



## Studies of removal of palladium(II) ions from chloride solutions on weakly and strongly basic anion exchangers

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### ABSTRACT

Palladium and its compounds find wide application in industry as a catalytic agent in different manufacture processes. Recovery of precious metals from industrial wastes is difficult and time consuming but in spite of these disadvantages it becomes profitable. Palladium(II) ions sorption from various chloride solutions of the composition: 0.1–6.0 M HCl–0.00056 M Pd(II), 1.0 M ZnCl<sub>2</sub>–0.1 M HCl–0.00056 M Pd(II), 1.0 M AlCl<sub>3</sub>–0.1 M HCl–0.00056 M Pd(II) on the weakly and strongly basic anion exchangers (Varion ATM, Varion ADM and Varion ADAM) was discussed. The sorption research of Pd(II) ions on these resins was carried out by means of static and dynamic methods. The dynamic processes were applied in order to determine the breakthrough curves of Pd(II) ions. Moreover, the working ion-exchange capacities as well as the weight and bed distribution coefficients were determined from the Pd(II) breakthrough curves. The recovery factors of Pd(II) ions (% R) depending on the phase contact time were obtained by means of static methods. The highest ion-exchange capacities for the 0.1–6.0 M HCl–0.00056 M Pd(II) systems were obtained for the weakly basic ion-exchange resin Varion ADAM.

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### 1. Introduction

Palladium is one of the noble metals which can catalyze many chemical reactions. Therefore palladium and its compounds find a wide application in various branches of industry. To improve catalytic properties of palladium catalyst (hardness of palladium alloys and mechanical resistance) copper, ruthenium and rhodium are added. Moreover, silver, gold and rhodium additives cause increasing corrosion resistance of palladium catalysts. The excellent chemisorption, resistance to oxidation at high temperature and selective activity towards reactants make palladium catalysts very effective. The forms (homogeneous, heterogeneous and colloidal) of palladium catalysts and the metal particle size of supported catalysts are the important factors affecting catalytic reaction. Supported catalysts of palladium can be produced by means of sol–gel or impregnating methods. Owing to these methods pure and of suitable porosity catalytic materials with the surface developed at low temperature can be obtained. This type of catalysts is also resistant to catalyst deactivation, sintering and poisoning [1].

Palladium catalysts find application in hydrogenation, hydrochlorination and hydrogenolysis processes [2–9]. Moreover, palladium catalysts can be used in oxidation reactions [10,11].

Because of increasing application of palladium in industry as well as in three-way catalyst and depleted sources of this metal, ion-exchange methods become useful for removal of palladium from spent catalysts and automobile catalytic converters.

Ion-exchange methods have been developed for most of the PGM metals and are based on differences in the affinity of similar complexes of noble metals towards resins. Various types of ion-exchange resins used in removal of noble metal ions have usually large ion-exchange capacities, which allow to concentrate metals. The concentration process of noble metals is necessary due to the fact that the waste materials contain precious metals of low concentration. Moreover, this method is quick and offers separation of noble metal ions from variety of other ions [12].

Numerous anion-exchange resins for palladium(II) ions are known [13,14]. They are characterized by high selectivity and high ion-exchange capacities for noble metal ions.

Strong base anion-exchange resins derive their functionality from quaternary ammonium exchange sites. The two main groups of strongly basic anion-exchange resins are Type 1 and Type 2, depending on the type of amine used during the chemical activation process. Type 1 anion resins have three methyl groups whereas

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in Type 2 an ethanol group replaces one of the methyl groups. Type 1 resins are more difficult to regenerate and they swell more from the chloride form to the hydroxide form than Type 2 ones. They are more resistant to high temperatures and can be used in high alkalinity. Type 1 resins are suitable for total anion removal in the case of all types of waters, Type 2 resins can be also applied for removal of all anions, but they are less effective in removing silica and carbon dioxide from waters. The best results can be obtained using the resins of Type 2 for anions removal from the waters containing free mineral acids, chlorides and sulfates.

Weakly basic anion-exchange resins contain polyamine functional groups. These weakly ionized resins can be regenerated efficiently by sodium hydroxide (nearly stoichiometric amount of base) which restore the exchange sites to the free base form. These type of resins find application in the removal of anions from the waters containing high concentration of sulfates or chlorides.

Gaita and Al-Bazi [15] used the weakly and strongly basic anion-exchange resins Amberlite IRA-93, Amberlite IRA-68 and Amberlite IRA-400 for selective separation of palladium, platinum and rhodium from the solutions obtained by leaching automobile catalytic converters. The macroporous anion exchanger Amberlite IRA-93 with dimethylamine functional groups and polystyrene–divinylbenzene matrix was the most efficient for the removal of palladium ions. Rhodium(III), palladium(II) and platinum(II) were desorbed from the anion exchanger bed by means of 6 M hydrochloric acid, 1% ammonia and 5% ammonia, respectively. Separation of palladium from platinum can be achieved either by reduction to the metallic state or by precipitation of  $(\text{NH}_4)_2\text{PdCl}_4$  and  $(\text{NH}_4)_2\text{PtCl}_6$  with the HCl solution.

