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Application of commercially available anion exchange resins for preconcentration of palladium(II) complexes from chloride–nitrate solutions

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ABSTRACT

The possibility of selective preconcentration of palladium(II) complexes by the polystyrene–divinylbenzene (Varion ATM, ADM) and polyacrylate (Varion ADAM) anion exchangers and the mechanism of their sorption onto these anion exchangers were investigated. The aim of this study was to find an appropriate model for the kinetics of Pd(II) complexes sorption and examine the influence of acids concentration and phase contact time on palladium(II) preconcentration.

The rate constants for the three models (pseudo-first and pseudo-second and intraparticle diffusion) and the correlation coefficients have been calculated in order to assess which model provides the best fit predicted data with experimental results. The pseudo-second order equation provides the best fit to experimental data.

1. Introduction

Preconcentration is an inevitable step in the determination of noble metals traces. In this procedure the analytes are preconcentrated from dilute solutions and separated from matrix elements which cause interferences during their determination. Ion exchange, solvent extraction, coprecipitation are the most commonly used preconcentration methods [1,2].

Ion exchange methods are mostly based on the separation of anionic chlorocomplexes of platinum metals from the matrix elements which occur in the cationic forms in dilute acid solutions.

At present various types of commercially available cation and anion exchangers Varion, are used in preconcentration processess [3,4], water treatment [5–9], removal [7,10–12], purification and separation processes [10,13].

The most popular Varion ion exchange resins are anion (Varion AD, ADA, ADM, ADAM, AT, ATM, AT-400, AT-660) and cation (Varion KS, KSM) exchange resins.

Literature does not provide the reply to the question about sorption behaviour of PGM metals and their preconcentration processes onto the Varion exchange resins. Its data on PGM metals are limited and incomplete. Due to this fact Varion ADM, ATM and ADAM are interesting and worth considering in the preconcentration process of palladium(II).

Hubicki and Leszczyńska. [14] used strongly (Varion AP), intermediate and weakly basic anion exchangers for palladium(II) removal from the chloride and chloride-nitrate solutions. Moreover, the effect of the addition of macrocomponents such as zinc(II) or aluminium(III) on the palladium(II) sorption from solutions under examination was observed. The strongly basic anion exchangers – Varion AP and Lewatit MP-500 as well as the weakly basic anion exchanger Duolite A-6 cannot be used in Pd(II) ions sorption from the solutions containing zinc(II) due to competitive sorptions of $[ZnCl4]^{2}$-complexes towards $[PdCl_4]^{2-}$. Duolite A-30 and Duolite A-7 give more promising results therefore the application of these resins for Pd(II) ions sorption in the presence of zinc(II) is worth considering. The affinity series of the anion exchangers towards palladium(II) complexes in solutions containing aluminium(III) was determined and is as follows:

$$\text{Varion AP} > \text{Duolite A-7} > \text{Lewatit MP 500} > \text{Duolite A-6} > \text{Duolit A 30 B}.$$

Leśniewska et al. [13] used cationic resins; Dowex 50 WX-8, Dowex 50 WX-2, Dowex HCR-S, Varion KS, Cellex-P for elimination of interferences during the palladium determination. After elimination of matrix ions (Al, Fe, Pb, Zn, Ni, Cu, Y) the anion exchange sorbent Cellex-T was used for palladium and platinum separation.

The aim of the paper was to study the possibility of palladium(II) complexes preconcentration from the chloride–nitrate solutions ($0.1 \div 0.9$ M HCl – $0.9 \div 0.1$ M HNO_3 – 100 mg/dm^3 Pd(II)), in order to understand the mechanisms of palladium(II) complexes sorption, find a suitable model for the kinetics and examined the influence of acids concentration and phases contact time.

Therefore applicability of the following anion exchange resins: Varion ADAM (weakly basic ion exchanger), Varion ATM (strongly

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Nomenclature

d_z	anion exchanger bed density (g/cm^3)
C_o	initial concentration of Pd(II) (mg/dm^3)
C_r	working ion exchange capacity (g/cm^3)
C_t	concentration of Pd(II) ions in solution after time t (mg/dm^3)
h	initial sorption rate (mg/g min)
k_1	equilibrium rate constant of the pseudo-second order sorption (1/min)
k_2	equilibrium rate constant of the pseudo-second order sorption (g/mg min).
k_{int}	interparticle diffusion rate constant ($mg/g\,min^{1/2}$)
m_j	weight of the dry ion exchanger (g)
q_1, q_2	amounts of Pd(II) adsorbed at equilibrium for the pseudo-first and second order sorptions (mg/g)
q_t	amount of Pd(II) adsorbed at t (mg/g)
U	effluent volume at $C = 0.5C/Co$ (cm^3)
U_o	dead volume in the column (cm^3)
V	volume of the solutions (dm^3)
V_i	void (inter-particle) anion exchanger bed volume (cm^3)
V_j	volume of ion exchanger bed put into the columns (cm^3)
V_p	volume of effluent between the first fraction and that to the breakthrough point (cm^3)

Greek letters

$\lambda_{Pd(II)}$	mass distribution coefficient of Pd(II)
$\lambda'_{Pd(II)}$	bed distribution coefficient of Pd(II)

basic ion exchanger, Type 1), Varion ADM (strongly basic ion exchanger, Type 2) was studied. Preconcentration of palladium(II) complexes from the chloride–nitrate solutions was carried out under dynamic and static conditions with a different phases contact time.

Due to the fact that palladium(II) and other noble metals can be brought to the solutions (leaching process) using diluted aqua regia, a mixture of mineral acids such as e.g., sulfuric, nitric and hydrochloric acids, a mixture of hydrochloric acid and sodium chloride as well as a mixture of hot hydrochloric acid and gaseous chlorine, chloride – nitrate solutions were considered in our studies [1,2,15]. Moreover, recovery processes of palladium(II) from scrap materials are carried out usually from chloride or chloride–nitrate solutions.

