to *Pd*, despite of their different physical and chemical structure. The nature of functional groups of the ion exchangers investigated allows to form the following types of chemical bonds during their contact with noble metal ions [5,6,19,20]:

- ionic, i.e. ion – ion interaction, which takes place on strong basic anion exchangers;
- coordination, forming as a result of conservation of electron pair between ligand (electron-pair donor), which is the nitrogen atom of resin functional groups, and the metal (electron-pair acceptor); this bond takes place on weak basic anion exchangers.

The fact that amphoteric ion exchanger ANKF-5 recovers *Pd(II)* ions from nitrate solutions on the same level (and even less) than anion exchanger AN-251 (both resins were synthesized on the basis of vinylpyridine), unambiguously points out to ionic state of *Pd(II)* in contacting solution. If cationic hydroxocomplexes or hydrated ions  $[Pd(H_2O)_4]^{2+}$  were present in this solution, the degree of palladium (II) recovery would probably be above 69% due to the activity of phosphorylic acid and pyridine nitrogen functional groups in weak acidic media.

Moreover, it is noteworthy that strong basic anion exchangers recover *Pd(II)* to a greater extent (**Table 3**), although the additional complex formation of palladium ions with functional groups of quaternary ammonium base is impossible (unlike the weak basic anion exchangers). Therefore, we consider highly probable that anionic palladium complexes  $[Pd(H_2O)(NO_3)_3]^-$  or  $[Pd(NO_3)_4]^{2-}$  exist in the systems investigated in the presence of 1 M  $KNO_3$ .

**Table 3.** Sorption of palladium from nitrate model solutions on ion exchangers investigated Initial *Pd(II)* concentration is  $5.0 \cdot 10^{-4}$  mol/L, pH = 2.

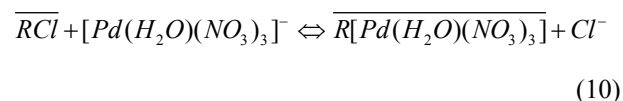
Trade name	log <i>D</i>	<i>R</i> (%)	Trade name	log <i>D</i>	<i>R</i> (%)
Purolite A 500	2.79	86	AV-17-8	2.77	85
Purolite A 530	2.87	88	AN-251	2.54	78
Purolite S 985	3.23	94	ANKF-5	2.34	69

As for sorption recovery of palladium (II) on anion exchanger Purolite S 985, which reaches 94%, there is little doubt that this recovery proceeds according not only to anion exchange, but also to complexation process, taking into account the presence of polyamine groups in the structure of this sorbent.

### 3.3. FT-IR Study of Palladium Sorption

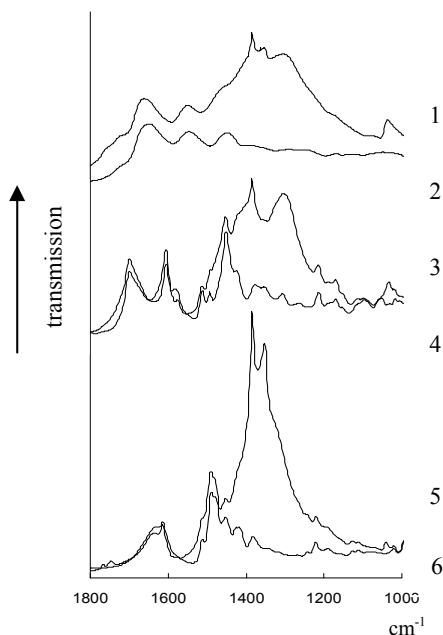
To study the palladium recovery from nitrate solutions in more detail, we have carried out IR-spectroscopic investigation. We have obtained IR-spectra of anion exchangers Purolite S 985, AV-17-8 and AN-251, the fragments of which are shown in **Figure 2**. IR-spectra of initial samples of these resins in chloride form are presented for comparison.

