

## Study of Pd(II) Sorption from Aqueous Solutions on the Natural and Acid-Modified Transcarpathian Clinoptilolite\*

by O. Korkuna<sup>1,2\*\*</sup>, T. Vrublevska<sup>1</sup> and W. Reschetilowski<sup>2</sup>

<sup>1</sup>Department of Analytical Chemistry, Ivan Franko National University,  
Kyryla and Mefodiya Str. 6, 79005 Lviv, Ukraine

<sup>2</sup>Institut für Technische Chemie der TU Dresden, Mommsenstr. 4, D-01062 Dresden, Germany  
\*\*e-mail: olga\_korkuna@yahoo.com

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The sorption of Pd(II) on the natural and acid-modified clinoptilolite under static conditions has been investigated. Optimal pH values for Pd(II) sorption are 4.5 from nitrate solutions and 10.0 from ammonia solutions for both sorbents respectively. The optimum grain size of both sorbents has been determined. It was found that the sorbent in the protonated form dried at 150–160°C and the natural sorbent dried at 100–110°C have highest sorption ability. The influence of inorganic salts of ammonium, alkali, heavy and platinum metal cations as well as some inorganic and organic anions on Pd(II) sorptive ability by the natural and H-clinoptilolite has been investigated. Pd(II) desorption from sorbents has been studied. The sorption capacity of natural and H-clinoptilolite towards Pd(II) from nitrate solutions (pH = 4.2) is 977 and 3440 µg/g respectively and for natural clinoptilolite from ammonia solutions (pH = 10.0) is 2404 µg/g.

**Key words:** zeolite, palladium(II), sorption, ion-exchange, clinoptilolite

In spite of small amounts of platinum metals present in wastes of jewellery, electrical engineering productions *etc.*, they are characterized by the allergen action on living organisms, some of their oxides can cause health problems (*e.g.* heart problems or malfunction of nervous system). Recent publications prove significant interest in platinum metals recovery by sorption and elaboration of different selective and sensitive methods of their determination followed by concentration and separation [1,2]. On the basis of literature data dealing with concentration and separation of palladium(II) it is established that most methods are intended for the combined separation of platinum group ions, mainly from chloride media, using expensive, not readily available sorbents, which in many cases are unstable in alkaline and strong-acid media [1,3]. Therefore, investigation of conditions of palladium(II) concentration and separation from nitrate and ammonia media using inexpensive, readily-available, chemical- and heat-resistant natural zeolites for elaboration of selective methods of sorption is practically significant.

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Natural zeolites, especially clinoptilolite are widely used for elimination of radioactive elements, for concentration and separation of heavy, alkali, alkaline earth metal ions, ammonium ions, and for gas adsorption. Owing to a number of specialities natural clinoptilolite is used for environmental protection, in medicine, agriculture and several industrial sectors [4,5]. Therefore, its application for separation of Pd(II) from wastes is prospective.

## EXPERIMENTAL

In our investigation we used the Transcarpathian clinoptilolite – crystalline aluminosilicate of high silicon content, which was employed from the deposit near the village Sokyrnytsa (Transcarpathian region, Ukraine). The mineralogy composition of this deposit is following: 85±6 wt.% of clinoptilolite, admixtures of quartz, mica, and feldspar. According to recent data [6], the formula of Transcarpathian clinoptilolite is:  $(K_{2.3}Na_{0.5}Ca_{2.1}Mg_{0.6}Fe(III)_{0.9}Fe(II)_{0.2}Ti_{0.2}) \cdot (Si_{31.4}Al_{6.5}O_{44}) \cdot 21.8H_2O$ .

To measure the Pd(II) sorptive concentration, the natural clinoptilolite was ground in a ball mill and fractionated by sieving to obtain the following particle fractions: 0.200–0.315; 0.315–0.355; 0.355–0.500; 0.500–0.710; 0.710–0.800 mm. The sorbent fractions were washed with distilled water, dried out in air and kept in a desiccator. Natural clinoptilolite has heterogeneous composition and contains different ion-exchangeable cations: Ca, K, Mg, Na ( $K > Ca \gg Mg > Na$ ). For the elimination of the dependence of sorption results on sorbents batch, it is necessary to modify clinoptilolite, namely to transform it into the H-form. Such high silicate zeolite as clinoptilolite can be transformed into the protonic form by mineral acids treatment [7–9]. Acid-modified clinoptilolite was obtained in the following way according to [10]. The grained sample of zeolite was pretreated with 12.0 mol/L solution of HCl for 24 h at 20±1°C. For treatment of 1 g of sorbent, 20 mL of acid were used. After modification the acid solution was poured out and the sorbent was properly washed with distilled water up to pH about 5.5–6.0; after that the sorbents were dried in air and kept in a desiccator.

