

Sorptive properties of natural and modified transcarpathian clinoptilolite and mordenite concerning palladium (II)

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The conditions of Pd(II) concentration on natural transcarpathian clinoptilolite and mordenite in the batch conditions: influence of *pH* solutions, heat treatment, influence of mineral salt background and extraneous ions have been investigated. The optimal conditions to obtain the H-forms of sorbents using different mineral acids for treatment (HCl, HNO₃, HClO₄, H₂SO₄) were chosen. The optimum conditions of Pd(II) ion-exchange on H-clinoptilolite and mordenite were established. The sorption capacities of natural and modified zeolites towards Pd(II) in the optimum sorption conditions were determined. Furthermore, we built the rows of effectiveness of ion exchangeable cations, which are reflected acidic modification of zeolites as well as Pd(II) sorption on them in different media. We also investigated Pd(II) sorption on clinoptilolite with immobilised selective organic reagents of a Pd(II).

1. INTRODUCTION

Analysis of the literary data, dealing with the concentration and separation of palladium (II) has showed that most described methods are intended for the combined separation of platinum group ions mainly from chloride solutions. The proposed methods use expensive, not readily available sorbents, which in many cases are unstable in alkaline and strong-acid media. Therefore, study of the conditions of palladium (II) concentration and separation from nitrate and ammonia media using inexpensive, available, chemically and heat-resistant natural zeolites for elaboration of selective methods of sorption is actual.

2. EXPERIMENTAL

We used the transcarpathian clinoptilolite employed from the deposit near the village of Sokyrnytsia and transcarpathian mordenite employed from the deposit near the village of Lypcha. The chemical composition (%) of transcarpathian clinoptilolite is as follows [1]: SiO₂ – 67.29; TiO₂ – 0.26; Al₂O₃ – 12.32; Fe₂O₃ – 1.26; FeO – 0.25; MgO – 0.29; CaO – 3.01; Na₂O – 0.66; K₂O – 2.76; H₂O – 10.90, whereby the content of the main mineral is 85±6%. The chemical composition (%) of transcarpathian mordenite is as follows [2]: SiO₂ – 64.56; TiO₂ – 0.23; Al₂O₃ – 12.02; Fe₂O₃ – 0.95; FeO – 0.83; MnO – 0.1; MgO – 0.68; CaO – 3.58; Na₂O – 0.94; K₂O – 2.03; P₂O₅ – 0.07; H₂O – 13.77. Accordingly to [2] the content of the main mineral is 72±6%.

Here we describe the establishment of optimal conditions of palladium (II) concentration on natural and acid-modified zeolites: clinoptilolite and mordenite and on clinoptilolite modified by organic reagents. We also describe the elaborated methods of palladium (II) sorption in certain objects.

Investigation of Pd(II) sorption have been carried out under batch conditions. For that sorbent in the definite amount (m , g) has been introduced into Pd(II) solution with the definite concentration (C , mol/L) and was shaken during definite time (t , h) on mechanical shaker. The equilibrium of Pd(II) ion-exchange under shaking on natural clinoptilolite and mordenite is established in 6 hours, and on H-forms of both sorbent it is established in 1 hour respectively.

The contents of sorbed palladium were determined by pulse voltammetry using a linearly varying potential (PO - 5122 model 03 oscillograph) from difference between the initial concentration and the concentration of Pd(II) in filtrates, which remained in the solutions after sorption ($[C]$, M). For that purpose 20.00 mL of Pd(II) solution were pipetted and 4.00 mL of concentrated $\text{NH}_3 \times \text{H}_2\text{O}$ ($\text{pH}=11.5$) were poured to it as the background electrolyte with next dilution to full volume 25.00 mL by distilled water. Palladium (II) is reduced using 1 mol/L NH_4OH + 1 mol/L NH_4Cl as the background electrolyte at a potential of -0.720 V saturated calomel electrode (SCE).