It can be seen from IR-spectra that appearance of intensive peaks in the range of 1400–1300  $cm^{-1}$  (1384, 1352 and 1300  $cm^{-1}$ ) is observed for all the ion exchangers, independently of their basicity and structure of polymeric matrix. These peaks are assigned to vibrations of N–O bonds of nitrate ion: peak at 1384  $cm^{-1}$  corresponds with stretching vibrations of free  $NO_3^-$  [20,39], whereas peaks at 1352 and 1300  $cm^{-1}$  can be assigned to the N–O stretching vibrations in palladium complex [39]. It should be noted that the greatest intensity of these peaks is revealed in IR-spectrum of strong basic anion exchanger AV-17-8 (**Figure 2**, spectrum 5). It was mentioned above that the functional groups of this resin (quaternary ammonium base) cannot react with palladium through additional coordination. Therefore, it can be concluded that the anion exchange takes place in this case:

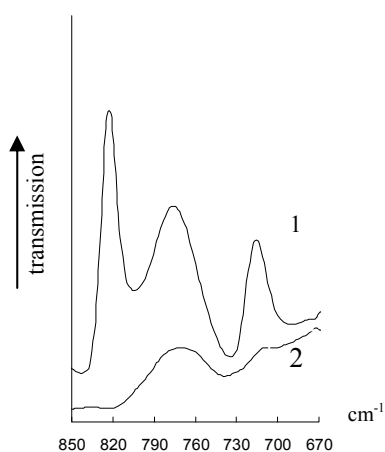


Since the similar but less intensive peaks are revealed in IR-spectra of weak basic anion exchangers Purolite S 985 and AN-251 (**Figure 2**, spectra 1 and 3), it can be concluded that the reaction (10) is to some extent attributable to these resins too.

However, in case of *Pd(II)* recovery on weak basic anion exchanger AN-251, the redistribution of the intensities in the range of 1700 – 1400  $cm^{-1}$ , corresponding to symmetric and asymmetric stretching vibrations of pyridine ring, is observed in IR-spectrum of this resin (**Figure 2**, spectrum 3). The absorption bands at 1600, 1558, 1494 and 1417  $cm^{-1}$  are assigned to C = C and C = N stretching in pyridine ring [20,39,40]. The reduction of peak intensity at 1510  $cm^{-1}$  and depression of that one at 1492  $cm^{-1}$  points out to the probable complexation between palladium and pyridine nitrogen [5,40].



**Figure 2.** IR-spectra fragments of anion exchanger samples Purolite S 985 (1), AN-251 (3), AV-17-8 (5) saturated from nitrate solutions of palladium (II)  $C_0(\text{Pd}) = 5.0 \times 10^{-4}$  mol/L;  $C_0(\text{HNO}_3) = 0.01$  mol/L;  $C_0(\text{KNO}_3) = 1.0$  mol/L Spectra (2), (4) and (6) correspond respectively to initial samples of Purolite S 985, AN-251 and AV-17-8 in chloride form.



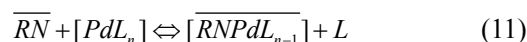
**Figure 3.** IR-spectra fragments of samples of anion exchanger Purolite S 985 saturated from nitrate palladium (II) solution (1) and of initial resin in chloride form (2)  $C_0(\text{Pd}) = 5.0 \times 10^{-4}$  mol/L;  $C_0(\text{HNO}_3) = 0.01$  mol/L;  $C_0(\text{KNO}_3) = 1.0$  mol/L.

The IR-spectrum of weak basic anion exchanger Purolite S 985 saturated with palladium shows the greatest changes compared to the spectrum of its initial sample in

chloride form (Figure 2, spectra 1 and 2). The peaks at 1384, 1352 and 1304  $\text{cm}^{-1}$ , which correspond to nitrate ion and are characteristic for anion exchange in accordance with reaction (10), also appear in the spectrum 1. In the range of stretching vibrations of aminogroups (1550 – 1530  $\text{cm}^{-1}$ ), the reduction of peak intensities takes place, and in the range of 1450–1420  $\text{cm}^{-1}$ , the peak disappears, corresponding to vibrations of methylene groups [5,40]. Such changes indicate that complexation processes in the sorbent's phase take place [5].

In case of Purolite S 985, special attention should be paid to the short-wavelength fragments of IR-spectra, shown in Figure 3. It contains an increase in peak intensity at 771  $\text{cm}^{-1}$  and appearance of bands at 822 and 711  $\text{cm}^{-1}$ . These changes correspond to deformation vibrations of  $N \rightarrow Pd$  bond, which is characteristic for coordination compounds [5,40,41].