The nitrate Pd(II) solution was obtained by dissolving the pure metal (99.99 wt.%) in nitric acid (1:1). Working solutions have been prepared by dilution of aliquot of the initial Pd(II) solution with distilled water. The ammonium Pd(II) solutions were prepared by the addition of 25 wt.% ammonia solution to the aliquot of the initial Pd(II) solution to obtain necessary pH value with dilution to 250 mL with distilled water. pH value of the solutions was controlled by a pH-573 pH-meter with saturated silver chloride reference electrode and adjusted by the addition of some amount of HNO<sub>3</sub>, NaOH and NH<sub>3</sub>·H<sub>2</sub>O solutions depending on the experimental conditions.

Investigations of Pd(II) sorption were carried out under static conditions. A definite amount of sorbent was placed in the Pd(II) solution and shaken using mechanical stirring. All investigations were repeated 3 times ( $\alpha = 0.95$ ).

The contents of sorbed palladium were determined by pulse voltammetry using a linearly varying potential (PO – 5122 model 03 oscillogpolarograph) and defined as the difference between the initial concentrations of Pd(II) and the concentrations in filtrates. For that purpose 20.00 mL of Pd(II) solution were pipetted and 4.00 mL of concentrated NH<sub>3</sub>·H<sub>2</sub>O (pH = 11.5) were added as the background electrolyte with next dilution to full volume (25 mL) using distilled water. Palladium(II) was reduced using 1 mol/L NH<sub>4</sub>OH + 1 mol/L NH<sub>4</sub>Cl as the background electrolyte at a potential of –0.720 V vs. saturated calomel electrode (SCE). A two-electrode thermostated cell (22±0.5°C) with an indicator mercury dropping electrode and a SCE were employed for such measurements; the capillary characteristics were as follows:  $m = 0.706 \text{ mg} \cdot \text{s}^{-1}$ ;  $\tau = 7.5 \text{ s}$ . Peak potentials were measured directly at the maximum point of the polarogram using a V7-21 voltmeter with precision ±1 mV. The investigated solution was purified from oxygen by blowing argon. Polarographic determination was carried out in the following regime of oscillogpolarograph work:  $E_{init} = -0.300 \text{ V}$ , rate of polarized potential  $V = 0.6 \text{ V} \cdot \text{s}^{-1}$ ,  $\tau_{ret} = 6 \text{ s}$ . Pd(II) determination was made by the method of comparative measurements and the method of standard additions.

The amount of sorbed Pd(II)  $m_{sorb}$  was determined by the following equation:  $m_{sorb} = m_{init} - m_{filt}$ , where  $m_{init}$  – Pd(II) mass in the initial solution,  $m_{filt}$  – Pd(II) mass in the filtrate.  $m_{init} = C_{init}MV_{sol}$ , where  $C_{init}$  – Pd(II) concentration in the initial solution in mol/L,  $M$  – molecular mass of Pd(II) in g/mol,  $V_{sol}$  – solution volume in L;  $m_{filt} = C_{filt}MV_{sol}$ , where  $C_{filt}$  – Pd(II) concentration in the filtrate. The extent of Pd(II) separation  $R$  (%) was calculated by the following equation:

$$R = \frac{m_{sorb}}{m_{init}} \cdot 100\%.$$

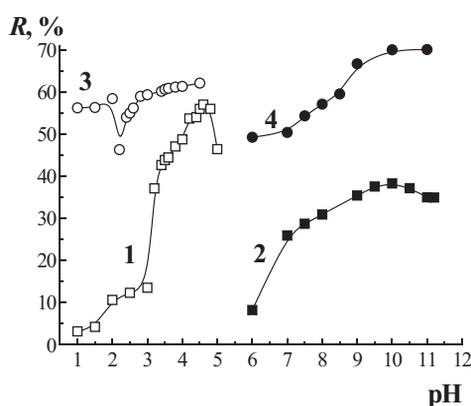
The Pd(II) sorption value  $a$  (g/g of sorbent) was calculated by means of the equation:

$$a = \frac{(C - C_{filt})MV_{sol}}{m}.$$

## RESULTS AND DISCUSSION

Clinoptilolite is a cation-exchangeable adsorbent since it has a negatively charged surface and possesses a sieve sorption mechanism. Acid treatment of clinoptilolite is usually connected with a partial elimination of aluminium from its structure. This leads to contraction of zeolite lattice and increase of  $\text{OH}^-$  groups number on the surface as well as inside the clinoptilolite structure. Therefore the optimum pH value of Pd(II) solutions during sorption by natural clinoptilolite can differ from the optimum pH value for the sorbent H-form. The extent of Pd(II) separation by natural and H-clinoptilolite as a function of pH value of the nitrate and ammonia solutions is shown in Fig. 1.