Degree of Pd(II) separation (II) R , % was calculated by means of formula: $R = \frac{m_{\text{sorb}}}{m_{\text{init}}} \times 100\%$,

where m_{sorb} – mass of Pd(II), which was sorbed by clinoptilolite with mass m , g; m_{init} – Pd (II) mass in initial solution; $m_{\text{sorb}} = m_{\text{init}} - m_{\text{filt}}$; $m_{\text{init}} = C \times M \times V$, where M – molecular mass of Pd(II), g/mol, V_{sol} – solution volume, L; $m_{\text{filt}} = [C] \times M \times V_{\text{sol}}$.

3. RESULTS AND DISCUSSION

Mineral acids are widely used for modification of such highly silica zeolites, as clinoptilolite and mordenite. As a rule, the modification causes change of sorption characteristics of the sorbent. Therefore, the influence of zeolites treatment by different mineral acids of different concentrations has been investigated [3, 4]. Optimum concentration of each used acid has been chosen for the best palladium (II) separation by the modified zeolites. The results of the investigations are shown in Table 1. For clinoptilolite the most effective modifier is 12.0 mol/L HCl, and for mordenite 3.0 mol/L HClO_4 . Acidic treatment results in the exchange of exchange cations by hydrogen ion, and also in the partial leaching of aluminium. This influences the change of sorptive characteristics of sorbents.

Table 1

Dependence of the amounts of Pd(II) separation on the acid treatment of natural clinoptilolite ($C_{\text{Pd(II)}}=3.70 \times 10^{-4}$ mol/L; $V_{\text{sol}}=150$ mL; $t_{\text{shaking}}=0.5$ hour) and mordenite ($C_{\text{Pd(II)}}=2.16 \times 10^{-6}$ mol/L; $V_{\text{sol}}=250$ mL; $t_{\text{shaking}}=1$ hour). $d_s=0.200-0.315$ mm; $m_s=0.5$ g.

Mineral	Acid treatment	pH	Degree of Pd(II) separation, %	Sorption capacity towards Pd(II),
				$\mu\text{g/g}_{\text{sorbent}}$
Clinoptilolite	7.0 mol/L HNO_3	11.50	—	5760
	12.0 mol/L HCl			11420
	0.75 mol/L HClO_4			6980
	1.5 mol/L H_2SO_4			4970
Mordenite	1.0 mol/L HNO_3	1.50	69	—
	12.0 mol/L HCl		60	
	3.0 mol/L HClO_4		76	
	0.5 mol/L H_2SO_4		67	

As can be see from Fig. 1, for both natural and H-clinoptilolite in the batch conditions of Pd(II) ion-exchange optimum pH value is 4.5 (nitrate medium) and $\text{pH}=10.0$ (ammonium medium). In former case

a palladium exists in the form of neutral aquahydroxo complex [5] and in the later one it exists as tetraammonium complex. However, degree of palladium (II) sorption from ammonium media by H-clinoptilolite is considerably higher than the one obtained for the natural analogue.

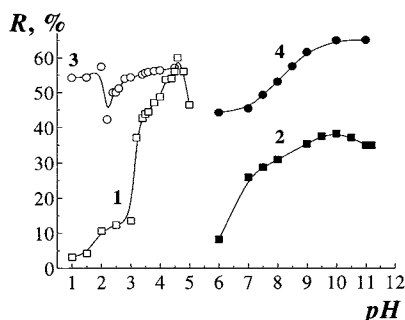


Fig. 1. Dependence of the degree of Pd(II) separation on the pH medium in batch conditions at $m_s=0.5$ g, $V_{sol}=250$ mL; $t_{shaking}=1$ hour: 1– on natural clinoptilolite ($d_s=0.355-0.500$ mm) from nitrate solutions $C_{Pd(II)}=7.68 \times 10^{-5}$ mol/L; 2– on natural clinoptilolite from ammonium solutions $C_{Pd(II)}=3.84 \times 10^{-5}$ mol/L; 3– on H-clinoptilolite ($d_s=0.200-0.315$ mm; $C_{Pd(II)}=3.84 \times 10^{-5}$ mol/L) from nitrate solutions; 4– on H-clinoptilolite from ammonium solutions.