Russian scientists applied anion and amphoteric exchangers for palladium(II) sorption from chloride solutions obtained from spent catalysts. The amphoteric ion exchangers VP-14K and ANKF-5 possess lower exchange capacity values than the anion exchanger AN-251M due to the fact that the acidic groups in the aminophosphorylic resin ANKF-5 facilitate the coordinative interactions between palladium ions and exchanger amino groups. The basic character of functional groups supports the increase of coordination and sorption ability of AN-251M. The pyridine-carboxylic resin VP-14K possesses also basic groups but this combination does not favour their active participation in the exchange process. Moreover, the amphoteric resin VP-14K possesses a deficient porosity of polymeric structure [16].

This paper describes the properties of strongly (Varion ADM and Varion ATM) and weakly (Varion ADAM) basic anion-exchange resins in sorption of palladium(II) ions from the chloride (0.1–6.0 M HCl–0.00056 M Pd(II)) solutions. The influence of macrocomponent (1.0 M  $\text{ZnCl}_2$  and 1.0 M  $\text{AlCl}_3$ ) addition on palladium(II) recovery from the 0.1 M HCl solution was also investigated.

Palladium from waste materials can be separated in hydrometallurgical processes. Waste materials are treated (leaching process) using a suitable agent or a mixture of agents. Palladium can be brought to the solutions using, e.g. mixture of nitric acid, sulfuric acid and hydrochloric acid (HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ); mixture of hydrochloric acid and chlorine (HCl– $\text{Cl}_2$ ) or mixture of hydrochloric acid and sodium chloride (HCl–NaCl). Palladium occurs in chloride solutions usually in the Pd-chlorocomplexes. Chloride solutions are very common therefore the recovery of Pd(II) ions from these solutions is very important.

## 2. Materials and methods

### 2.1. Preparations of solutions

The aqueous Pd (II) stock solution was obtained from solid  $\text{PdCl}_2$  (>99.99%, POCh, Poland) and standardized HCl solutions in the amounts required for maintaining  $\text{H}^+$  concentration at 0.1 M.

Working solutions of palladium ions (0.00056 M Pd(II)) were prepared by dilution with HCl in order to obtain a desired value  $\text{H}^+$  concentration. Appropriate amounts of  $\text{AlCl}_3$  and  $\text{ZnCl}_2$  (POCh, Poland) were dissolved in 0.1 M hydrochloric acid to obtain Pd(II) working solutions with the macrocomponents (1.0 M  $\text{AlCl}_3$  and 1.0 M  $\text{ZnCl}_2$ ).

The other reagents were of analytical grade from POCh (Poland).

### 2.2. Characteristics of anion exchangers

Macroporous Varion ATM, Varion ADM, Varion ADAM resins were used for sorption studies. Important physical and chemical properties of these resins are presented in Table 1.

### 2.3. Determination of the recovery factors

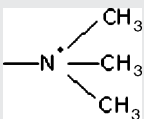
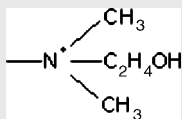
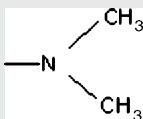
Anion exchangers were dried at room temperature. 0.5 g of the resin was put into the conical flask and 50  $\text{cm}^3$  of the solution was added. The flask was shaken mechanically using a 358S laboratory shaker (Elpin type, Poland) from 1 to 240 min at 298 K. Then the raffinate was separated from the ion exchanger by filtration and the concentration of Pd(II) ions was determined using the spectrophotometric iodide method.

The recovery factor (% R) of Pd(II) was calculated from the following equation:

$$\%R = \frac{c_w}{c_0} \times 100 \quad (1)$$

where  $c_w$  is the amount of Pd(II) adsorbed calculated as the difference between the initial concentration ( $c_0$ ) and the concentration after sorption in the aqueous solutions.

**Table 1**  
Characteristics of the anion exchangers

Description	Varion ATM	Varion ADM	Varion ADAM
Structure Type	Macroporous Strongly basic	Macroporous Strongly basic	Macroporous Weakly basic
Functional groups			
Ionic form as shipped	$\text{Cl}^-$	$\text{Cl}^-$	$\text{Cl}^-$
Matrix		Polystyrene–divinylbenzene	Polyacrylate
Bead size (mm)	0.315–1.25	0.315–1.25	0.315–1.25
Operating pH range	0–14	0–14	0–14
Total exchange capacity (meq/ $\text{cm}^3$ )	1.2	1.2	1.2

#### 2.4. Determination of breakthrough curves for palladium(II) ions

The dynamic processes were applied in order to determine the breakthrough curves of Pd(II) ions. The columns used in the dynamic method were filled with the proper water-swollen anion exchanger in the amount of 10 cm<sup>3</sup>. Then the solutions of palladium(II) ions of the concentration 0.00056 M were passed through the anion exchanger bed at the rate of 0.4 cm<sup>3</sup>/min. The eluate was collected in the fractions and the content of palladium(II) ions was determined.