Therefore, it can be concluded that palladium sorption from nitrate weak acidic solutions on weak basic anion exchangers proceeds not only according to anion exchange mechanism (reaction (10)), but also is accompanied by coordination:



where  $L = \text{H}_2\text{O}; \text{NO}_3^-; n = 2 - 4$ .

### 3.4. Sorption Isotherm Studies

The isotherms of palladium sorption from nitrate solutions on anion exchangers Purolite S 985, A 500 and A 530 are represented in Figure 4. It is known [29,33] that the shape of these curves is an evidence of sorption selectivity. It can be seen from Figure 4 that all the isotherms are convex curves and they are classified to Langmuir isotherms, which are described as follows:

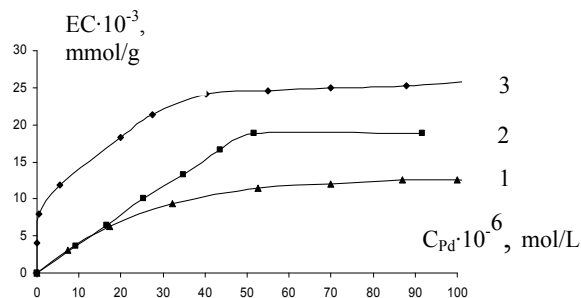
$$EC = EC_\infty \cdot \frac{\overline{K}_{eq} \cdot C_{eq}}{1 + \overline{K}_{eq} \cdot C_{eq}} \quad (12)$$

where  $EC_\infty$  is the maximal equilibrium exchange capacity of the resin to palladium, mmol/g;  $\overline{K}_{eq}$  is the apparent constant of ion exchange equilibrium, L/mmol.

By transforming the Eq. (12) to the linear form, we calculated ion exchange equilibrium constants and determination coefficients ( $r^2$ ), which are presented in Table 4. It can be seen from these data that coefficients  $r^2$  are close to 1. This fact supports our hypothesis about Langmuir-type isotherms for palladium sorption.

### 3.5. Kinetics Studies

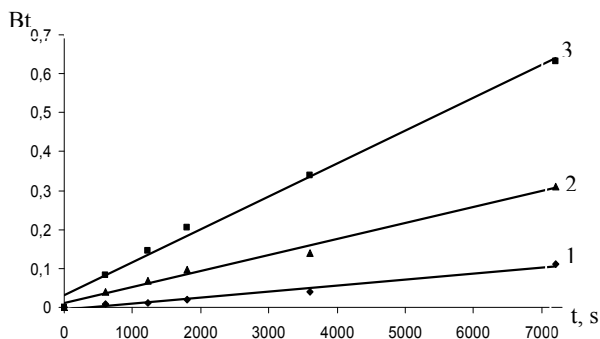
The successful application of ion exchangers in industrial conditions requires their good kinetic properties. That is why the research on kinetics of  $\overline{Pd(II)}$  sorption on Purolite ion exchangers in the investigated systems is both of theoretical and practical interest. The



**Figure 4.** Isotherms of palladium sorption on anion exchangers Purolite A 530 (1), A 500 (2) and S 985 (3)  $C_0(\text{HNO}_3) = 0.01$  mol/L;  $C_0(\text{KNO}_3) = 1.0$  mol/L.

**Table 4.** Apparent constants of ion exchange equilibrium ( $K_{eq}$ ) and determination coefficients ( $r^2$ ) during recovery of palladium (II) from nitrate model solutions.

Trade name	$\overline{K_{eq}}$	$r^2$
Purolite A 500	135	0.894
Purolite A 530	34.4	0.991
Purolite S 985	588	0.975



**Figure 5.** Kinetic dependencies of  $Bt$  function on time  $t$  for anion exchangers Purolite A 530 (1), S 985 (2) and A 500 (3).

**Table 5.** Kinetic parameters of palladium (II) sorption from nitrate model solutions  $C_0(\text{Pd}) = 5.0 \times 10^{-4}$  mol/L;  $C_0(\text{HNO}_3) = 0.01$  mol/L;  $C_0(\text{KNO}_3) = 1.0$  mol/L.