As shown in Fig. 1 (curve 1), from pH 1.0 up to 3.2, Pd(II) is weakly sorbed by natural clinoptilolite, that may be due to the Pd(II) forms, namely domination of the complex  $[\text{Pd}(\text{OH})(\text{H}_2\text{O})_3]^+$  in this pH range in nitrate solutions [11]. From pH = 3.0,



**Figure 1.** Dependence of the extent of Pd(II) separation by different clinoptilolite forms on the pH medium under the static conditions at  $t_{shaking} = 1$  h,  $m_s = 0.5$  g,  $V_{sol} = 250$  mL: 1) – by the natural form from the nitrate solutions;  $C_{Pd(II)} = 7.68 \cdot 10^{-5}$  mol/L;  $d_s = 0.355$ – $0.500$  mm; 2) – by the natural form from the ammonia solutions;  $C_{Pd(II)} = 3.84 \cdot 10^{-5}$  mol/L;  $d_s = 0.355$ – $0.500$  mm; 3) – by H-form from the nitrate solutions  $C_{Pd(II)} = 3.84 \cdot 10^{-5}$  mol/L;  $d_s = 0.200$ – $0.315$  mm; 4) – by H-form from the ammonia solutions;  $d_s = 0.200$ – $0.315$  mm;  $C_{Pd(II)} = 3.84 \cdot 10^{-5}$  mol/L.

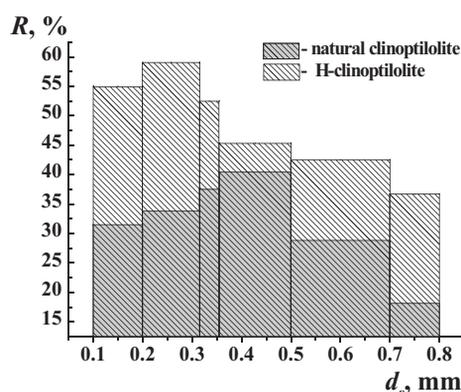
the Pd(II) sorption considerably increases, that can be explained by the formation of the mixed aquahydroxocomplexes of the type  $[\text{Pd}(\text{OH})_2(\text{H}_2\text{O})_2]^0$  [11], which possess better affinity for clinoptilolite. The maximum extent of Pd(II) separation is achieved at pH = 4.5, where this complex is dominant. At pH higher than 4.5, the Pd(II) sorption gradually decreases, that may result from polymerization of Pd(II) complexes and formation of colloid parts. This leads to precipitation of  $\text{Pd}(\text{OH})_2$  and therefore investigation of Pd(II) sorption in such conditions is hindered.

In the case of H-clinoptilolite (curve 3) the extent of Pd(II) separation slowly increases from pH = 1.0 up 4.5 and the maximum sorption value is achieved as in the case of natural clinoptilolite. However, H-clinoptilolite better sorbed the complexes of  $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ , which are dominant up to pH = 2.0 in the nitrate medium. Such difference of sorption character between the natural and the H-clinoptilolite can be explained by the changing of the window size of the sorbent channels during acid treatment.

Curves 2 and 4 in Fig. 1 illustrate the extent of Pd(II) separation from ammonia solutions by the natural and the H-clinoptilolite. The shape of these curves is explained by domination of complex  $\text{Pd}(\text{NH}_3)_4^{2+}$  and the increase in the dissociation of the surface OH-groups. As a result of OH-dissociation, the surface  $-\text{O}^-$  groups are formed, which can coordinate tetraammonia complexes of Pd(II). However, at pH > 10.5 the ionic strength of solutions considerably increases, which leads to slight decrease of the Pd(II) complexes separation. However, the extent of Pd(II) ammonium complexes separation on H-clinoptilolite (curve 4) is considerably higher than that on the natural analogue. It is due to the difference in pores size of natural and acid-modified zeolite [12] as well as to smaller grain size of H-clinoptilolite. In this case the "sieve effect" has greater contribution to the sorption process.