The working capacities, the weight and bed distribution coefficients were calculated from the Pd(II) breakthrough curves.

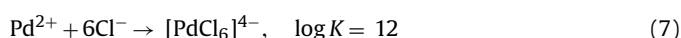
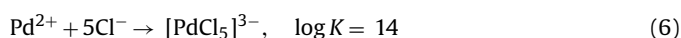
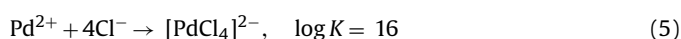
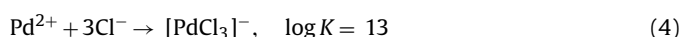
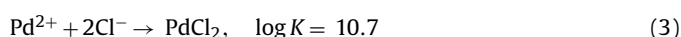
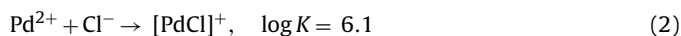
#### 2.5. Analytical procedure

Palladium(II) concentration in the eluate was determined using the spectrophotometric iodide method. In the presence of an excess of potassium iodides, palladium(II) ions form the red-brown complex [PdI<sub>4</sub>]<sup>2-</sup>. Commonly, ascorbic acid as a reducing agent is added to the solution in order to avoid oxidation of iodides by oxygen from the air. Absorbance was measured at 408 nm in a 1-cm cell against water as the reference [17].

### 3. Results and discussion

Like the other transition metals the PGMs form a range of complexes with a variety of different ligands. Aqueous chloride solutions are a cost-effective medium in which all the PGMs can be brought into solutions and concentrated. All of the PGMs in their tetravalent oxidation state form hexachlorocomplex anions ([MCl<sub>6</sub>]<sup>2-</sup>, where M are the metals like Pd, Pt, Ir, Ru, Rh and Os) predominantly in strong chloride solutions.

Palladium can form stable chlorocomplexes such as [PdCl]<sup>+</sup>, PdCl<sub>2</sub>, [PdCl<sub>3</sub>]<sup>-</sup> and [PdCl<sub>4</sub>]<sup>2-</sup> in the acidic chloride medium:



At 0.1 M Cl<sup>-</sup> and higher, the predominant species in solutions is [PdCl<sub>4</sub>]<sup>2-</sup>. Due to the fact that palladium complexes occur in the anionic form they are capable of undergoing anion-exchange reactions.

Anion exchangers used in this work fall into two categories such as strong (Varion ADM and Varion ATM) and weak (Varion ADAM) base anion exchangers. Strong bases are protonated much more readily than weak bases and this means that they can behave as ion exchangers at relatively low acid concentration. Weak base anion exchangers protonate significantly, and therefore behave as ion exchangers, only at high acid concentration.

The anionic species of palladium ([PdCl<sub>4</sub>]<sup>2-</sup> and [PdCl<sub>3</sub>]<sup>-</sup>) are more favourable than cationic ones ([PdCl]<sup>+</sup> and Pd<sup>2+</sup>) or the non-ionic form (PdCl<sub>2</sub>) for anion exchanges. The Pd-chlorocomplexes form ion pairs with the anion-exchange resins. The tendency of the anion exchanger for the formation of PGM-chlorocomplexes is as follows: [MCl<sub>6</sub>]<sup>2-</sup> > [MCl<sub>4</sub>]<sup>2-</sup> >> [MCl<sub>6</sub>]<sup>3-</sup> > aqua species [18].

Palladium(II) and base metal-complexes may be bound to the resins through solvation or ion-exchange mechanisms. When the resin has one or more coordinate atoms in its functional group

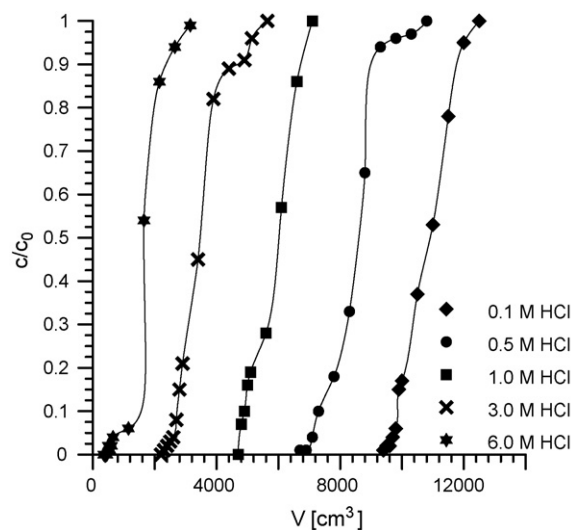
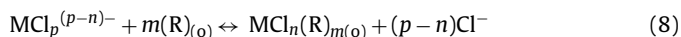


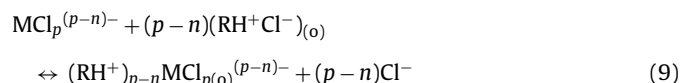
Fig. 1. Influence of HCl concentration on the breakthrough curves of Pd(II) in the 0.1–6.0 M HCl systems for the weakly basic anion exchanger Varion ADAM.

chloride ligands from the palladium complexes can be replaced by bonding using a solvent mechanism according to the equation:



where M is the metal such as Pd, Zn, Al, etc., R is a resin, and (o) represents a stationary phase (resin).