2. Experimental

2.1. Characteristics of the anion exchange resins used in the studies

Varion ADAM is a weakly basic anion exchange resin including tertiary amine functional groups ($-N(CH_3)_2$) on the polyacrylate matrix. It has a macroporous structure, of the total ion exchange capacity 1.2 meq/cm^3, particle sizes 0.315–1.25 mm. It can be used in the operating pH range from 0 to 14.

Varion ATM and ADM are strongly basic anion exchange resins. Both resins are macroporous, polystyrenic but belonging to different types. Varion ATM is a strongly basic anion exchange resin Type 1 while Varion ADM Type 2. Type 1 anion exchange resin has three methyl groups ($-N^+(CH_3)_3$) whereas in Type 2 an ethanol group replaces one of the methyl groups ($-N^+(CH_3)_2C_2H_4OH$). The total ion exchange capacity and particle sizes is equal 1.2 meq/cm^3 and 0.315–1.25 mm, respectively for both anion resins.

2.2. Methods

2.2.1. Static method

The static method was used to determine the amount of palladium(II) complexes sorbed onto anion exchange resins. Laboratory experiment was carried out in the conical 100 cm^3 flasks dosed with a ground-in stopper. 20 cm^3 proper aqueous phase (chloride–nitrate solutions: 0.1 M HCl – 0.9 M HNO_3; 0.2 M HCl – 0.8 M HNO_3; 0.5 M HCl – 0.5 M HNO_3; 0.8 M HCl – 0.2 M HNO_3; 0.9 M HCl – 0.1 M HNO_3) containing 100 mg/dm^3 Pd(II) and 0.2 g ion exchanger were put into a conical flask and shaken mechanically using the laboratory shaker, (Elphin+, type 357, produced in Poland) for 1–240 min at 20 °C. Then the anion exchanger was filtered off in order to determine the concentration of palladium(II) complexes in the solution. The amount of palladium(II) complexes $[PdCl_4]^{2-}$ sorbed onto anion exchangers, q_t, was calculated by the mass-balance relationship (Eq. (1)):

$$q_t = (C_o - C_t)\frac{V}{m_j} \tag{1}$$

where C_o is the initial concentration of Pd(II) complexes in the aqueous phase, C_t is the concentration of Pd(II) complexes in solution after time t, V is the volume of the solution, m_j is the weight of the dry ion exchanger used [16–17].

2.2.2. Kinetic investigations

Kinetics of palladium(II) complexes sorption from the chloride–nitrate solutions by the static method was studied. In order to investigate the mechanism of sorption and potential rate controlling steps, the pseudo-first and second order equations and the interparticle diffusion equation have been used to test the experimental data. The rate constants for the three models have been determined and the correlation coefficients have been calculated in order to assess which model provides the best fit of the predicted data with the experimental results.

In order to investigate the mechanism of sorption and potential rate controlling steps the pseudo-first and -second order kinetic models have been used. The Legergren's equation and the pseudo-first order equation are generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \tag{2}$$

After integration and applying the boundary conditions such as $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Eq. (2) becomes:

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1}{2.303}t \tag{3}$$

where q_1 and q_t are the amounts of palladium(II) complexes sorbed at equilibrium and at t, respectively, and k_1 is the rate constant of the pseudo-first order sorption [17–20].

The pseudo-second order equation based on adsorption equilibrium capacity was also used in the data analysis. Such an equation can be expressed as [20,21]:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \tag{4}$$

Integrating this equation for the boundary conditions gives:

$$\frac{1}{(q_2 - q_t)} = \frac{1}{q_2} + k_2 t \tag{5}$$

where q_2 is the amount of palladium(II) complexes sorbed at equilibrium, k_2 is the equilibrium rate constant of the pseudo-second order sorption.