One of the factors, that influence the sorbents sorption ability, is the size of their grains. Ion-exchange in clinoptilolite takes place on its surface as well as inside its channels. The crystal structure of clinoptilolite has 2-D view channels: channels A (10-member rings, free diameters  $0.44 \times 0.72$  nm) and B (8-member rings, free diameters  $0.41 \times 0.47$  nm) which are parallel to each other, while C channels (8-member rings, free diameters  $0.40 \times 0.55$  nm) intersect both A and B channels [13]. In the natural clinoptilolite the ion-exchangeable positions are engaged by big cations  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , which block entrance to small zeolite channels, therefore ion-exchange takes place mostly in large channels. In H-clinoptilolite the ion-exchangeable positions are engaged by small cations  $\text{H}^+$  that allow Pd(II) to enter the small channels. The clinoptilolite grains of different sizes have a different number of smaller and larger channels. Therefore, the extent of Pd(II) separation by the natural clinoptilolite grains of different sizes and those modified with 12.0 mol/L HCl to compare their sorption ability was studied (see Fig. 2).

It was established that the maximum extent of Pd(II) separation by natural clinoptilolite is achieved by the grain fraction with  $d_s = 0.355\text{--}0.500$  mm. Considerable sorbent crushing leads to the increase of dead rocks numbers because they have

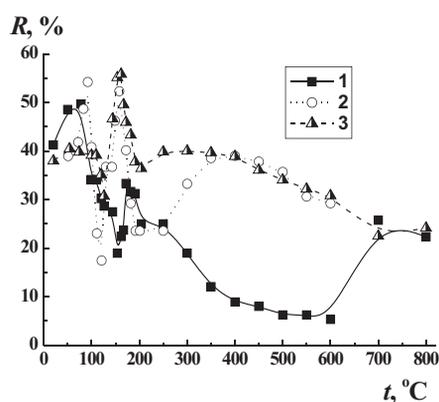


**Figure 2.** Dependence of the extent of Pd(II) separation by natural (pH = 10.0) and H-clinoptilolite (pH = 4.5) on the grain size of sorbent under the following conditions:  $C_{Pd(II)} = 4.26 \cdot 10^{-5}$  mol/L;  $V_{sol} = 250$  mL;  $m_s = 0.5$  g;  $t_{shaking} = 1$  h.

smaller hardness than clinoptilolite and are rapidly crushed. This is a reason for the decreased Pd(II) separation by small clinoptilolite grain fractions. As follows from Fig. 2, the H-sorbent has the highest Pd(II) separation extent on the grains with  $d_s = 0.200$ – $0.315$  mm in contrast to the natural clinoptilolite, since acid treatment leads to washing out of dead rocks.

During thermal treatment of the mineral clinoptilolite containing different types of water, a number of changes takes place. At first it loses water and then undergoes amorphization. All these changes during thermal treatment have strong influence on sorbent sorption properties. Therefore, we investigated the influence of thermal treatment of the natural clinoptilolite on its sorptive ability towards Pd(II) (see Fig. 3, curve 1).

The obtained dependence of the extent of Pd(II) separation by natural clinoptilolite on the sorbent thermal treatment shows that the maximum separation of Pd(II) is achieved in the temperature range  $70$ – $80^\circ\text{C}$ , where the physically adsorbed water is lost. The next sorption maximum appears on the curve at  $170^\circ\text{C}$ , which can be connected with elimination of ligands water or with dissociation of water molecules by polar cations during dehydration. As a result, hydroxide bonds with cations can be formed and the additional OH groups during interaction of  $\text{H}^+$  with the framework of  $\text{O}^{2-}$  ions also can appear [14]. Additionally, OH-groups can take part in ion-exchange with Pd(II) ions. At  $> 350^\circ\text{C}$  the Pd(II) separation extent considerably decreased, that could be a result of sorbent structure reformation [6]. Similar effects are reported in [15,16], in which it is shown that at  $300$  and  $400^\circ\text{C}$  the successive changes of clinoptilolite occur leading to the increase in the number of OH-groups in the zeolite structure.



**Figure 3.** Dependence of extent of Pd(II) separation on the sorbent thermal treatment: 1) by the natural clinoptilolite; the ammonia solution, pH = 10.0;  $C_{Pd(II)} = 5.48 \cdot 10^{-5}$  mol/L;  $d_s = 0.500\text{--}0.710$  mm; 2) by H-clinoptilolite; the nitrate solution pH = 4.1;  $d_s = 0.315\text{--}0.355$  mm;  $C_{Pd(II)} = 1.14 \cdot 10^{-5}$  mol/L; 3) by H-clinoptilolite; the ammonia solution, pH = 10.0;  $d_s = 0.200\text{--}0.315$  mm;  $C_{Pd(II)} = 5.48 \cdot 10^{-5}$  mol/L. In all cases  $V_{sol} = 250$  mL;  $m_s = 0.5$  g;  $t_{shaking} = 1$  h.