In the second mechanism the system requires an acid environment to protonate the organic reagent. In acidic media, palladium complexes are bonded through the protonated nitrogen of the amine group of the resins:



The Varion ADM, Varion ATM and Varion ADAM resins selected in this study contain coordinating N atoms and amino groups which are readily associated with H<sup>+</sup> in acid solutions. During the pre-concentration of palladium(II) ions, the Varion resins may form coordinate complexes with these anions by replacing the chloride ions or forming ion pair compounds by association through the chloride ions in the complex, or both processes may occur at the same time [19–22].

As follows from the research results presented in Tables 2–4 and Figs. 1–10, the working ion-exchange capacities ( $C_r$ , g/cm<sup>3</sup>) as well as the weight ( $\lambda$ ) and bed ( $\lambda'$ ) distribution coefficients of Pd(II) ions for anion exchangers of various basicity depend on hydrochloric acid concentration in the 0.1–6.0 M HCl–0.00056 M Pd(II) system.

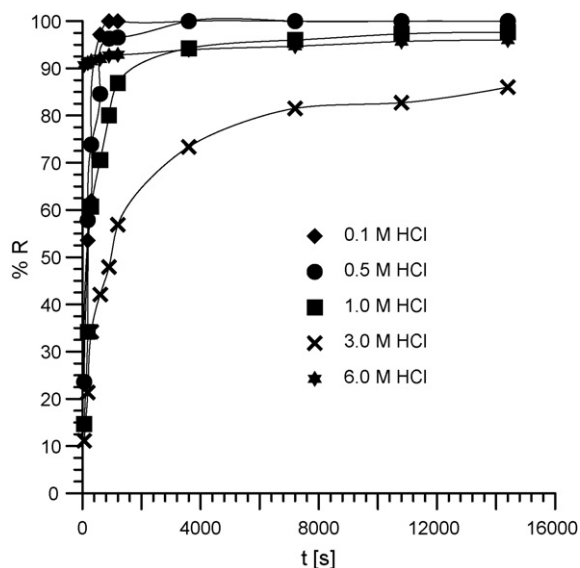
The values of working ion exchange capacities ( $C_r$ , g/cm<sup>3</sup>) for the weakly basic anion exchanger of polyacrylate matrix, Varion ADAM,

Table 2

Working ion-exchange capacities compared with the weight and bed distribution coefficients of Pd(II) ions in the 0.1–6.0 M HCl system determined for the weakly basic anion exchanger

Model system	Varion ADAM <sup>a</sup>		
	Working ion-exchange capacities, $C_r$ (g/cm <sup>3</sup> )	Weight distribution coefficients, $\lambda$	Bed distribution coefficients, $\lambda'$
0.1 M HCl	0.0930	2680.1	1090.8
0.5 M HCl	0.0650	2111.5	859.4
1.0 M HCl	0.0460	1477.1	601.2
3.0 M HCl	0.0210	359.7	146.4
6.0 M HCl	0.0030	401.0	163.2

<sup>a</sup>  $d_z = 0.4070$  g/cm<sup>3</sup>,  $d_z$  is the density of Varion ADAM.



**Fig. 2.** Influence of HCl concentration on the recovery factors of Pd(II) in the 0.1–6.0 M HCl–0.00056 M Pd(II) systems for the weakly basic anion exchanger Varion ADAM.

decrease with the increasing hydrochloric acid concentration in the 0.1–6.0 M HCl solutions, as presented in Fig. 1.

The differences in the values of working ion-exchange capacities ( $C_r$ , g/cm<sup>3</sup>) as well as in the distribution coefficients (weight ( $\lambda$ ) and bed ( $\lambda'$ )) for the weakly basic Varion ADAM are depicted in Table 2.

For the strongly (Varion ATM and Varion ADM) and the weakly (Varion ADAM) basic anion exchangers the distribution coefficients start at a maximum and drop with the increasing hydrochloric acid strength due to the increasing competition between Cl<sup>-</sup> and metal-complex anions. These competitions lead to a reduced capacity, too. Moreover, as for Varion ADAM capacity, its functional groups contain N donor atom which can be protonated. Higher values of capacity for Varion ATM compared to Varion ADM could be explained by different substituents linked to the nitrogen atom. For Varion ATM the interaction of palladium(II) complexes with the resin is probably due not only to the ion exchange but also to the presence of the hydroxyl group which contributes to the palladium retention. Moreover, based on the hard and soft acids and bases theory (HSAB), the ion exchangers of the functional groups containing S, O or N donor atoms interact strongly with the soft acids like precious metal ions therefore the hydroxyl group as a coordination activity group is capable of coordination with the palladium(II)-chlorocomplexes.