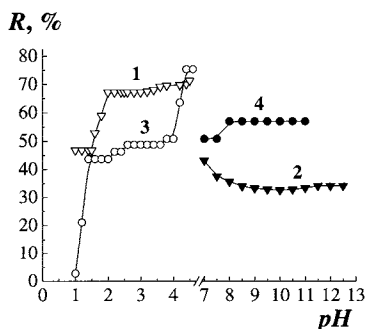


Fig. 2. Dependence of the degree of Pd(II) separation on the pH medium in batch conditions at $m_s=0.5$ g, $V_{sol}=250$ mL; $t_{shaking}=1$ hour: 1– on natural mordenite from nitrate solutions $d_s=0.200-0.315$ mm; $C_{Pd(II)}=1.50 \times 10^{-5}$ mol/L; 2– on natural mordenite from ammonium solutions $C_{Pd(II)}=6.55 \times 10^{-6}$ mol/L; $d_s=0.500-0.700$ mm; 3 – on H-clinoptilolite ($d_s=0.200-0.315$ mm; $C_{Pd(II)}=1.91 \times 10^{-5}$ mol/L) from nitrate solutions; 4– on H-clinoptilolite from ammonium solutions.

For natural and H-mordenite, as follows from Fig. 2, the optimum pH value of palladium (II) ion-exchange from nitrate medium is also 4.5. However, degree of Pd(II) separation for natural mordenite is somewhat lower. In the ammonium media the Pd(II) separation by H-mordenite is achieved in a higher degree than by natural mordenite.

So far, as water is included to the crystal structure of the sorbent, we investigated influence of the sorbent heat treatment on their sorption qualities towards palladium (II). As follows from Fig. 3, the greatest sorption value of Pd(II) on natural clinoptilolite is achieved in the interval of drying 110-120°C (loss of the physically bonded water), the similar dependence is observed for natural mordenite (Fig. 4). As a result of acid treatment of natural zeolites, the number of H_3O^+ groups increases and a number of H_2O , which sorbent can lose during heat treatment also increases respectively. It leads to a change of the sizes of entrance channels and sorbent pores. As follows from Fig. 3, the greatest degree of Pd(II) separation is observed on H-clinoptilolite roasted at 150°C, where the stronger physically adsorbed water is lost. For sorption properties of H-mordenite heat treatment appears to be not effective (Fig. 4).

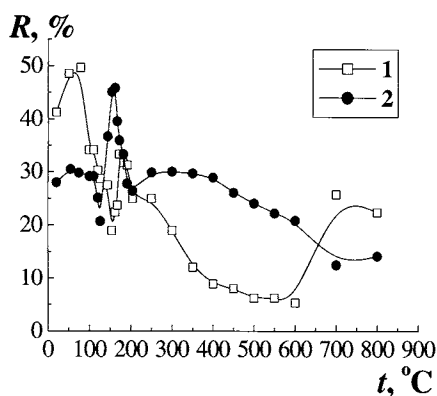


Fig. 3. Dependence of the degree of Pd(II) separation from ammonium solution on the sorbent heat treatment ($t_{\text{air}}=2.5$ hour, $\text{pH}=10.0$; $V_{\text{sol}}=250$ mL; $C_{\text{Pd(II)}}=5.48 \times 10^{-5}$ mol/L; $m_s=0.5$ g; $t_{\text{shaking}}=1$ hour: 1) by natural clinoptilolite, $d_s=0.500-0.710$ mm; 2) by H-clinoptilolite, $d_s=0.200-0.315$ mm.

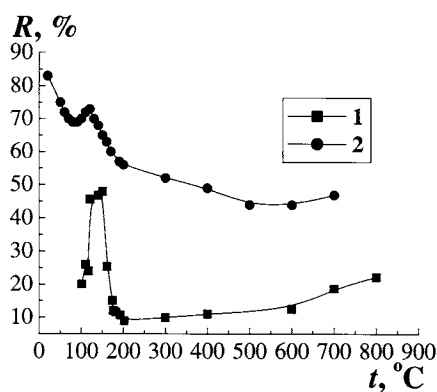


Fig. 4. Dependence of the degree of Pd(II) separation from nitrate solution on the sorbent heat treatment ($t_{\text{air}}=2.5$ hour, $\text{pH}=1.50$; $m_s=0.5$ g; $t_{\text{shaking}}=1$ hour: 1) by natural mordenite: $C_{\text{Pd(II)}}=2.42 \times 10^{-7}$ mol/L; $d_s=0.200-0.315$ mm; $V_{\text{sol}}=100$ mL; 2) by H-mordenite: $d_s=0.500-0.710$ mm; $V_{\text{sol}}=250$ mL; $C_{\text{Pd(II)}}=1.14 \times 10^{-5}$ mol/L.