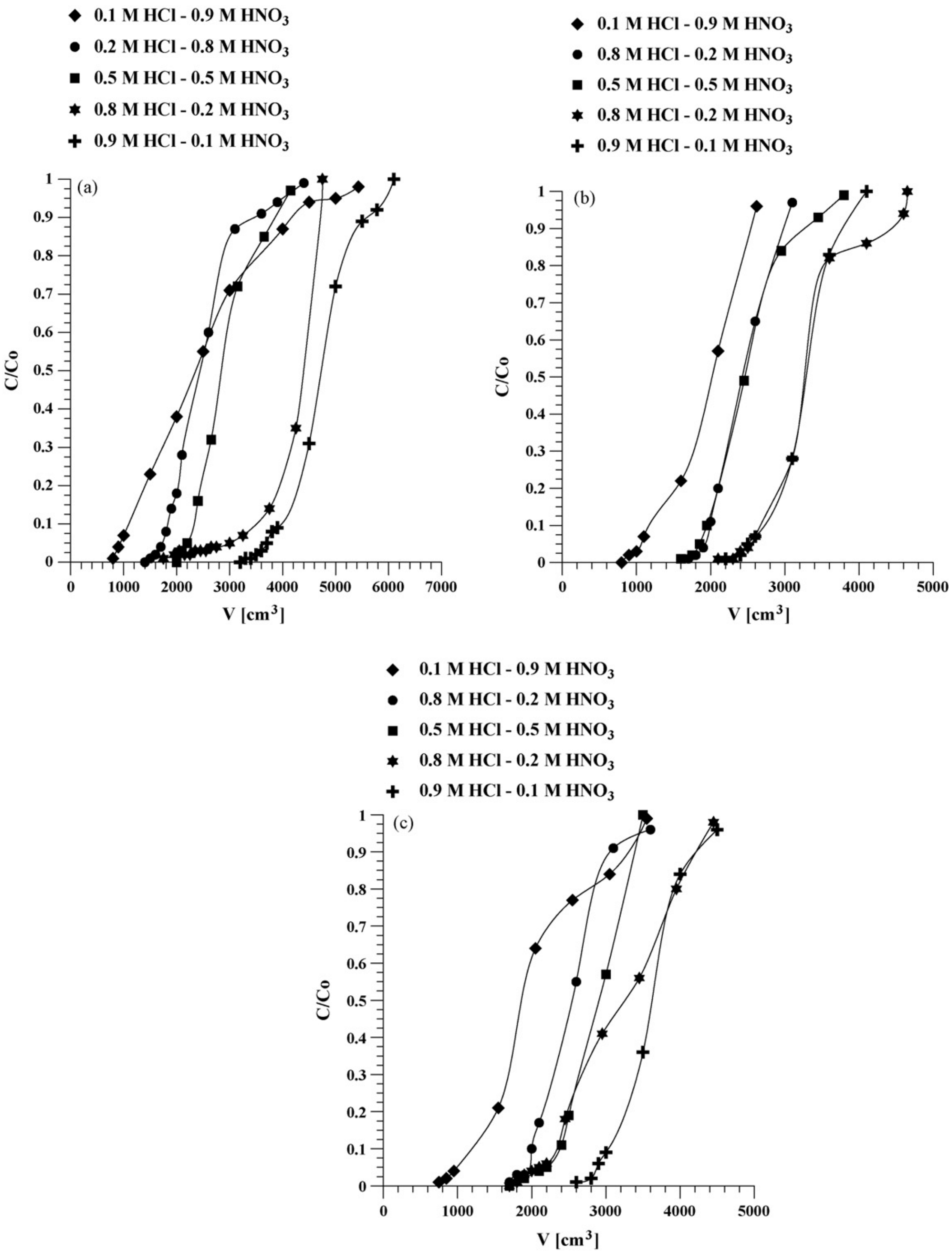

Fig. 1. (a) Breakthrough curves for palladium(II) ions in the 0.1–0.9 M HCl – 0.9–0.1 M HNO_3 systems for the weakly basic anion exchange resin Varion ADAM. (b) Breakthrough curves for palladium(II) ions in the 0.1–0.9 M HCl – 0.9–0.1 M HNO_3 systems for the strongly basic anion exchange resin Varion ADM. (c) Breakthrough curves for palladium(II) ions in the 0.1–0.9 M HCl – 0.9–0.1 M HNO_3 systems for the strongly basic anion exchange resin Varion ATM.

The integrated linear form of Eq. (5) is

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \qquad (6)$$

The initial sorption rate is:

$$h = k_2 q_2^2 \qquad (7)$$

The initial rate of the interparticle diffusion is as follows:

$$q_t = f(t^{1/2}) \qquad (8)$$

The rate parameter (k_{int}) for the interparticle diffusion can be defined as:

$$q_t = k_{int} t^{1/2} \qquad (9)$$

where k_{int} is the interparticle diffusion rate constant [20].

Table 1
Working ion exchange capacities compared with the mass and bed distribution coefficients in the 0.1 ÷ 0.9 M HCl – 0.9 ÷ 0.1 M HNO_3 systems for the anion exchange resins of various basicity.

Ion exchanger	System	Working ion exchange capacity, C_r (g/cm^3)	Weight distribution coefficient; $\lambda_{Pd(II)}$	Bed distribution coefficient; $\lambda'_{Pd(II)}$
Varion ADAM[a]	0.1 M HCl – 0.9 M HNO_3	0.0070	578.4	235.4
	0.2 M HCl – 0.8 M HNO_3	0.0130	598.0	243.4
	0.5 M HCl – 0.5 M HNO_3	0.0190	697.5	283.9
	0.8 M HCl – 0.2 M HNO_3	0.0150	1079.1	439.2
	0.9 M HCl – 0.1 M HNO_3	0.0310	1160.7	472.4
Varion ADM[b]	0.1 M HCl – 0.9 M HNO_3	0.0070	620.2	201.2
	0.2 M HCl – 0.8 M HNO_3	0.0160	745.7	241.9
	0.5 M HCl – 0.5 M HNO_3	0.0150	756.5	245.4
	0.8 M HCl – 0.2 M HNO_3	0.0200	1007.7	326.9
	0.9 M HCl – 0.1 M HNO_3	0.0180	1012.9	328.6
Varion ATM[c]	0.1 M HCl – 0.9 M HNO_3	0.0050	585.2	185.4
	0.2 M HCl – 0.8 M HNO_3	0.0160	801.5	253.9
	0.5 M HCl – 0.5 M HNO_3	0.0120	916.0	290.2
	0.8 M HCl – 0.2 M HNO_3	0.0150	1026.5	325.2
	0.9 M HCl – 0.1 M HNO_3	0.0250	1142.0	361.8

[a] d_z = 0.4070 g/cm^3.

[b] d_z = 0.3244 g/cm^3.

[c] d_z = 0.3168 g/cm^3; d_z –density of anion exchange resins.

2.2.3. Dynamic method

1 cm diameter columns joined to the feeder by means of the ground glass joint were used in the dynamic method. Ion exchange resins after suitable preparation (removal of mechanical impurities, contact with water to swelling) were packed to the columns in the amount of 10 cm^3. Then proper solutions containing different concentrations of hydrochloric and nitric acids and the same concentration of palladium(II) complexes were passed through the anion exchanger bed. The speed of solutions flow was stable and equal to 0.4 cm/min. The eluate was collected in the fractions. The contents of palladium(II) complexes were determined by the spectrophotometric iodide method. The working ion exchange capacity, C_r, (g/cm^3) (Eq. 10), the mass $\lambda_{Pd(II)}$ (Eq. 11) and bed $\lambda'_{Pd(II)}$ (Eq. 12) distribution coefficients were calculated from the breakthrough curves of palladium(II) complexes which are presented in Fig. 2(a)–(c).

$$C_r = \frac{(V_p C_o)}{V_j} \tag{10}$$

where V_p is the collected volume of effluent between the first fraction and that to the breakthrough point (cm^3), C_o is the initial concentration of microcomponent ($C_{o\ Pd(II)}$ = 100 mg/dm^3), V_j is the volume of anion exchanger bed put into the columns – 10 cm^3 in our investigations.

