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Effect of matrix and structure types of ion exchangers on palladium(II) sorption from acidic medium

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ABSTRACT

Influence of matrix and structure types of the weakly basic anion exchange resins such as Amberlyst A-23, Amberlyst A-24 and Dowex-WGR-2 onto palladium(II) sorption from the chloride and chloride–nitrate media was investigated. The addition of sodium chloride as well as the effect of acids concentration on Pd(II) sorption were taken into account. The batch and column methods were applied. Moreover, the isotherm for the most efficient resin – Amberlyst A-23 was determined. The Langmuir, Freundlich and Temkin–Pyzhev equations, which are commonly used for describing sorption equilibrium were applied in the analysis of the obtained results. The breakthrough curves of palladium(II) and the sorption parameters (distribution coefficients (K_d, K'_d), ion exchange capacities (C_r, C_t), time required for the moving and formation of exchange zone (t_m, t_f)) were determined. In order to trace the sorption process the FT-IR spectra of the pure anion exchange resins and those loaded with palladium(II) were recorded, too. Satisfactory results were obtained for all examined resins but the largest sorption capacities were found for Amberlyst A-23 (9.99–7.61 mg/g). Sodium chloride addition, high concentrations of hydrochloric and nitric acids cause reduction of equilibrium and working sorption capacity values.

1. Introduction

Ion exchange has been successfully and widely applied in industrial, drinking and wastewater treatment areas. Its application is based on a variety of standard and selective commercially available ion exchangers. The conventional ion exchange resins have found application in many fields, but their use in hydrometallurgy has been limited due to a lack of selectivity [1].

Ion exchange resins are insoluble polymeric or macromolecular substances with fixed ions or reactive ionic groups. The reactive groups have been encorporated during the manufacture of synthetic ion exchangers and are able to dissociate as well as to undergo ion exchange reactions [2–5]. The high demand for ion exchange materials led to the development of new products of special properties. Nowadays, the most widely used ion exchangers are organic materials based on synthetic polymers. The beginning of the era of synthetic polymers is attributed to the work by Adams and Holmes [6]. In the wide group of commercially available ion exchangers whose properties and methods of preparation have changed during the last century the strongly and weakly basic anion exchange resins play a great role in ion chromatography. Selectivity of anion exchange resins depends on their polymeric matrix, structure as well as the functional group type [7]. The weakly basic anion exchange resins which effectively exchange only anions of weaker acids due to their low basicity, possess primary ($-NH_2$), secondary ($=NH$) or tertiary-amine ($\equiv N$) functional groups. In some cases mixtures of these groups are involved [2]. Depending on the matrix types weakly basic anion exchange resins (e.g. acrylic, styrene-divinylbenzene, epoxy-amine and phenol-formaldehyde) possess different properties and show various selectivity towards the same ions. Polystyrene crosslinked with divinylbenzene (PS-DVB) as a resin matrix offers remarkable chemical and physical stability, more stable than phenol-formaldehyde matrices. On the other hand, the exchange rates on PS-DVB resins are low. Resins with the fast exchange rate are those based on hydrophilic macroporous copolymers. Moreover, the strong hydrophobic nature of PS-DVB materials unfavourably affects the sorption process and results in their restricted application in some areas [1,8]. Therefore, numerous attempts have been made to increase the hydrophilicity of PS-DVB resins e.g. the hydrophilic functional groups (hydroxymethyl, sulfonic, carboxylic) chemically attached to the aromatic rings of the PS-DVB resins or coating of the hydrophobic surface with hydrophilic polymers of poly(vinyl alcohol), poly(oxyethylenes) [8,9]. Acrylic polymers as the most important weakly basic anion exchange resins have been successfully applied in the fields where high levels of organic compounds are present. In this case this type of resins shows higher values