The calculated values of the working capacities for Varion ADAM are higher compared to Varion ADM and Varion ATM. The dif-

**Table 3**

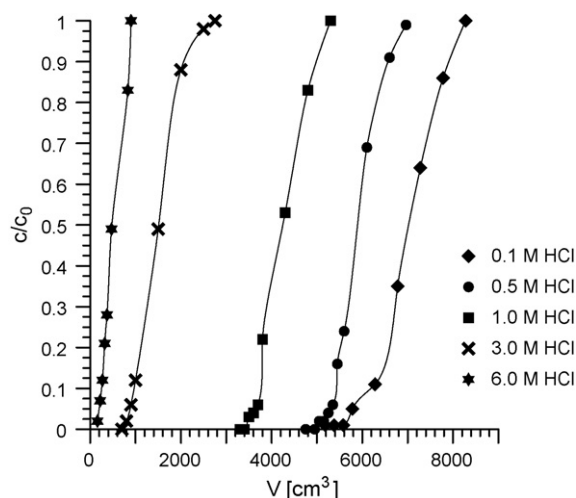
Working ion-exchange capacities compared with the weight and bed distribution coefficients of Pd(II) ions in the 0.1–6.0 M HCl system determined for the strongly basic anion exchangers

Model system	Varion ADM <sup>a</sup>			Varion ATM <sup>b</sup>		
	$C_r$ (g/cm <sup>3</sup> )	$\lambda$	$\lambda'$	$C_r$ (g/cm <sup>3</sup> )	$\lambda$	$\lambda'$
0.1 M HCl	0.0480	2001.8	649.4	0.0490	2214.0	701.4
0.5 M HCl	0.0380	1631.3	529.2	0.0450	1858.9	588.9
1.0 M HCl	0.0290	1255.9	407.4	0.0320	1339.0	424.2
3.0 M HCl	0.0050	417.4	135.4	0.0050	475.4	150.6
6.0 M HCl	0.0010	127.6	41.4	0.0010	149.0	47.2

$C_r$  (g/cm<sup>3</sup>), working ion-exchange capacities;  $\lambda$ , weight distribution coefficient;  $\lambda'$ , bed distribution coefficient;  $d_z$ , density of anion exchangers.

<sup>a</sup>  $d_z = 0.3244$  g/cm<sup>3</sup>.

<sup>b</sup>  $d_z = 0.3168$  g/cm<sup>3</sup>.

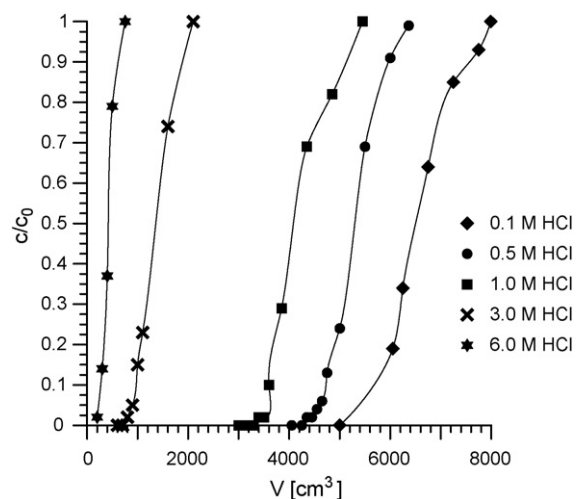


**Fig. 3.** Influence of HCl concentration on the breakthrough curves of Pd(II) in the 0.1–6.0 M HCl system for the strongly basic anion exchanger Varion ATM.

ferences in the values of the working ion-exchange capacities of strongly basic styrenedivinylbenzene anion exchangers (Varion ADM and Varion ATM) and weakly basic polyacrylate anion exchanger (Varion ADAM) can be caused by different types of the skeleton. Not only tertiary amine groups present in the surface layer of the anion exchangers but also those inside the skeleton are responsible for sorption of Pd(II) complexes because their access is facilitated at low HCl concentration.

The fundamental difference in basicity of anion-exchange resins determines the way in which the complex anions are recovered or re-exchanged. In the case of weakly basic exchangers, the changes of value of working capacities ( $C_r$ ) can be reversed by simply reducing the acid concentration, thereby deprotonating the base. Reducing the acid concentration does not reverse the protonation of strong bases significantly and so recovery of the complex anions is achieved partially by introducing large quantities of competing anions.

As follows from the static studies in the 0.1–6.0 M HCl system for the weakly basic anion exchanger, the equilibrium between the aqueous phase and the anion exchanger was achieved at a contact time of 3600 s for 0.1 and 0.5 M HCl. In the range 1.0–3.0 M of hydrochloric acid the equilibrium between both phases is achieved after a longer period of time. The shape of the curves indicates



**Fig. 4.** Influence of HCl concentration on the breakthrough curves of Pd(II) in the 0.1–6.0 M HCl systems for the strongly basic anion exchanger Varion ADM.