The breakthrough point occurs when the ratio C/C_o achieves proper values and microcomponent ions are found in the effluent.

$$\lambda_{Pd(II)} = \frac{(U - U_o - V_i)}{m_j} \tag{11}$$

where U is the effluent volume at $C = 0.5\ C/C_o$ (cm^3), U_o is the dead volume in the column (cm^3) (liquid volume in the column between the bottom edge of the anion exchanger bed and the outlet – the estimated value of the dead volume is 2 cm^3), V_i is the void (interparticle) anion exchanger bed volume (which amounts to ca. 0.4), m_j is the dry anion exchanger weight (g).

$$\lambda'_{Pd(II)} = \lambda_{Pd(II)} \cdot d_z \tag{12}$$

where d_z is the anion exchanger bed density [22].

2.2.4. Determination of palladium(II) complexes

The concentration of palladium(II) chloro–nitrate complexes in eluate were determined using the spectrophotometric iodide method and the spectrophotometer Specord M 42 produced by Carl Zeiss Jena, Germany. Palladium(II) complexes in the presence of an excess of potassium iodides formed the red–brown complex $[PdI_4]^{2-}$. A reducing agent (usually ascorbic acid) is added to the solutions in order to avoid oxidation. The solution under investigations containing not more than 0.2 mg Pd(II) was put into a 50 cm^3 flask. Then 5 cm^3 of 6 M HCl, 10 cm^3 of 20% KI solutions and 6 cm^3 of 1% ascorbic acid solutions were added. The solutions were diluted with distilled water to a certain volume. After stirring, absorbance was measured at 408 nm in a 1 cm cell against water as the reference [23,24].

3. Results and discussion

Aqueous chloride–nitrate solutions are a cost-effective medium in which all the PGM can be brought into solutions and concentrated.

In aqueous solutions containing Cl^- and $NO_3{}^-$ ions, the chemical morphology of chloropalladium(II), nitratepalladium(II) and chloride–nitratepalladium(II) complexes is one of the most important factors that affect the preconcentration of palladium(II) and make the sorption mechanism a little more complicated.

Palladium(II) in chloride solutions can form different kinds of stable chloro-, hydroxy-chloride and hydroxide complexes. To identify the predominant Pd species under the various experimental conditions, the speciation of palladium was determined as a function of pH and total Cl^- concentration using the stability constants proposed by Baes and Mesmer [25].

The equations for determining Pd speciation are as follows:

$$[Pd_{tot}] = [Pd^{2+}]\left\{1 + \sum_{n=1}^{4}(\beta_{Cln}[Cl^-]^n + \beta_{OHn}[H^+]^{-n})\right\},$$

$$[Pd^{2+}] = \frac{[Pd_{tot}]}{1 + \sum_{n=1}^{4}(\beta_{Cln}[Cl^-]^n + \beta_{OHn}[H^+]^{-n})},$$

$$[PdCl_n^{2-n}] = \beta_{Cln}[Pd^{2+}][Cl^-]^n, \quad n = 1, 2, 3, 4,$$

$$[Pd(OH)_n^{2-n}] = \beta_{OHn}[Pd^{2+}][H^+]^{-n}, \quad n = 1, 2, 3, 4,$$

$$[Cl_{tot}] = [Cl^-] + \sum_{n=1}^{4} n[PdCl_n^{2-n}],$$

where $[Pd_{tot}]$ is the total Pd concentration, $[Cl_{tot}]$ the total Cl^- concentration [26].