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Nomenclature

q_t (mg/g)	amount of palladium(II) adsorbed at time t
C_0 (mg/dm^3)	initial concentration of palladium(II)
C_t (mg/dm^3)	concentration of palladium(II) at time t
C_e (mg/dm^3)	concentrations of palladium(II) at equilibrium
V (dm^3)	volume of the solution
W (g)	mass of the dry anion exchanger
q_e (mg/g)	sorption capacity
C_r (g/cm^3)	working anion exchange capacity
C_t (g/cm^3)	total anion exchange capacity
V_p (dm^3)	effluent volume to the break point
V_j (cm^3)	volume of anion exchanger in the column
U (cm^3)	effluent volume at $C = 0.5C/C_0$
K_d	mass distribution coefficient
K'_d	bed distribution coefficient
U_0 (cm^3)	dead volume in the column
V_v	void (inter-particle) ion exchanger bed volume (which amounts to ca. 0.4)
m_j (g)	dry ion exchanger weight
t_f	time required for formation of exchange zone
t_m	time required for moving exchange zone
$V_z = V_t - V_p$	distinction between the total volume of effluent, V_t and volume collected till the break point appearance, V_p (cm^3)
U_r (cm^3/min)	flow rate
S (cm^2)	total column cross-section area, $S = \prod r^2$
r	radius of column
Q_0 (mg/g)	Langmuir constant related to the monolayer capacity
b (dm^3/g)	equilibrium constant of Langmuir
k_F (mg/g)	Freundlich constant
$1/n$	Freundlich constant
R	gas constant (8.314 J/mol K)
T (K)	temperature
b_T (J/mol)	Temkin constant related to heat of sorption
A (dm^3/g)	Temkin constant
R_L	equilibrium parameter of the Langmuir model

of anion exchange capacities compared with the PS-DVB resins [2]. The weakly basic anion exchange resins are available on market as gel, macroporous (macroreticular) or hyper-crosslinked. The macroporous beads are formed by clusters of small polymeric spherical particles of gel type and contain particles with micro-, meso- and macro-pores (a few), whereas the mesopores have the greatest contribution to the pore volume of the anion exchangers. The gel resins do not have permanent porosity. Depending on the swelling and crosslinking degrees the gel resins are characterized by different sizes of micropores and mesopores (<4 nm) which are formed when the resin is swelled in water [10].

This paper is a continuation of our previous works [11,12] whose aim is to find the most suitable ion exchangers which can be successfully applied in the recovery of palladium(II) ions from scrap materials e.g. used auto catalysts, industry catalysts, anodic slime, waste waters etc. The literature data concerning sorption of palladium(II) ions on different types of ion exchangers are incomplete due to the fact that the studies have not taken into account the most important properties of ion exchangers such matrix and structure type. The previous works [11,12] focus mainly on applicability of strongly basic ion exchangers with the styrene-divinylbenzene matrix (Dowex MSA-1, Dowex MSA-2, Varion ADM, Varion ATM), but those under studies – weakly basic ion exchangers with different matrix types are a new trend in our investigations. Making comparison between the previously obtained results of palladium(II) sorption on the ion exchangers with the styrene-divinylbenzene matrix and the ones presented in this paper, the preliminary selection of the ion exchangers suitable for such a purpose can be made.

The objective of the present work is to investigate the sorption potential of the weakly basic anion exchange resins with different matrices and structure types: Amberlyst A-24 (acrylic, gel), Amberlyst A-23 (phenol-formaldehyde, macroporous) and Dowex-WGR-2 (epoxy-amine, macroporous) for removing palladium(II) from the aqueous, acidic medium: chloride (HCl); chloride–nitrate (HCl–HNO_3) and chloride with sodium chloride addition (HCl–NaCl). The Langmuir and Freundlich models were used to describe the equilibrium isotherms for Amberlyst A-23. The breakthrough curves were determined, sorption parameters were calculated and FT-IR spectra were recorded to describe the sorption mechanism of palladium(II) on the weakly basic anion exchange resins mentioned above.

The use of the chlorine/hydrochloric acid, mixture of mineral acids and chloride–nitrate (aqua regia) solutions as leaching agents has found several industrial applications. Thus there is an increasing interest in preconcentration, recovery and separation of PGM metal ions from acidic media. The leaching process with acidic sodium chloride solutions of spent catalysts containing palladium is one of the most effective methods for secondary raw materials treatment [12–14]. Therefore in this paper the sorption process of palladium(II) was carried out from acidic solutions with and without sodium chloride addition.

2. Experimental

2.1. Reagents and solutions

The palladium(II) stock solution was prepared from solid $PdCl_2$, A.R. Grade, >99.99% $PdCl_2$ (POCh, Poland) in 1.0 M HCl. Appropriate volumes of hydrochloric acid standardized solution were added to adjust the H^+ concentration to the desired value.

Aqueous chloride (0.1–3.0 M HCl; 0.1–2.0 M HCl–1.0 M NaCl; 0.1–2.0 M HCl–2.0 M NaCl) and chloride–nitrate (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) solutions of palladium(II) were prepared by dilution with concentrated HCl or with HCl and HNO_3 in order to obtain a desired value of H^+ concentration. The working solutions were found to contain 100 mg/dm^3 Pd(II). In the case of chloride solutions with sodium chloride addition sodium chloride salt (POCh, Poland) was dissolved in distilled water before dilution with HCl. Other reagents used were of analytical grade from POCh (Poland).