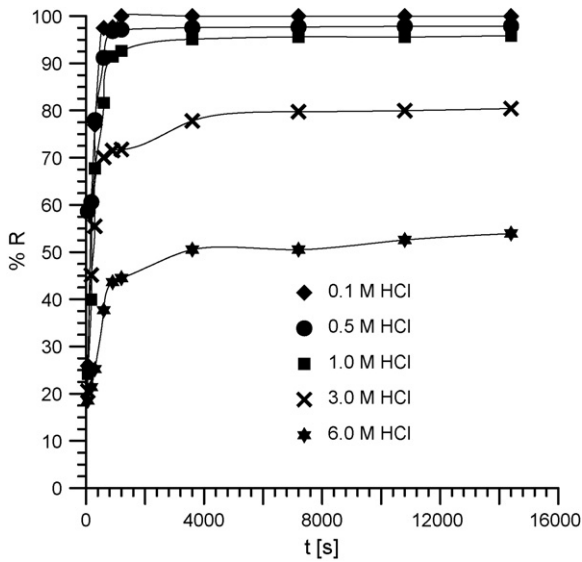


Fig. 5. Influence of HCl concentration on the recovery factors of Pd(II) in the 0.1–6.0 M HCl–0.00056 M Pd(II) systems for the strongly basic anion exchanger Varion ATM.

that recovery factors (% R) of Pd(II) ions depend on the phase contact time and decrease insignificantly with the hydrochloric acid concentration increase (Fig. 2). For 0.1 and 0.5 M HCl the recovery factors achieve very high values approximately equal to 100% in the range from 1200 to 14,400 s of phase contact time. A similar dependence of the working ion-exchange capacities and the distribution coefficients of Pd(II) ions on the hydrochloric acid concentration in the 0.1–6.0 M HCl system was obtained for the strong base anion exchangers, Varion ADM and Varion ATM (Table 3). The breakthrough curves of Pd(II) ions for Varion ATM and Varion ADM are presented in Figs. 3 and 4, respectively.

The recovery factors of Pd(II) ions in the 0.1–6.0 M HCl system for the strongly basic anion exchangers also depend on hydrochloric acid concentration. Making comparison between the recovery factors of Pd(II) ions for the weakly and strongly basic anion exchangers values of more substantial change can be observed for

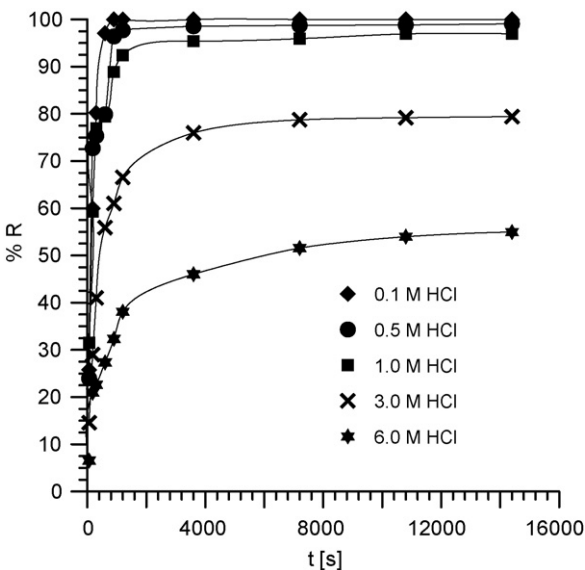


Fig. 6. Influence of HCl concentration on the recovery factors of Pd(II) in the 0.1–6.0 M HCl–0.00056 M Pd(II) systems for the strongly basic anion exchanger Varion ADM.

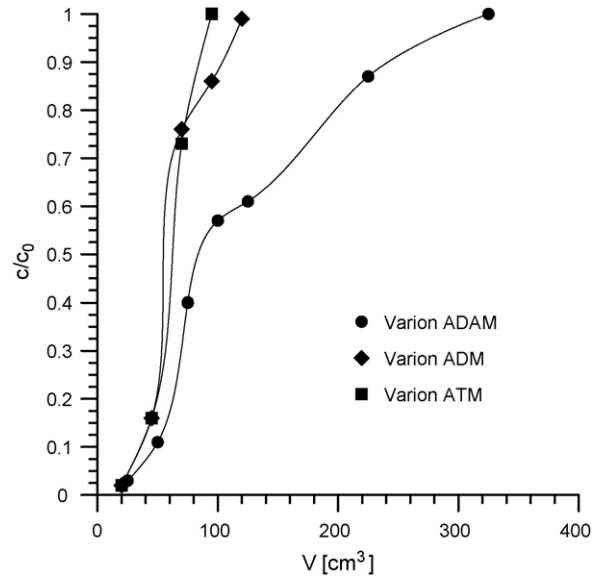


Fig. 7. Breakthrough curves of Pd(II) ions in the 1.0 M ZnCl<sub>2</sub>–0.1 M HCl system for the anion exchangers of various basicity.

the strongly basic anion exchangers. The recovery factors for Pd(II) ions depending on the phase contact time in the 0.1–6.0 M HCl system for the strong base anion exchangers for Varion ATM and Varion ADM are shown in Figs. 5 and 6, respectively.