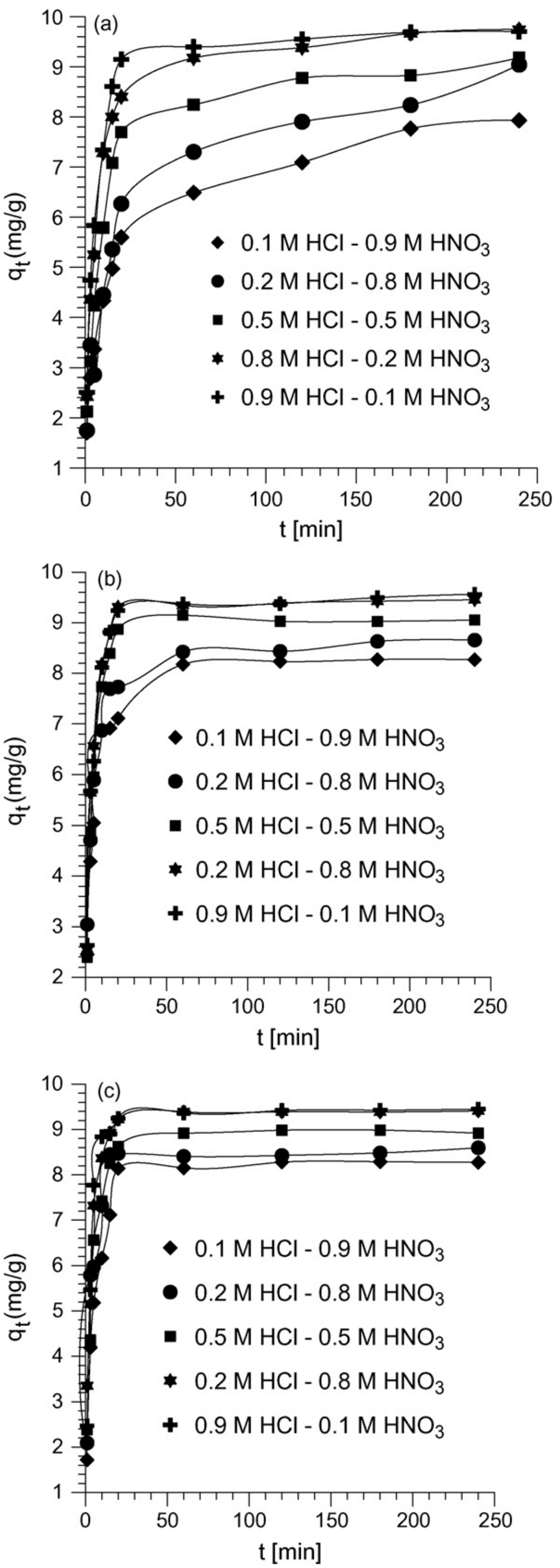

Fig. 2. (a) Effect of hydrochloric acid concentration on the sorption of palladium(II) complexes onto the weakly basic anion exchanger Varion ADAM. (b) Effect of hydrochloric acid concentration on the sorption of palladium(II) complexes onto the strongly basic anion exchanger Varion ADM. (c) Effect of hydrochloric acid concentration on the sorption of palladium(II) complexes onto the strongly basic anion exchanger Varion ATM.

The anionic species of palladium(II) complexes and the reaction scheme are presented below:

$$Pd^{2+} + Cl^- \rightarrow [PdCl]^+, \quad K = 10^{4.47}$$

$$Pd^{2+} + 2Cl^- \rightarrow [PdCl_2], \quad K = 10^{7.76}$$

$$Pd^{2+} + 3Cl^- \rightarrow [PdCl_3]^-, \quad K = 10^{10.17}$$

$$Pd^{2+} + 4Cl^- \rightarrow [PdCl_4]^{2-}, \quad K = 10^{11.54}$$

$$Pd^{2+} + 2H_2O \rightarrow [Pd(OH)]^+ + H_3O^+, \quad K = 10^{-2.3}$$

$$Pd^{2+} + 4H_2O \rightarrow [Pd(OH)]_2 + 2H_3O^+, \quad K = 10^{-4.2}$$

$$Pd^{2+} + 6H_2O \rightarrow [Pd(OH)_3]^- + 3H_3O^+, \quad K = 10^{-12}$$

$$Pd^{2+} + 8H_2O \rightarrow [Pd(OH)_4]^{2-} + 4H_3O^+, \quad K = 10^{-14}$$

The major species in the acidic solution containing 0.1 M and higher chloride concentration is $[PdCl_4]^{2-}$. At higher pH values than 8, formation of another hydroxide–chloride or hydroxide complexes begins [27,28].

The PGM chlorocomplexes occur in acidic chloride media mostly in the anionic form therefore they are capable of undergoing anion exchange reactions. The anionic species of palladium $[PdCl_4]^{2-}$, $[PdCl_3]^-$ are more favorable than cationic species $[PdCl]^+$, Pd^{2+} or the nonionic form $[PdCl_2]$ for anion exchange. The Pd(II) chlorocomplexes form ion pairs with the anion exchange resins. The tendency of the anion exchanger for formation of PGM chlorocomplexes is following:

$$[MCl_6]^{2-} > [MCl_4]^{2-} \gg [MCl_6]^{3-} > \text{aqua species}.$$

In aqueous nitrate solutions palladium(II) may be forming a series of anionic complexes with nitrate ions. The formation of various nitrate complexes of palladium(II) are given below:

$$Pd^{2+} + NO_3{}^- \Leftrightarrow [Pd(NO_3)]^+$$

$$Pd^{2+} + 2NO_3{}^- \Leftrightarrow [Pd(NO_3)]_2$$

$$Pd^{2+} + 3NO_3{}^- \Leftrightarrow [Pd(NO_3)_3]^-$$

$$Pd^{2+} + 4NO_3{}^- \Leftrightarrow [Pd(NO_3)_4]^{2-}$$

Moreover, free palladium(II) ion $[Pd(H_2O)_4]^{2+}$ can form a nitrate–hydroxide complexes of palladium(II) [29–32]:

$$[Pd(H_2O)_4]^{2+} + NO_3{}^- \Leftrightarrow [Pd(H_2O)_3(NO_3)]^+$$

$$[Pd(H_2O)_4]^{2+} + 2NO_3{}^- \Leftrightarrow [Pd(H_2O)_2(NO_3)_2]$$

$$[Pd(H_2O)_4]^{2+} + 3NO_3{}^- \Leftrightarrow [Pd(H_2O)(NO_3)_3]^-$$

$$[Pd(H_2O)_4]^{2+} + 4NO_3{}^- \Leftrightarrow [Pd(NO_3)_4]^{2-}$$

As follows from the presented results (Fig. 1(a)–(c) and Table 1), the weakly basic anion exchanger Varion ADAM and the strongly basic anion exchangers Varion ADM and ATM are suitable for preconcentration of Pd(II) complexes from the chloride–nitrate solutions.

The working ion exchange capacities, the bed and mass distribution coefficients depend on hydrochloric acid concentration. The weakly basic anion exchanger Varion ADAM is characterised by the highest values of working ion exchange capacities in the 0.1 M HCl – 0.9 M HNO_3, 0.5 M HCl – 0.5 M HNO_3, 0.9 M HCl – 0.1 M

HNO_3 solutions. Making comparison between the values of working ion exchange capacities for the strongly basic anion exchangers it was found that both resins possess comparable values of these parameters. The differences in working capacity may result from the matrix structure. The weakly basic anion exchanger Varion ADAM is of polyacrylate matrix whereas Varion ADM and ATM are styrene copolymers with divinylbenzene. Moreover, strongly basic anion exchangers are protonated much more readily than weakly basic therefore they can behave as ion exchangers at relatively low acid concentration. Weakly basic anion exchangers are protonated significantly but only at high acid concentration.