2.2. Instrumentation

The analysis of palladium(II) concentrations was carried out by means of the UV-VIS spectrophotometer Specord M42; Carl Zeiss Jena, Germany.

The FT-IR spectra of the resins under discussion before and after loading by palladium(II) ions were recorded using the Alpha spectrometer with ATR attachment (Bruker Optics, Germany).

The thermostatic shaker; Elpin+, type 375 S, Poland was used to mix (mechanically shake) the solid and liquid phases.

2.3. Weakly basic anion exchange resins characteristics

The three weakly basic anion exchange resins: Amberlyst A-23, Amberlyst A-24 (Rohm and Haas Co., France) and Dowex-WGR 2 (Dow Chemical Co., USA) [15] with different matrices and structure types were employed in the sorption studies of palladium(II) ions from the chloride and chloride–nitrate acidic media.

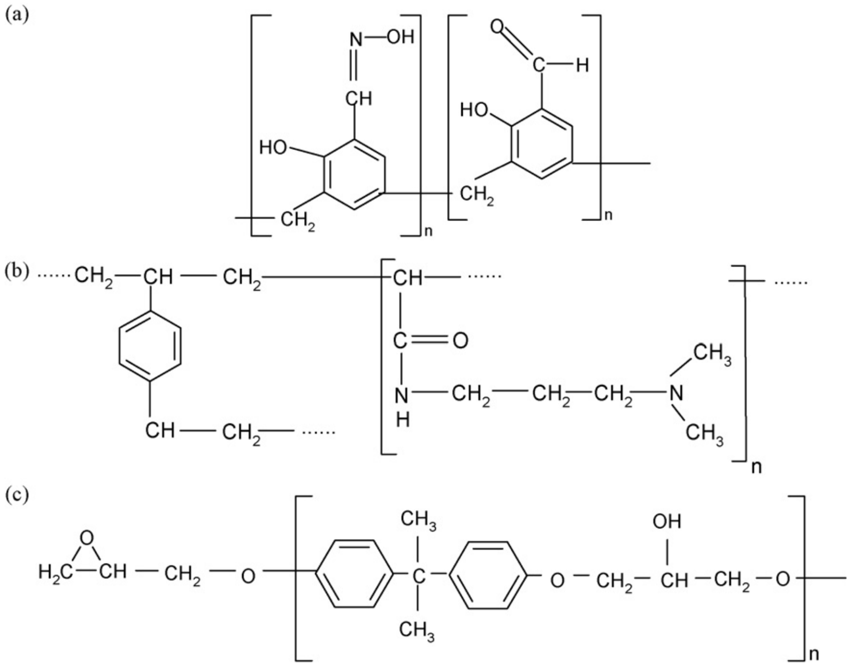

Fig. 1. Chemical structure of (a) phenol-formaldehyde, (b) acrylic and (c) epoxy-amine resins matrix.

Amberlyst A-23 is a macroporous anion exchanger including tertiary-amine functional groups on the phenol-formaldehyde matrix (Fig. 1a). It occurs in the form of granules coloured from green to grey. The total anion exchange capacity provided by the producer is equal or higher than 1.8 equiv./dm^3 (free base form). The resin water retention is in the range 60–65% and the grain size from 0.47 to 0.74 mm. The resin is stable up to 353 K.

Amberlyst A-24 possesses acrylic matrix (Fig. 1b) and the tertiary-amine functional groups. It has a gel structure, of the total ion exchange capacity $\geq$1.6 equiv./dm^3 (free base form), water retention 56–64% and transparent white beads of the size 0.7–0.95 mm.

Dowex-WGR-2 similar to Amberlyst A-23 possesses a macroporous structure. It has an epoxy-amine matrix (Fig. 1c) and preliminary, secondary and tertiary-amine groups (polyfunctionality). The total ion exchange capacity is equal to 9.6 mequiv./g (dry basis) and the beads size is in the range from 0.3 to 1.2 mm [15].

The chemical structures of the resin matrices are shown in Fig. 1.

2.4. Anion exchange experiments

The sorption of palladium(II) from the acidic solutions was investigated in the batch mode and under column conditions.

2.4.1. Batch adsorption studies

The equilibrium isotherms and kinetics of palladium(II) sorption were accomplished through the batch mode experiments which were performed in 100 cm^3 Erlenmeyer flasks by the addition of 0.05 dm^3 of palladium(II) solution into 0.05 g of the desired anion exchange resins. In all experiments, the flasks were shaken mechanically at 180 rpm on the shaker for 1–720 min at ambient temperature (295 ± 2 K). The time of 240 min was enough to reach phases equilibrium. The resin was separated by filtration after the sorption and the liquid phase was analyzed by the UV-VIS iodide method to determine concentrations of palladium(II) ions [3,16–18]. All collected values in this paper are the average of three independent experiments. The precision of the parallel measurements was ±3% standard deviation.