Concentration and separation of palladium is often carried out from the concentrated solutions of electrolytes, in the presence of matrix components which also can sorb on a zeolite, or form complexes with the palladium ions. Therefore, we investigated the influence of the salt effect made by inorganic salts on palladium (II) sorption by natural and H-clinoptilolite. As follows from the obtained data (Fig. 5), the highest degree of the Pd(II) separation is observed at salts content less than 0.2 mol/L, at the subsequent increase of salt background the degree of palladium separation sharply decreased. It is related to the laboured migration of palladium (II) ions to the sorbent surface and, simultaneously, free access of its ions to the entrance of channels windows of clinoptilolite block. However, a competitive complexation palladium (II) with salts anions is also possible. The influence of salt background is similar for both forms of mordenite. The only exception is that satisfactory ion-exchange is achieved at salts concentration up to 0.5 mol/L.

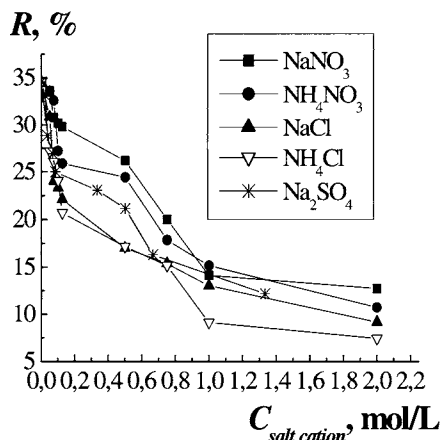


Fig. 5. Dependence of the degree of Pd(II) separation by natural clinoptilolite on concentration of inorganic salts cations. $pH=10.00$; $d_s=0.315-0.355$ mm; $V_{sol}=250$ mL; $C_{Pd(II)}=4.26 \times 10^{-5}$ mol/L; $m_s=0.5$ g; $t_{shaking}=1.5$ hour.

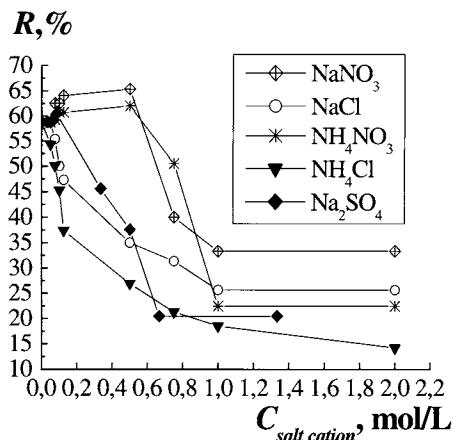


Fig. 6. Dependence of the degree of Pd(II) separation by natural mordenite on concentration of inorganic salts cations. $pH=4.00$; $d_s=0.200-0.315$ mm; $V_{sol}=250$ mL; $C_{Pd(II)}=1.14 \times 10^{-5}$ mol/L; $m_s=0.5$ g; $t_{shaking}=1$ hour.

Table 2

The influence of extraneous components on Pd(II) sorption by H-clinoptilolite. ($d_s=0.200-0.315$ mm; $pH=4.20$; $C_{Pd(II)}=4.27 \times 10^{-5}$ mol/L; $V_{sol}=250$ mL; $t_{shaking}=3$ hour; $m_s=0.5$ g.)