Clinoptilolite calcined at  $>600^\circ\text{C}$  has better sorption ability towards Pd(II), which can be explained by heating out of the structure with a formation of siloxane bonds in the places of tetrahedral vacancies [15,16].

During acid modification of natural clinoptilolite, the number of hydroxide groups which the sorbent can lose during thermal treatment is increased [17]. This can cause the change in the size of the entrance channels and sorbent pores. Therefore, it was important to investigate the influence of thermal treatment of H-clinoptilolite on its sorption ability towards Pd(II) from nitrate and ammonia media.

As can be seen in Fig. 3 (curve 2), the two maxima of Pd(II) sorption from the nitrate medium have been observed for H-clinoptilolite dried at  $100^\circ\text{C}$  and  $160^\circ\text{C}$ . The maximum value of Pd(II) sorption from ammonia media (curve 3, Fig. 3) is achieved on the zeolite dried in the temperature range  $150\text{--}160^\circ\text{C}$ . At these temperatures hygroscopic and ligands water was eliminated from H-clinoptilolite. Such type of curve 2 is logical if we take into consideration, that the aquahydroxo complex of palladium(II), which exists in a nitrate medium, has a smaller size than that of ammonium, thus it can enter the incompletely blocked clinoptilolite channels (after the elimination of hygroscopic water). From  $250^\circ\text{C}$  the extent of Pd(II) separation from the nitrate medium insignificantly increases, which is related to the contraction of zeolite lattice and which may perhaps hinder the access of palladium(II) complexes at pH = 4.1 inside the pores.

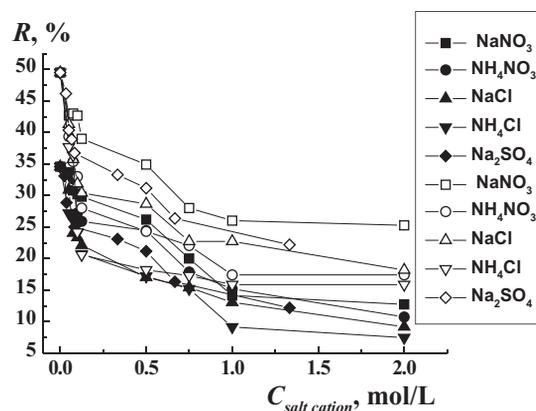
The extent of Pd(II) separation in the ammonia medium on the dried sorbent at  $>250^\circ\text{C}$  gradually decreases. It is connected with the structural sorbent reconstruction, which draws narrowing of channels thus playing an important part in the “sieving effect” of sorption. At  $>600^\circ\text{C}$  the extent of Pd(II) separation from both media

considerably decreases, which can be explained by the sample amorphization as demonstrated in previous research [19].

Consequently, in agreement with the experimental data elsewhere [19], H-clinoptilolite dried in the temperature range of 150–160°C has better sorption ability than natural clinoptilolite dried in the temperature range of 70–80°C (pH = 10.0).

As the real objects containing Pd(II) are wastes of industrial enterprises or geological samples, therefore they can contain plenty of extraneous compounds which are suitable for competitive sorption on a zeolite or can take part in the reaction of complexation with Pd(II) ions. Therefore, we investigated the influence of the salt effect created by inorganic salts on palladium(II) sorption by natural and H-clinoptilolite (Fig. 4).

As shown in Fig. 4, in the cases when salt content is less than 0.125 mol/L, a large extent of Pd(II) separation is observed. With a further increase in the salt background the extent of palladium separation sharply decreased. The ammonia salts exhibit the most negative influence on Pd(II) sorption. This effect is connected with the laboured migration of palladium(II) ions to the sorbent surface and, simultaneously, with the blocking of free access for Pd(II) ions to the entrance of channels windows of clinoptilolite. That is why before carrying out sorption the real concentrated solutions of productions and natural objects must be diluted. In the case of such anions as chloride and sulphate it is also possible that competitive complexation of palladium(II) takes place. These complexes of Pd(II) have negative charge and are not sorb on clinoptilolite.



**Figure 4.** Dependence of extent of Pd(II) separation by natural (empty symbols) and H-clinoptilolite (full symbols) on the concentration of inorganic cations. The ion-exchange conditions:  $V_{\text{sol}} = 250 \text{ mL}$ ;  $m_s = 0.5 \text{ g}$ ;  $t_{\text{shaking}} = 1.5 \text{ h}$ . 1) natural clinoptilolite; pH = 10.0;  $C_{\text{Pd(II)}} = 4.26 \cdot 10^{-5} \text{ mol/L}$ ;  $d_s = 0.315\text{--}0.355 \text{ mm}$ ; 2) H-clinoptilolite; pH = 4.2;  $d_s = 0.200\text{--}0.315 \text{ mm}$ ;  $C_{\text{Pd(II)}} = 4.26 \cdot 10^{-5} \text{ mol/L}$ .