Different values of capacity for Varion ADM and Varion ATM could be explained by different substituents linked to the nitrogen atom. Varion ATM consist the hydroxyl group. This means that this resin possess a different surrounding compared with another resins. The interaction between palladium(II) complexes and resins may be ion exchange or can follow from the presence of hydroxyl groups (solvation mechanism). Palladium(II) complexes may be bound to the resins through solvation (a) or ion exchange mechanisms (b):

$$\mathrm{MCl_p}^{(p-n)-} + \mathrm{m(R)_{(o)}} \leftrightarrow \mathrm{MCl_n(R)_{m(o)}} + (p-n)\mathrm{Cl^-} \qquad (a)$$

$$\mathrm{MCl_p}^{(p-n)-} + (p-n)(\mathrm{RH^+Cl^-})_{(o)} \leftrightarrow (\mathrm{RH^+})_{p-n}\mathrm{MCl_{p(o)}}^{(p-n)-} + (p-n)\mathrm{Cl^-} \qquad (b)$$

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

When the resin has one or more co-ordinate atoms in its functional group the interaction between the palladium(II) complexes and resins can be solvent mechanism. In acidic media, palladium(II) complexes are bonded through the protonated nitrogen of the amine group of the resins.

Based on HSAB theory (the hard and soft acids and bases), the donor atoms such as S, O or N are capable of co-ordination with the palladium(II) complexes and interact strongly with the soft acids like precious metal ions.

For all investigated ion exchangers the values of mass and bed distribution coefficients depend on hydrochloric and nitric acid concentration. The mass and bed distribution coefficients increased with the increasing ratio of hydrochloric acid to nitric acid. When the HCl:HNO_3 ratio is 1:9 the distribution coefficients achieve the smallest values. Decrease of chemical yield at higher nitric acid concentration can be caused by competitive sorption between NO_3^- and $[H(NO_3)_2]^-$ ions which are formed in the aqueous phase and increasing competition between Cl^- and metal-complex anions.

A series of contact time experiments was undertaken at various time of agitation and the results showing the plots of the amount of palladium(II) complexes sorbed per 0.2 g of anion exchanger, q_t (mg/g), against time, t (min) are presented in Fig. 2(a)–(c). The amount of Pd(II) complexes increase with time t and it remains constant after the contact time of about 60 min for Varion ADM and ATM or 240 min for Varion ADAM. The time profile of palladium(II) complexes uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of Pd(II) on the surface of anion exchangers.

In the kinetics studies, determined r^2 was used to fit the best kinetic expression. The equilibrium data following the linerarized form of Lagergren pseudo-first order kinetics (Eq. (3)) was obtained from the slope and intercept of plot $\log(q_1 - q_t)$ versus time. A straight line of $\log(q_1 - q_t)$ versus time suggest the applicability of this kinetic model to fit the experimental data. The equilibrium sorption capacity, q_e, is required to fit the data, but in many cases q_e remains unknown due to slow adsorption processes. For this reason, it is necessary to obtain the real equilibrium adsorption capacity, q_e, by extrapolating the experimental data to $t = \infty$ or by using a

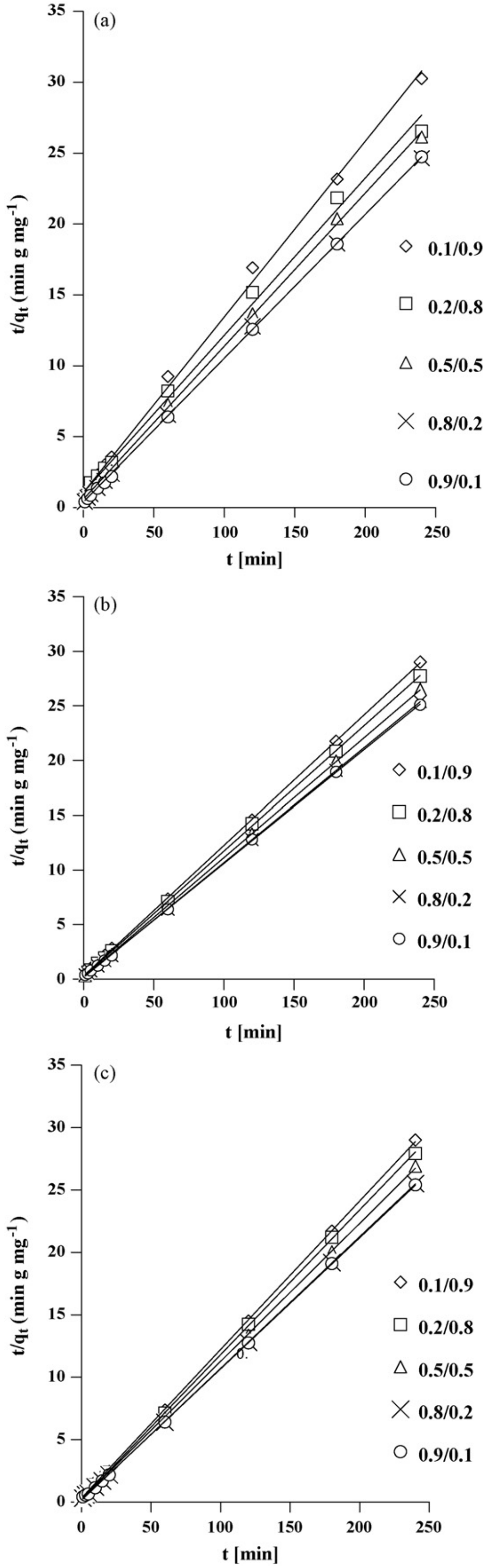

Fig. 3. (a)–(c) Plots of the kinetic equation for the sorption of palladium(II) complexes onto the anion exchangers, the pseudo-second order sorption kinetics of Pd(II) onto Varion ADAM (a), Varion ADM (b), Varion ATM (c) from chloride–nitrate solutions.