Ion	[Pd] : [Ion]	R, %	Ion	[Pd] : [Ion]	R, %
-	-	55.9	Fe(III)*	1:5	41.3
Pt(IV)	1:1	0	Mn(II)*	1:1	23.9
Rh(III)	1:1	8.9	Cl ⁻	1:1	39.9
Os(IV)	1:10	36.8	NO ₃ ⁻	1:500	40.9
Ir(IV)	1:0,5	31.7	SO ₄ ⁻	1:500	41.8
Ru(IV)	1:1	41.6	CO ₃ ⁻	1:1000	55.5
Au(III)	1:1	0	PO ₄ ³⁻	1:1	19.6
Ag(I)	1:1	31.7	C ₂ O ₄ ²⁻	1:1	7.1
Cu(II)	1:500	45.9	Tart ²⁻	1:1	10.6
Zn(II)	1:1	21.7	Cit ³⁻	1:1	7.1
Ni(II)	1:10	42.2	EDTA	1:1	6.2
Pb(II)	1:1	0			

As can be concluded from Table 2 the presence of Os(IV), Ni(II), Fe(III), Ru(IV) in the shown rates does not prevent the Pd(II) ion-exchange on H-clinoptilolite and Cu(II) increases the palladium (II) ion-exchange. The influence of extraneous ions on Pd(II) sorption by H-mordenite is shown in Table 3. As follows from the Table 3, platinum metals, copper and lead at contents less than 100-multiple

* at the experimental conditions these elements form sediment, however in their presence the sorption can be carried out at $pH=1.50$.

excesses prevent the palladium (II) separation on mordenite. At the same time 100-multiple excesses of extraneous anions prevent the Pd(II) concentration in a less degree. Therefore, effective Pd(II) concentration in solutions with more than 100-multiple excesses of extraneous ions is impossible.

Table 3

The selectivity of Pd(II) separation by H-mordenite. $d_s=0.200-0.315$ mm; $pH=1.50$; $V_{sol}=100$ mL; $C_{Pd(II)}=2.42 \times 10^{-7}$ mol/L; $m_s=0.5$ g; $t_{shaking}=1$ hour; $[X]:[Pd]=100:1$.

X	-	Pt(IV)	Ir(IV)	Os(VI)	Ru(IV)	Rh(IV)	Fe(III)
R, %	81	66	59	56	57	58	76
X	Cu(II)	Pb(II)	Al(III)	Mn(II)	Citrate	Tartrate	Sulphate
R, %	66	50	74	64	75	79	65

After the separation of metal ions from multicomponent solutions by sorbent an important task for the subsequent analysis is their desorption. Therefore, the desorption conditions of Pd(II) from clinoptilolite and mordenite have been investigated. Mineral acids and salts of different concentrations were used as desorbents. The best desorbents of Pd (II) from clinoptilolite are 1.5 mol/L HCl and 2.0 mol/L NaCl. Complete desorption is achieved in these cases 0.1 mol/L HCl; 0.1 mol/L and 2.0 mol/L NH_4Cl are the best Pd(II) desorbents from mordenite. Such regularity can be explained by the complexation of Pd^{2+} with Cl^- ions as well as by the greater relating of the Na^+ -ion to Pd^{2+} in the process of ionic exchange.

The sorption capacity is the basic characteristic of the sorbent. The values of sorption capacity of natural and H-forms for both zeolites in the optimum conditions of Pd(II) sorption from ammonium and nitrate solutions are resulted in a Table 4. As follows from Table 4 natural forms of the clinoptilolite sorbs the most amount of Pd (II) from an ammonium medium, however its sorption ability is low enough. Natural mordenite in a nitrate medium has 2.4-times higher sorption capacity than natural clinoptilolite. Comparison of the sorption properties of natural and H-clinoptilolite clearly shows, that sorption capacity of both sorbent towards Pd(II) is higher in ammonium medium, however in the case of H-form it is 18-times greater. Sorption capacity of H-clinoptilolite towards Pd(II) in nitrates solutions is 3.6-times greater, than of its natural analogue, but is more than 3-times less, than in ammonium medium. Sorption capacity of H-mordenite at $pH=4.5$ is substantially higher, though sorption from more acidic medium takes place from more concentrated Pd(II) solution. It should be noted that the sorption capacity of H-mordenite towards Pd(II) ($pH=4.50$) is 2.8-times higher, than in natural mordenite. However, sorption capacity of H-clinoptilolite is almost 2-times greater than H-mordenite.