We investigated also the dependence of Pd(II) sorption by natural and H-clinoptilolite from water solutions on the presence of some ions which can be most often found in composite industrial and natural objects, and also reagents which are used for the separation and masking in analysis. The experimental results are presented in Table 1.

**Table 1.** The influence of extraneous compounds on Pd(II) sorption ( $V_{sol} = 250$  mL;  $m_s = 0.5$  g;  $t_{shaking} = 3$  h) by natural clinoptilolite: pH = 10.0;  $C_{Pd(II)} = 4.25 \cdot 10^{-5}$  mol/L;  $d_s = 0.315$ – $0.355$  mm; and by H-clinoptilolite: pH = 4.2;  $C_{Pd(II)} = 4.27 \cdot 10^{-5}$  mol/L;  $d_s = 0.200$ – $0.315$  mm.

Ion	Natural clinoptilolite		H-clinoptilolite	
	[Pd] : [Ion]	R, %	[Pd] : [Ion]	R, %
–	–	43.3	–	55.9
Pt(IV)	1:0.5	26.5	1:1	0
Rh(III)	1:1	32.7	1:1	8.9
Os(IV)	1:5	34.2	1:10	36.8
Ir(IV)	1:10	32.6	1:0.5	31.7
Ru(IV)	1:5	31.2	1:1	41.6
Au(III)	1:1	33.6	1:1	0
Ag(I)	1:10	26.6	1:1	31.7
Cu(II)	1:10	69.1	1:500	45.9
Zn(II)	1:1	30.8	1:1	21.7
Ni(II)	1:10	33.6	1:10	42.2
Pb(II)	1:10	29.4	1:1	0
Fe(III)*	not invest.	not invest.	1:5	41.3
Mn(II)*	not invest.	not invest.	1:1	23.9
Cl <sup>-</sup>	1:100	38.4	1:1	39.9
NO <sub>3</sub> <sup>-</sup>	1:>1000	57.0	1:500	40.9
SO <sub>4</sub> <sup>-</sup>	1:10	42.2	1:500	41.8
CO <sub>3</sub> <sup>2-</sup>	1:10	34.9	1:1000	55.5
PO <sub>4</sub> <sup>3-</sup>	1:5	41.6	1:1	19.6
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1:500	37.3	1:1	7.1
Tart <sup>2-</sup>	1:1000	41.1	1:1	10.6
Cit <sup>3-</sup>	1:1000	46.7	1:1	7.1
EDTA	1:500	39.5	1:1	6.2

\*At the experiment conditions these elements form sediment, therefore in their presence the sorption was carried out at pH = 1.5.

The data of Table 1 show, that the presence of 10-fold excess of Ag(I), Ir(IV), Ni(II), Pb(II), 5-fold excess of Os(IV) and Ru(IV), commensurable amounts of Rh(III), Au(III) and Zn(II), and half less amount of Pt(IV) considerably decreased the Pd(II) sorption in the ammonia medium. It was observed that Pd(II) sorption in the

presence of Cu(II) increases, moreover such effect of sorption increase is proportional to the increase of Cu(II) concentration in the ammonia solution as well as nitrate media. The presence of Pt(IV), Rh(III), Au(III), Pb(II) hinders the selective separation of Pd(II) from the nitrate solutions. However, the selective Pd(II) separation is possible in the presence of 10-multiple excesses of Os(IV), Ni(II), 5-multiple excesses of Fe(III), commensurable amounts of Ru(IV). Among anions, phosphate, sulphate and carbonate ions exhibit the most perceptible influence on the decrease of Pd(II) sorption in the ammonia medium. Chlorides, which form the anionic complexes of palladium(II), obviously do not hinder significantly sorption in the ammonia media. The presence of nitrate ions leads to the increase of Pd(II) sorption, that can be explained by the sorption effectiveness at the moderate ionic force strength ( $<0.05$  mol/L). Effective Pd(II) sorption by H-clinoptilolite can be carried out only in the carbonate, sulphate and nitrate media.

Consequently, the obtained data showed that Pd(II) sorption from the ammonia media by natural clinoptilolite is more selective than its sorption from the nitrate solutions by a H-form, because in the ammonia medium palladium(II) separation can be carried out in the presence of larger excess of most extraneous elements.

The sorption capacity is the basic sorbents characteristics. The sorption capacities of natural and H-clinoptilolite under the optimum conditions of Pd(II) sorption from the ammonia and nitrate solutions were established. The experimental data are presented in Table 2.