Table 2
Kinetic parameters for palladium (II) ions sorption onto the anion exchangers with various basicity.

Anion exchanger	The systems	$q_{e,exp}$	Pseudo-first order kinetic equation			Pseudo-second order kinetic equation				Interparticle diffusion equation	
			q_1	k_1	$r_1{}^2$	q_2	k_2	h	$r_2{}^2$	k_{int}	r^2_{int}
Varion ADAM	0.1 M HCl – 0.9 M HNO_3	7.93	0.21	0.02	0.95	8.07	0.01	0.94	0.99	0.38	0.86
	0.2 M HCl – 0.8 M HNO_3	9.04	0.20	0.01	0.88	9.02	0.01	0.93	0.99	0.44	0.86
	0.5 M HCl – 0.5 M HNO_3	9.18	0.25	0.02	0.82	9.26	0.02	1.69	0.99	0.41	0.71
	0.8 M HCl – 0.2 M HNO_3	9.74	0.27	0.02	0.90	9.86	0.03	2.54	0.99	0.39	0.39
	0.9 M HCl – 0.1 M HNO_3	9.70	0.32	0.03	0.89	9.82	0.04	3.52	0.99	0.36	0.57
Varion ADM	0.1 M HCl – 0.9 M HNO_3	8.27	0.32	0.04	0.91	8.39	0.04	3.09	0.99	0.30	0.61
	0.2 M HCl – 0.8 M HNO_3	8.66	0.39	0.03	0.88	8.73	0.05	3.56	0.99	0.28	0.60
	0.5 M HCl – 0.5 M HNO_3	9.06	0.51	0.03	0.76	9.14	0.06	5.22	0.99	0.31	0.48
	0.8 M HCl –0.2 M HNO_3	9.45	0.60	0.03	0.71	9.52	0.06	5.63	0.99	0.30	0.30
	0.9 M HCl – 0.1 M HNO_3	9.56	0.50	0.02	0.70	9.62	0.05	4.85	0.99	0.31	0.49
Varion ATM	0.1 M HCl – 0.9 M HNO_3	8.29	0.64	0.03	0.66	8.40	0.05	3.19	0.99	0.32	0.54
	0.2 M HCl – 0.8 M HNO_3	8.60	0.89	0.02	0.39	8.61	0.07	5.15	0.99	0.26	0.40
	0.5 M HCl – 0.5 M HNO_3	8.98	0.64	0.02	0.52	9.04	0.06	4.92	0.99	0.31	0.48
	0.8 M HCl – 0.2 M HNO_3	9.41	0.77	0.03	0.67	9.47	0.08	7.14	0.99	0.27	0.27
	0.9 M HCl – 0.1 M HNO_3	9.45	0.73	0.03	0.74	9.51	0.08	6.94	0.99	0.27	0.38

$q_{e,exp}$ (mg/g); k_1, k_2 (1/min); h (mg/g min).

trial and error methods. In many cases, the Lagergen equation does not fit well for the whole range of contact time and is generally applicable over the initial stage of adsorption processes.

The plots of $\log(q_1 - q_t)$ for three anion exchangers in the chloride–nitrate solutions are not shown in the paper. The calculated rate constant k_1, predicted $q_{e,exp}$ and q_1 values and corresponding $r_1{}^2$ value were listed in Table 2. The values of correlation coefficients are low in the range from 0.82 to 0.95, 0.70 to 0.91, 0.39 to 0.74 for Varion ADAM, ADM and ATM, respectively. Moreover, the calculated q_1 values obtained from the pseudo-first order kinetic models do not give reasonable values, which are too low to compare with experimental $q_{e,exp}$ values. This finding suggest that the sorption of palladium(II) complexes onto Varion anion exchange resins is not the pseudo-first order reaction.

Pseudo-second order equation (Eq. (6)) was also applied. If the pseudo-second order kinetics are applicable, the plot t/q_t versus t should show a linear relationship. There is no need to know any parameters beforehand and q_2 and k_2 can be determined from the slope and intercept of the plot. Moreover, this procedure is more likely to predict the behaviour over the whole range of sorption.

The straight lines in plot t/q_t versus t show good agreement of experimental data with the pseudo-second order kinetic model for all resins (Fig. 3). The values of the k_2 and q_2 and correlation coefficients r_2^2 are also presented in Table 2. The correlation coefficients for the pseudo-second order kinetic model were grater than 0.99 for all resins. The calculated q_2 values also agree very well with the experimental data in the case of the pseudo-second order kinetics.

The interparticle diffusion is described by linear plot q_t versus $t^{0.5}$. The k_{int} and r^2_{int} for the interparticle diffusion kinetic model were calculated from the slopes and intercepts of the plr^2_{int}ot q_t versus $t^{0.5}$ and the calculated values were added to Table 2. The relationships between q_t and $t^{0.5}$ are not linear and the correlation coefficients achieve a very low values. Due to these above facts this model cannot applied to explain the palladium(II) complexes sorption onto Varion ADAM, ADM and ATM.

4. Conclusions

The experimental attempts led to the following conclusions:

- The values of the working ion exchange capacities, the mass and bed distribution coefficients and the amount of palladium(II) complexes sorbed onto anion exchangers depend on the hydrochloric and nitric acids ratio.
- The weakly basic anion exchanger is characterised by the highest values of the working ion exchange capacities, the bed and mass distribution coefficients.
- The anion exchangers Varion ADAM, ATM and ADM studied in this paper can be applied in preconcentration of Pd(II) complexes from the chloride–nitrate solutions owing to their selectivity towards palladium(II) complexes and high values of the working ion exchange capacities.
- The Varion ADAM shows the best performance for palladium(II) complexes preconcentration from the chloride–nitrate solution.
- The amounts of palladium(II) complexes sorbed onto the anion exchangers increase with the increasing phase contact time.
- The sorption of palladium(II) complexes on the anion exchangers Varion ADAM, ADM and ATM can be best described by the pseudo-second order kinetic model.