The rows of effectiveness of ion exchangeable cations of sorbent under the acid modification of clinoptilolite by 12.0 mol/L HCl and mordenite by 3.0 mol/L of $HClO_4$ are built: $K^+ > Na^+ > Mg^{2+} > Fe^{3+} > Ca^{2+} > Mn^{2+}$ and $Ca^{2+} > Na^+ \approx K^+ > Mg^{2+} > Fe^{3+} > Fe^{2+} > Mn^{2+}$ accordingly. The effectiveness of ion-exchangeable cation of zeolites was calculated as part from the summ of concentrations of all determined exchangeable cations in μg -equiv/ml. The carried out investigations showed that K^+ is basic exchange cation while treating the clinoptilolite by 12.0 mol/L HCl, and Ca^{2+} is the most preferable while treating the mordenite by 3.0 mol/L $HClO_4$ and it is ineffective to obtain the H-clinoptilolite. In both samples considerable dealumination under acid modification take place. It is the principal reason of growth of sorption ability of sorbents H-form, because H^+ has low ion exchangeable efficiency. The rows of effectiveness of ion exchangeable cations of sorbent under palladium (II) sorption by natural clinoptilolite have been obtained: $Na^+ > Ca^{2+} > Mg^{2+} > Fe^{2+} > Al^{3+} > K^+$ ($pH=4.2$) and $Ca^{2+} > K^+ > Na^+ > Mg^{2+} > Al^{3+}$ ($pH=10.0$) and by H-clinoptilolite: $Na^+ > Ca^{2+} > H^+ > Mg^{2+} > K^+ > Al^{3+}$ ($pH=4.2$) and $Ca^{2+} > K^+ > Mg^{2+} > Na^+ > Al^{3+}$ ($pH=10.0$). For natural and H-mordenite those rows are similar. The effectiveness of exchangeable cation was calculated as part from the summ of amount of all determined ion-exchangeable cations in μg -equiv/g of sorbent. Consequently, Na^+ and Ca^{2+} are basic

exchangeable cations of the investigated zeolites at palladium (II) sorption from nitrate media, and K^+ and Na^+ – from ammonium media.

Table 4

Sorption capacity of natural and H-clinoptilolite, modified by 12.0 mol/L HCl and natural and H-mordenite, modified by 3.0 mol/L $HClO_4$. $t_{stabilizing}=2.5$ hour.

Concentration of Pd(II), mol/L	d_{sorb} , mm	Volume of Pd(II) solution, mL	pH	Sorbent	Sorption capacity, $\mu g/g$
1.36×10^{-4}	0.355-0.500	250	4.20	Nat. clinoptil.	977
1.36×10^{-4}	0.355-0.500	250	10.00	Nat. clinoptil.	2404
1.36×10^{-4}	0.200-0.315	250	4.20	H-clinoptilolite	3440
4.35×10^{-4}	0.200-0.315	150	11.50	H-clinoptilolite	11420
4.35×10^{-4}	0.200-0.315	150	11.50	Nat. clinoptil.	635
1.19×10^{-4}	0.200-0.315	250	4.50	Nat. mordenite	2330
1.19×10^{-4}	0.200-0.315	250	1.50	Nat. mordenite	600
1.19×10^{-4}	0.200-0.315	250	4.50	H-mordenite	6480
4.86×10^{-4}	0.200-0.315	100	1.50	H-mordenite	4190

The methods of sorption of Pd(II) microamounts ($C_{Pd(II)}=2.42 \times 10^{-7}$ mol/L) in model solutions containing total 100-multiple excesses of the following ions: Pt(IV), Ir(IV), Os(VI), Ru(IV), Rh(IV), Fe(III), Mn(II), Cu(II), Pb(II), Al(III) have been elaborated. The results of experiment are presented in Table 5.