**Table 2.** Sorption capacity of natural and H-clinoptilolite, modified by 12.0 mol/L HCl.  $C_{Pd(II)} = 1.36 \cdot 10^{-4}$  mol/L;  $V_{sol} = 250$  mL;  $m_s = 0.5$  g;  $t_{shaking} = 2.5$  h.

$d_{sorb}$ , mm	pH	Form of clinoptilolite	Sorption capacity, $\mu\text{g/g}$
0.355–0.500	4.2	Natural	977
0.350–0.500	10.0	Natural	2404
0.200–0.315	4.2	H-form	3440

On comparing the sorption properties of natural and H-clinoptilolite, it is clear, that sorption capacity of H-clinoptilolite towards Pd(II) in the nitrate solutions is nearly 4 times larger than that of the natural analogue. The sorption capacity of natural clinoptilolite towards Pd(II) in the ammonia medium is 2.5 times larger than that in the nitrate medium. According to [10], the sorption capacity of H-clinoptilolite in the ammonia media (11420  $\mu\text{g/g}$ ) under other sorption conditions ( $C_{Pd(II)} = 4.35 \cdot 10^{-4}$  mol/L; pH = 11.5;  $V_{sol} = 150$  ml) is 18 times greater. It is necessary to take into account the fact that the initial concentration of Pd(II) nitrate solution was smaller, than that of the palladium ammonia solution in [7] because of formation of sediment under the experiment conditions at pH = 4.2.

Consequently, sorption of palladium(II) on H-clinoptilolite is more effective than the ammonia solution.

After the separation of metal ions from multicomponent solutions by sorbent an important task for next determination is their desorption. Therefore, the ion-reexchange conditions of Pd(II) from natural and H-clinoptilolite were investigated. Aqueous solutions of mineral acids and salts of different concentrations were used. The experimental data are presented in Tables 3 and 4.

From Table 3 it can be seen that the best desorbents of Pd(II) are 1.5 mol/L HCl and 2.0 mol/L NaCl. 100% desorption is achieved in these cases. This effect can be explained by complexation of Pd<sup>2+</sup> with Cl<sup>-</sup> ions as well as by greater affinity for the Na<sup>+</sup> ions in the process of ionic exchange. With palladium(II) desorption by mineral acids it is necessary to note that the higher desorption extent is achieved using more diluted acids in the case of HCl and H<sub>2</sub>SO<sub>4</sub>. This is connected with acids strength (Hammet acidity function), which diminishes in the series HClO<sub>4</sub> > H<sub>2</sub>SO<sub>4</sub> > HCl > HNO<sub>3</sub> [18], as well as with their ability to destroy a zeolite structure, that decreases desorption by the use of highly concentrated acidic solutions. Salts of bivalent cations are practically useless for desorption of Pd(II) from natural clinoptilolite.

**Table 3.** Dependence of extent of Pd(II) desorption from natural clinoptilolite on the desorbent concentration. Desorption conditions:  $V_{des} = 10$  mL;  $t_{des} = 15$  min. Sorption conditions:  $d_s = 0.355$ – $0.500$  mm;  $m_s = 0.5$  g; pH = 10.0;  $C_{Pd(II)} = 4.27 \cdot 10^{-5}$  mol/L;  $V_{sol} = 250$  mL;  $t_{shaking} = 2$  hours.

C(HCl), mol/L	0.1	1.0	<b>1.5</b>	3.0	6.0
R <sub>des.</sub> , %	56	80	<b>100</b>	53	53
C(H <sub>2</sub> SO <sub>4</sub> ), mol/L	0.1	1.0	2.0	4.5	9.0
R <sub>des.</sub> , %	17	40	60	62	48
C(HNO <sub>3</sub> ), mol/L	0.1	1.0	2.0	3.2	6.4
R <sub>des.</sub> , %	10	38	39	46	55
C(HClO <sub>4</sub> ), mol/L	0.1	1.0	1.5	2.9	5.9
R <sub>des.</sub> , %	6	34	44	52	55
C(NaNO <sub>3</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	4	12	28	31	41
C(NaCl), mol/L	0.1	1.0	1.5	<b>2.0</b>	<b>3.0</b>
R <sub>des.</sub> , %	15	58	80	<b>100</b>	<b>100</b>
C(NH <sub>4</sub> NO <sub>3</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	0	31	44	56	69
C(NH <sub>4</sub> Cl), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	1	16	16	30	36
C(Ba(NO <sub>3</sub> ) <sub>2</sub> ), mol/L	0.05	0.1	0.2	0.3	0.45
R <sub>des.</sub> , %	3	4	5	5	5
C(BaCl <sub>2</sub> ), mol/L	0.1	0.5	0.75	1.0	1.5
R <sub>des.</sub> , %	4	6	6	10	13
C(Ca(NO <sub>3</sub> ) <sub>2</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	1	3	3	5	11
C(CaCl <sub>2</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	1	3	7	14	18