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References

[1] C.R.M. Rao, G.S. Reddi, Platinum group metals (PGM); occurrence, use and recent trends in their determination, Trends Anal. Chem. 19 (2000) 565–586.
[2] B. Godlewska-Żyłkiewicz, Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium, Microchim. Acta 147 (2004) 189–210.
[3] Z. Hubicki, A. Wołowicz, M. Leszczyńska, Studies of removal of palladium(II) ions from chloride solutions on weakly and strongly basic anion exchangers, J. Hazard. Mater. 159 (2008) 280–286.
[4] K. Brajter, K. Słonawska, Matrix separation of palladium and iridium by the cellulose anion exchanger Cellex T and the subsequent determination of palladium at the μg/g-level, Microchim. Acta 97 (1989) 137–143.
[5] C.S. Barton, D.I. Stewart, K. Morris, D.E. Bryant, Performance of three resin-based materials for treating uranium-contaminated groundwater within a PRB, J. Hazard. Mater. 116 (2004) 191–204.
[6] M. Dimova-Todorova, I. Dobrevsky, T. Panayotova, Coagulation of natural waters with modified ion exchangers, Desalination 164 (2004) 71–76.
[7] M. Apolinarski, M. Roman, Technical and economical efficiency of some selected methods for nitrate removal from groundwater, Water Supply 10 (1992) 65–70.
[8] J. Naumczyk, L. Szpyrkowicz, F.Z. Grandt, Organics isolation from fresh and drinking waters by macroporous anion-exchange resins, Water Res. 23 (1989) 1593–1597.
[9] A.B. Kiss, E. Dani, Investigation of ion exchangers – for obtaining high purity ion exchange water – by means of UR Spectrophotometric and supplementary methods, Tungsram Tech. Mitt. 29 (1976) 1248–1259.
[10] I. Orszag, F. Ratkovics, B. Szeiler, Purification of ammonium nitrate containing condensed water by ion-exchangers, Hung. J. Ind. Chem. 9 (1981) 241–249.
[11] D. Rozycka, Recovery of fluorine from dilute aqueous solutions of anionites – sorption and desorption of F** minus ions, Przem. Chem. 57 (1978) 149–151.
[12] I. Bàlint-Ambró, The ion-exchange behaviour of arsenic(III) on Varion anion-exchange resins, J. Chromatogr. 102 (1974) 457–460.
[13] B.A. Leśniewska, B. Godlewska-Żyłkiewicz, A. Ruszyński, E. Bulska, A. Hulanicki, Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry, Anal. Chim. Acta 564 (2006) 236–242.
[14] Z. Hubicki, M. Leszczyńska, Studies of sorption od Pd(II) microquantities on strongly basic polyacrylate anion exchangers, Desalination 175 (2005) 289–295.
[15] J. Szymanowski, Development of release and separation technologies for noble metals, Rudy Metale 34 (1989) 54–58 (in Polish).
[16] M. Özacar, I.A. Şengil, Adsorption of reactive dyes on calcined alunite from aqueous solutions, J. Hazard. Mater. B98 (2003) 211–224.
[17] M. Özacar, I.A. Şengil, A kinetic study of metal complex dye sorption onto pine sawdust, Process Biochem. 40 (2005) 565–572.
[18] Z. Aksu, Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modelling, Biochem. Eng. J. 7 (2001) 79–84.
[19] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[20] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater. B136 (2006) 681–689.
[21] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[22] J. Minczewski, J. Chwastowska, R. Dybczyński, Separation and Preconcentration Methods in Inorganic Trace Analysis, John Wiley & Sons, New York, 1982.
[23] Z. Marczenko, A.P. Ramsza, Differential spectrophotometric determination of palladium in catalyst using the dimethylglyoxime and iodide methods, Chem. Anal. 23 (1978) 23–27.
[24] M.C. Bruzzoniti, C. Mucchino, E. Tarasco, C. Sarzanini, On-line preconcentration, ion chromatographic separation and spectrophotometric determination of palladium at trace level, J. Chromatogr. A 1007 (2003) 93–100.
[25] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976, p. 264.
[26] Y.H. Kim, Y. Nakano, Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modelling, Water Res. 39 (2005) 1324–1330.
[27] G. Levitin, G. Schmuckler, Solvent extraction of rhodium chloride from aqueous solutions and its separation from palladium and platinum, React. Funct. Polym. 54 (2003) 149–154.
[28] M. Ruiz, A.M. Sastre, E. Guibal, Palladium sorption on glutaraldehyde-crosslinked chitosan, React. Funct. Polym. 45 (2000) 155–173.
[29] K.A. Venkatesan, B.R. Selvan, M.P. Antony, T.G. Srinivasan, P.R. Vasudeva Rao, Extraction of palladium(II) from nitric acid medium by imidazolium nitrate immobilized resin, Hydrometallurgy 86 (2007) 221–229.
[30] M.M. Raj, A. Dharmaraja, K. Panchanatheswaran, K.A. Venkatesan, T.G. Srinivasan, P.R. Vasudeva Rao, Extraction of fission palladium(II) from nitric acid by benzoylmethylenetriphenylphosphorane (BMTPP), Hydrometallurgy 84 (2006) 118–124.
[31] E.C. Frias, H.K. Pitsch, T.J. Ly, C. Poitrenaud, Palladium complexes in concentrated nitrate and acid solution, Talanta 424 (1995) 1675–1683.
[32] F.L. Bernardis, R.A. Grant, D.C. Sherrington, A review of methods of separation of the platinum-group metals through their chloro-complexes, React. Funct. Polym. 65 (2005) 205–217.