Trade name	$\overline{D} \cdot 10^6$ (mmol/g·s)	$\overline{D_s} \cdot 10^8$ (cm <sup>2</sup> /s)	$t_{1/2}$ (s)
Purolite A 500	11.70	8.26	1558
Purolite A 530	2.06	0.58	23164
Purolite S 985	9.26	5.94	2390

calculated main kinetic parameters are summarized in **Table 5** and **Figure 5** contains the dependencies  $Bt = f(t)$ .

It can be seen from **Figure 5** that dependencies  $Bt = f(t)$  are the straight lines for all the resins Purolite investigated and comply with criterion of gel kinetics, i.e. the whole sorption process is controlled by interdiffusion of the ions exchanged in a resin grain [29,30,33]. As for the main kinetic parameters, it should be noted that average rate of ion exchange process is higher on strong basic anion exchanger Purolite A 500 (**Table 5**). Consequently, the value of average diffusion coefficient for this resin exceeds such values for the other sorbents and the half-exchange time is lesser. A comparison of kinetic process between anion exchangers Purolite S 985 and A 500 shows that such behavior of these sorbents is in good consistence with our above-mentioned assumptions about sorption mechanism. Since the palladium sorption on Purolite A 500 is not complicated by additional complexation (in contrast to Purolite S 985), the rate of this process is higher and diffusion coefficient values are also bigger, whereas the half-exchange times are lesser for this resin. However, it is interesting to note that the strong basic anion exchanger Purolite A 530, which is not practically distinguished from A 500 in its sorption properties (**Table 3**), compares much unfavorably with A 500 in its kinetic properties (**Table 5**). The average rate of ion exchange process on Purolite A 530 is about 5 times lower than on Purolite A 500. Also the average diffusion coefficient values for A 530 are by one order smaller and the half-exchange time is by one order greater (**Table 5**). Such behavior of anion exchanger Purolite A 530 in comparison with also strong basic resin A 500 can be probably explained by its exchange capacity, which is less by half than this value for A 500, and by its lesser swelling as well (**Table 1**). Moreover, it can be assumed that the sorbed complex ions of palladium (II), which possess a square spatial configuration [42], have not enough time to reach the active centers of the sorbent A 530, where the anion exchange occurs, because of its small exchange capacity (there are few available exchange centers on a resin surface). Certainly this phenomenon requires a special study, but from the practical point of view the anion exchanger Purolite A 500 is preferable than sorbent Purolite A 530 for recovery of palladium (II) from nitrate solutions.

### 3.6. Sorption of Palladium from Nitrate Solutions of Spent Catalysts

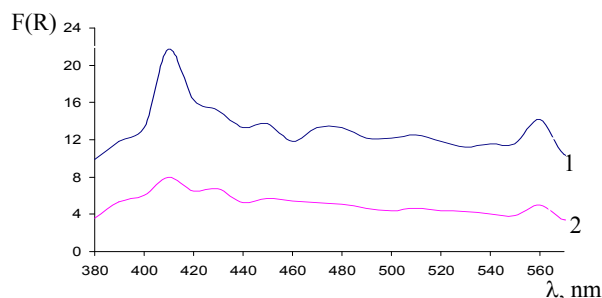
Further we have studied the sorption recovery of palladium (II) from solutions of spent catalysts on some anion exchangers chosen on the basis of their good sorption and kinetic properties. The results are summarized in **Table 6**.

It can be seen from these data that the anion exchangers in general possess good sorption ability to  $\text{Pd(II)}$  ions, but this characteristic is slightly lower in compari-

son with the data obtained for model solutions, excluding anion exchanger AV-17-8 (Table 3). Partly the decrease in  $Pd(II)$  recovery from real solutions can be explained by complex composition of initial solution of spent catalyst (Table 2), where a number of ions produce a competing effect on palladium sorption process.