As follows from Table 4 only in the case of 1.0 mol/L HCl and 4.5 mol/L H<sub>2</sub>SO<sub>4</sub> complete desorption of Pd(II) from H-clinoptilolite is achieved. Among other salts only chlorides give an acceptable result. Such results are similar to desorption from natural clinoptilolite, although in this case Pd(II) was sorbed from ammonia solutions. Consequently, as follows from Table 4, the most effective desorbent is acid by means of which H-clinoptilolite is obtained.

**Table 4.** Dependence of extent of Pd(II) desorption from H-clinoptilolite on the desorbent concentration. Desorption conditions:  $V_{des} = 10$  mL;  $t_{des} = 15$  min. Sorption conditions:  $d_s = 0.200\text{--}0.315$  mm;  $m_s = 0.5$  g; pH = 4.2;  $C_{Pd(II)} = 4.27 \cdot 10^{-5}$  mol/L;  $V_{sol} = 250$  mL;  $t_{shaking} = 2$  hours.

C(HCl), mol/L	0.1	<b>1.0</b>	<b>1.5</b>	<b>3.0</b>	<b>6.0</b>
R <sub>des.</sub> , %	44	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
C(H <sub>2</sub> SO <sub>4</sub> ), mol/L	0.1	1.0	2.0	<b>4.5</b>	9.0
R <sub>des.</sub> , %	14	40	44	<b>100</b>	79
C(HNO <sub>3</sub> ), mol/L	0.1	1.0	2.0	3.2	6.4
R <sub>des.</sub> , %	8	13	17	50	28
C(HClO <sub>4</sub> ), mol/L	0.1	1.0	1.5	2.9	5.9
R <sub>des.</sub> , %	4	15	34	50	63
C(NaNO <sub>3</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	7	8	9	9	9
C(NaCl), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	9	40	50	56	67
C(NH <sub>4</sub> NO <sub>3</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	6	15	16	18	22
C(NH <sub>4</sub> Cl), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	39	47	43	30	53
C(Ba(NO <sub>3</sub> ) <sub>2</sub> ), mol/L	0.05	0.1	0.2	0.3	0.45
R <sub>des.</sub> , %	10	10	11	11	12
C(BaCl <sub>2</sub> ), mol/L	0.1	0.5	0.75	1.0	1.5
R <sub>des.</sub> , %	22	54	55	51	44
C(Ca(NO <sub>3</sub> ) <sub>2</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	2	2	4	4	4
C(CaCl <sub>2</sub> ), mol/L	0.1	1.0	1.5	2.0	3.0
R <sub>des.</sub> , %	9	15	14	16	20

## CONCLUSIONS

Palladium(II) sorption on natural and acid-modified with 12.0 mol/L HCl clinoptilolite has been investigated. Optimum palladium(II) sorption under the static conditions on grains of the size: 1) 0.355–0.500 mm – natural clinoptilolite and 2) 0.200–0.315 mm – H-clinoptilolite at pH = 4.5 from the nitrate solutions and pH = 10.0 from the ammonia solutions is achieved. Sorptive properties of sorbent H-form dried

at 150–160°C are similar to those of the natural form dried at 70–80°C. It was established that selectivity of the Pd(II) separation by different forms of clinoptilolite in the presence of inorganic salts with  $C > 1.0$  mol/L decreases considerably. It was found that the presence of the 5-fold excesses of Ag(I), Ir(IV), Ni(II), Pb(II) and commensurable amounts of Os(IV) and Ru(IV) do not inhibit palladium(II) sorption on natural clinoptilolite in the ammonia medium, and also the presence of the 10-fold excesses of Os(IV), Ni(II), 5-fold excesses of Fe(III) and commensurable amounts of Ru(IV) do not inhibit sorption in the nitrate medium on H-clinoptilolite. The capacity of natural and H-clinoptilolite (treatment with 12.0 mol/L HCl) in relation to Pd(II) from the nitrate solutions (pH = 4.2):  $a = 977$   $\mu\text{g/g}$  and  $a = 3440$   $\mu\text{g/g}$ , respectively as well as capacity of natural clinoptilolite from the ammonia solutions (pH = 10.0):  $a = 2404$   $\mu\text{g/g}$  was determined. HCl and NaCl are the most effective desorbents for both sorbent forms.

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