Table 4

Working ion-exchange capacities compared with the weight and bed distribution coefficients of Pd(II) ions in the 1.0 M ZnCl<sub>2</sub>–0.1 M HCl and 1.0 M AlCl<sub>3</sub>–0.1 M HCl systems determined for the weakly and strongly basic anion exchangers

Type of resins	Model systems					
	1.0 M ZnCl <sub>2</sub> –0.1 M HCl			1.0 M AlCl <sub>3</sub> –0.1 M HCl		
	C <sub>r</sub> (g/cm <sup>3</sup> )	λ	λ'	C <sub>r</sub> (g/cm <sup>3</sup> )	λ	λ'
Varion ADAM	0.00025	19.4	7.8	0.0175	841.8	338.4
Varion ATM	0.00020	17.7	5.6	0.0110	522.2	169.4
Varion ADM	0.00020	15.1	4.9	0.0110	557.4	176.6

C<sub>r</sub> (g/cm<sup>3</sup>), working ion-exchange capacities; λ, weight distribution coefficient; λ', bed distribution coefficient.

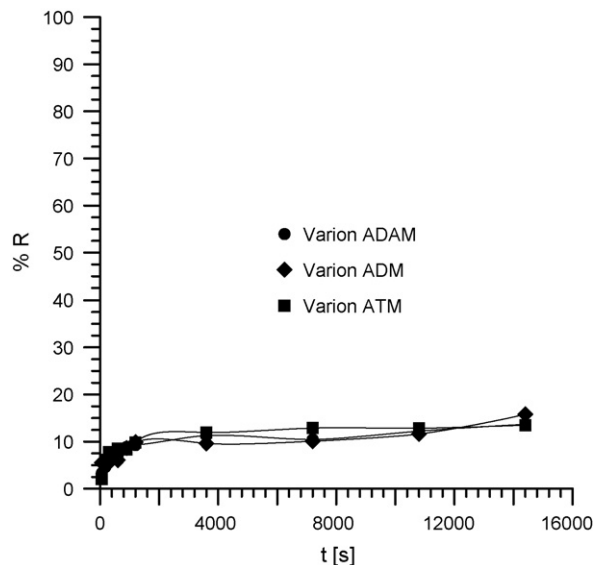


Fig. 8. Influence of phase contact time on the recovery factors of Pd(II) ions from the 1.0 M ZnCl<sub>2</sub>–0.1 M HCl system for the anion exchangers of various basicity.

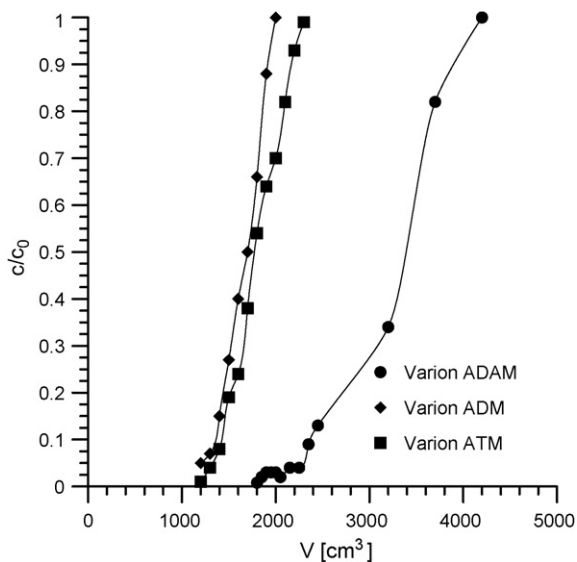


Fig. 9. Breakthrough curves of Pd(II) ions in the 1.0 M  $\text{AlCl}_3$ -0.1 M HCl system for the anion exchangers of various basicity.

The static studies carried out in chloride solutions indicate that the weakly basic anion exchanger of the functional diamine groups and the polyacrylic matrix can find practical application in technologies of Pd(II) recovery from the industry scrap materials due to high values of Pd(II) recovery factors when the equilibrium is reached.

The strong base anion exchangers are also suitable for recovery of Pd(II) ions but from diluted solutions where concentrations of chlorides are low. At higher concentration of hydrochloric acid, the values of recovery factors are low and the removal of Pd(II) ions is not complete and satisfactory.

Due to the fact that zinc is one of the commonly used reducing agents in hydrometallurgy processes and aluminium chloride mixed with hydrochloric acid is used for leaching of PGM metals, the influence of these microcomponents addition was examined.