Table 5

Results of Pd(II) sorption from model solutions by H-mordenite and its desorption by 0.1 mol/L HCl ($n=3$; $\alpha=0.95$)

Sample number	Pd(II) : X_{total}	R_{sorb} , %	R_{des} , %	$S_{r,sorb}$
1	1:100	66	92	0.07
2	1:95	66	90	0.09
3	1:90	67	92	0.05

The Pd(II) concentration by natural clinoptilolite in wastes of jeweller production have been carried out with its further determination by pulse voltammetry using a linearly varying potential. The elaborated method is incultated at the Lviv state jeweller plant. The results of experiment are shown in Table 6.

Table 6

Content of Pd(II) separated from jeweller industry wastes after concentration on clinoptilolite ($n=3$; $\alpha=0.95$)

Sample number	Sample volume, L	Content of Pd(II), mg; $x \pm \frac{t_{\alpha} S_r}{\sqrt{n}}$	S_r
1	3.0	8.0 ± 1.4	0.07
2	2.5	18.5 ± 4.1	0.09
3	2.8	37.2 ± 4.6	0.05

In order to increase the selectivity of zeolite sorption towards Pd(II) ions, we studied the possibility to modify the clinoptilolite by specific organic reagents using immobilisation and grafting them to

sorbent. As a reagents 1-(2-piridilazo)-2-naphthol (PAN), chrome azurol S (CAS), acetylaceton (AA) and dioxime acetylaceton (DAA) were tested. Immobilisation of PAN and CAS was carried out by evaporation, and grafting of AA and DAA by 3 stage organic syntheses. Palladium sorption on the modified sorbent takes place due to the reaction of its complexation with the groups of reagent, adsorbed by only on the sorbent surface. So far as a reagent has enough largeness, it blocks channels for the Pd(II) access. As follows from the Table 7 H-form of sorbent modified by PAN from hexane, demonstrate the largest sorption capacity. The resulted data of sorption of chloride solutions of Pd(II) on clinoptilolite with grafted groups of acetylaceton and dioxime acetylaceton are presented in Table 8. As follows from the results of investigation, sorption of Pd(II) from its chloride solutions on mentioned above modified sorbents takes place effectively. It is a positive effect, because in practice, most industrial wastes contain chlorides complexes of Pd(II) which do not sorb on natural and H-modified clinoptilolite, because these sorbents are cationexchangers. Colour of samples with a sorbed palladium considerably differs from the initial ones and that can be used for half-quantity determination of palladium in the industrial wastes, as a test system. Compounds of palladium with these grafted reagents have the brightly yellow colour.

Table 7

Sorption capacity of natural and H- and clinoptilolite modified by PAN CAS in batch sorption conditions. $C_{Pd(II)}=3.49 \times 10^{-4}$ mol/L; $pH=2.7$; $d_s=0.200-0.315$ mm; $V_{sol}=150$ mL; $m_s=0.5$ g; $t_{shaking}=2.5$ hour.

Reagent content on sorbent surface, mg/g	0.125 PAN (hexan)	0.5 PAN (hexan)	0.125 PAN (chl.)	0.5 PAN (chl.)	0.27 CAS (ethanol)	1.08 CAS (ethanol)
Sorption capacity, $\mu\text{g/g}$ (Nat-clin)	3105	3340	3080	3215	3090	3220
Sorption capacity, $\mu\text{g/g}$ (H-clin)	3110	3345	3085	3215	3090	3220

Table 8

Sorption value of different forms of palladium(II) on H-clinoptilolite, with the grafted groups of acetylaceton (A, 0.21 mmol/g) and dioxime acetylaceton (B, 0.17 mmol/g) depending on the conditions of sorption.

No	$C_{Pd(II)}$, mg/mL	V_{sob} , mL	pH	t_{sorp} , hour	m_{ss} , g	a , mg/g	
A	1	0.0150	75.00	3.00	4	4.99	
	2	0.1500	75.00	2.65	2.75	0.150	20.22
	3	0.7500	20.00	2.75	4.75		30.41
B	1	0.0150	75.00	3.00	4	0.150	2.09
	2	0.1500	75.00	2.65	2.75	0.150	24.55
	4	0.7500	20.00	2.75	4.75	0.100	21.66

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