In order to determine the form of palladium in contacting solution of spent catalyst as well as in the phase of strong basic anion exchanger, we have obtained the diffuse reflectance spectra presented in Figure 6. It can be seen from these data that the maximum in diffuse reflectance spectra is located at 410 nm. It corresponds with the maximum in absorption spectrum at 390 nm (Figure 1), since the bathochromic shift of maximum in diffuse reflectance spectra is observed during sorption concentration of noble metal ions in view of matrix effect of solid phase [43,44]. Therefore, the prevailing form of  $Pd(II)$  existence in nitrate weak acidic solutions of spent catalysts is its complex  $[Pd(H_2O)(NO_3)_3]^-$

It is known [2-5,15] that the desorption of noble metals from highly selective ion exchangers is hardly achievable process because of strong retention of adsorbed metal ions by functional groups of resins. Due to that, for the successful regeneration of these sorbents it is necessary to use the elution agents which form more stable complexes with the recovered metal ions than the complexes of these metals existing in the resin phase. From this point of view, the acidic or basic thiourea solutions are widely applied as eluting agent [1,15,19,22-24,27]. We have also used in the present work the thiourea solutions for palladium desorption after its sorption recovery. The results are shown in Table 7. It can be seen from the presented data that the palladium (II) elution degrees after its recovery from model solutions reach the level of 78-82% – the result which is considered quite satisfactory. However, the palladium desorption after its recovery from solutions of spent catalysts proceeds on the level of 22–25%. When carrying out this process, we have changed thiourea concentration and used its solutions in  $HNO_3$  or  $NaOH$ , but the best result we could reach was ~ 25% by palladium elution with 1 M thiourea solution in 1 M  $NaOH$ . It should be noted that the recovery of noble metals from industrial solutions after their sorption on highly selective ion exchangers is often carried out by burning of such resins, since the value of noble metals exceeds the costs of ion exchange materials, even selective ones [2,4,24,45]. Therefore, it is necessary to continue the research for improving the palladium recovery after its sorption on selective ion exchangers from solutions of spent catalysts.



**Figure 6.** Diffuse reflectance spectra of anion exchangers' samples AV-17-8 (1) and Purolite A 500 (2) saturated with palladium (II) from nitrate solutions of spent catalysts.  $C_0(Pd) = 5.0 \times 10^{-4}$  mol/L;  $C_0(HNO_3) = 0.01$  mol/L;  $C_0(KNO_3) = 1.0$  mol/L  $F(R)$  – diffuse reflectance coefficient.

**Table 6.** Sorption recovery of palladium (II) from nitrate solutions of spent catalysts  $C_0(Pd) = 5.0 \times 10^{-4}$  mol/L;  $C_0(HNO_3) = 0.01$  mol/L;  $C_0(KNO_3) = 1.0$  mol/L.

Trade name	log $D$	$R(\%)$
Purolite A 500	2.31	65
Purolite S 985	2.86	88
AV-17-8	2.72	84

**Table 7.** Elution of palladium from anion exchangers investigated by thiourea solution (1.0 mol/L) in 0.01 M  $HNO_3$  after palladium sorption from nitrate weak acidic model solutions.

Trade name	Desorption degree (%)
Purolite S 985	78
Purolite A 500	82

## 4. CONCLUSIONS

Sorption recovery of palladium (II) from nitrate weak acidic model solutions and solutions of spent catalysts on some ion exchangers with different physical and chemical structure was investigated. Based on electron absorption spectra, it was determined that complexes  $[Pd(H_2O)(NO_3)_3]^-$  prevail in contacting solutions. It was shown that ion exchangers investigated possess good sorption and kinetic properties.

The mechanism of palladium sorption recovery on strong and weak basic anion exchangers from nitrate weak acidic solution was outlined by means of FT-IR-spectroscopy. It was shown that strong basic anion exchangers sorb palladium according to anion exchange, whereas weak basic resins recover  $Pd(II)$



complexes not only by anion exchange, but also by means of additional coordination with nitrogen atoms of functional groups.

The palladium (II) desorption after its recovery on selective ion exchangers from model solutions and solutions of spent catalysts was carried out using thiourea solutions. It was shown that the degree of palladium elution by 1 M thiourea solution in 0.01 M  $HNO_3$  after its sorption from model solutions is on the level of 78 – 82 %, whereas this value does not exceed 25% after  $Pd(II)$  sorption from solutions of spent catalysts. The improvement of this process should be a subject for further research.

Based on results of present investigation, the anion exchangers AV-17-8 as well as Purolite S 985 and A 500 can be recommended for selective recovery of palladium (II) from nitrate weak acidic solutions.

## 5. ACKNOWLEDGEMENT

The authors would like to express profound gratitude to the team of Moscow office of Purolite International Ltd, who kindly provided us with ion exchanger samples.

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