In the case of removal of Pd(II) ions microquantities from the 1.0 M  $\text{ZnCl}_2$ -0.1 M HCl solution on the anion exchangers of var-

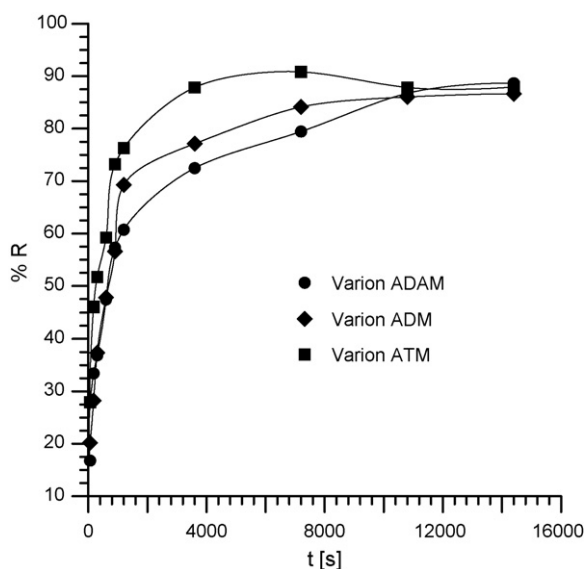


Fig. 10. Influence of phase contact time on the recovery factors of Pd(II) ions from the 1.0 M  $\text{AlCl}_3$ -0.1 M HCl system for the anion exchangers of various basicity.

ious basicity, the values of working ion-exchange capacities are very low, which is due to competitive sorption of  $[\text{ZnCl}_4]^{2-}$  complexes towards  $[\text{PdCl}_4]^{2-}$ . The ion-exchange capacities and the distribution coefficients calculated from the breakthrough curves of Pd(II) ions from the 1.0 M  $\text{ZnCl}_2$ -0.1 M HCl solution compared with the same parameters for 1.0 M  $\text{AlCl}_3$ -0.1 M HCl for all examined resins are shown in Table 4. The breakthrough curves of Pd(II) ions for the weakly and strongly basic anion exchangers in the 1.0 M  $\text{ZnCl}_2$ -0.1 M HCl solution are presented in Fig. 7. As follows from the studies, the strongly basic anion exchangers – Varion ADM and Varion ATM – as well as the weakly basic anion exchanger Varion ADAM, cannot be used in the sorption of Pd(II) ions from the 1.0 M  $\text{ZnCl}_2$ -0.1 M HCl solutions. Moreover, this fact is confirmed by the low values of recovery factors (Fig. 8) determined by means of the static method.

From the values of ion-exchange capacities (Table 4 and Fig. 9) and recovery factors (Fig. 10) in the 1.0 M  $\text{AlCl}_3$ -0.1 M HCl system it was found that all anion exchangers can be used in the recovery of Pd(II) ions from chloride solutions due to the fact that these resins show a high selectivity and affinity towards palladium-chlorocomplexes.

Based on the calculated values of working ion-exchange capacity the affinity series of palladium(II) ions for the anion exchangers of various basicity in the 1.0 M  $\text{AlCl}_3$ -0.1 M HCl system is as follows: Varion ADAM > Varion ATM  $\approx$  Varion ADM.

The best results in recovery of Pd(II) ions from waste materials can be obtained using the weak base anion exchanger Varion ADAM of polyacrylic matrix. The basicity of the functional groups as well as the type of skeleton have an influence on the sorption of Pd(II) ions in the 1.0 M  $\text{AlCl}_3$ -0.1 M HCl system.

#### 4. Conclusion

The experimental attempts led to the following conclusions:

- The values of the working ion-exchange capacities, the bed and weight distribution coefficients decrease with the increasing hydrochloric acid concentration.
- Based on the calculated values of working ion-exchange capacities, the affinity series of palladium(II) ions for the anion exchangers in the systems under examination is as follows:
  - 0.1 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.093 g/cm<sup>3</sup>) > Varion ADM (0.048 g/cm<sup>3</sup>)  $\approx$  Varion ATM (0.049 g/cm<sup>3</sup>).
  - 0.5 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.065 g/cm<sup>3</sup>) > Varion ATM (0.044 g/cm<sup>3</sup>)  $\approx$  Varion ADM (0.038 g/cm<sup>3</sup>).
  - 1.0 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.046 g/cm<sup>3</sup>) > Varion ATM (0.032 g/cm<sup>3</sup>)  $\approx$  Varion ADM (0.029 g/cm<sup>3</sup>).
  - 3.0 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.021 g/cm<sup>3</sup>) > Varion ATM (0.005 g/cm<sup>3</sup>)  $\approx$  Varion ADM (0.005 g/cm<sup>3</sup>).
  - 6.0 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.003 g/cm<sup>3</sup>) > Varion ATM (0.001 g/cm<sup>3</sup>)  $\approx$  Varion ADM (0.001 g/cm<sup>3</sup>).
  - 1.0 M  $\text{AlCl}_3$ -0.1 M HCl-0.00056 M Pd(II):  
Varion ADAM (0.017 g/cm<sup>3</sup>) > Varion ATM (0.001 g/cm<sup>3</sup>)  $\approx$  Varion ADM (0.001 g/cm<sup>3</sup>).
- The above-mentioned anion exchangers can be used in removal of palladium(II) ions from the chloride solutions (0.1–6.0 M HCl; 1.0 M  $\text{AlCl}_3$ -0.1 M HCl) but Varion ADAM is the most promising.
- The effect of macrocomponent addition causes decrease in Pd(II) ions uptake.

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