The sorption capacities of the weakly basic anion exchange resins were calculated from the following equations:

- Amount of palladium(II) adsorbed at time t, q_t (mg/g), q_t (mg/g):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t are the concentrations of palladium(II) in the solution at the beginning and after time t, respectively (mg/dm^3); V is the volume of the solution (dm^3); W is the mass of the dry anion exchanger (g).

- Sorption capacity, q_e (mg/g):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_e is the concentration of palladium(II) in the solution at equilibrium [16–20].

2.5. Column loading

The dynamic procedure was applied to determine the breakthrough curves of palladium(II) ions (plots C/C_0 vs. V [cm^3]; C – the concentration of Pd(II) ions in the eluate; C_0 – the initial Pd(II) concentration; V – the volume of effluent). Columns of a 1 cm diameter were filled with swollen anion exchange resins – the bed volume of the anion exchanger – 0.01 dm^3. Then the solution of initial palladium(II) concentration equal to 100 mg/dm^3 was passed through the anion exchange resins bed. The passing rate of the solutions through the column was constant and equal to 0.4 cm^3/min. During the column loading process by Pd(II) ions the eluate was collected in the fractions and the content of Pd(II) was measured. Based on the course of the breakthrough curves the values of V_p (volume of effluent to break point appearance), and U at C/C_0 = 0.5 were obtained (determined graphically) and applied to calculate the total and working anion exchange capacities as well as distribution coefficients (mass and bed).

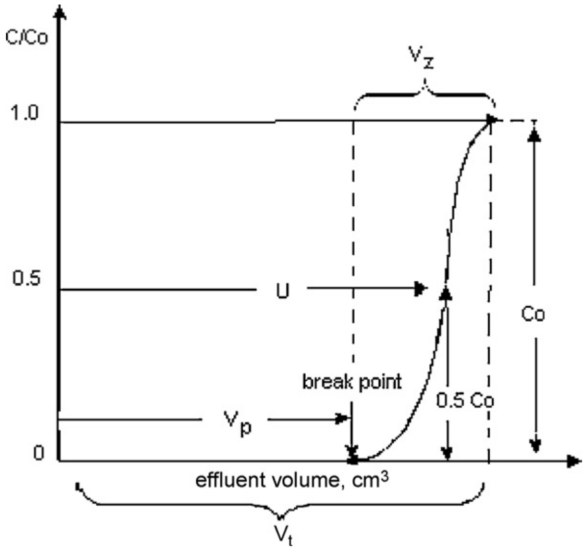

Fig. 2. Typical exchange isoplane (breakthrough curve).

The working anion exchange capacity, C_r (Fig. 2) obtained by dynamic procedures was calculated from the following equation:

$$C_r = \frac{V_p \cdot C_0}{V_j} \tag{3}$$

whereas the total anion exchange capacity, C_t (Fig. 2) from Eq. (4):

$$C_t = \frac{U \times C_0}{V_j} \tag{4}$$

where V_p – the effluent volume to the break point (dm^3), C_0 – the initial concentration of Pd(II) solution (mg/dm^3), V_j – the volume of anion exchanger in the column (cm^3) and U – the effluent volume at $C/C_0 = 0.5$ (cm^3).

The distribution coefficients, K_d, K'_d of palladium(II) were calculated, too (Eqs. (5) and (6)):

- The mass distribution coefficient:

$$K_d = \frac{U - U_0 - V_v}{m_j} \tag{5}$$

- The bed distribution coefficient:

$$K'_d = \frac{U - U_0 - V_v}{V_j} \tag{6}$$

where U_0 – the dead volume in the column (cm^3), V_v – the void (inter-particle) ion exchanger bed volume (which amounts to ca. 0.4) and m_j – the dry ion exchanger weight (g) [16,18,21,22].

During the loading process of anion exchange bed, at any time the ion exchange takes place in only a portion of bed called exchange zone or interchangeably the mass transfer zone.

Exchange zone moves down through the anion exchange bed. The direction of the moving of exchange zone and the acidic solutions (chloride or chloride–nitrate) flow are the same. After the exchange zone the anion exchange bed is exhausted whereas underneath it is still fresh. When the exchange zone reaches the end of the anion exchange bed, palladium ions leak in the effluent. Based on the column parameters and breakthrough curves the time required for the formation, t_f and moving of the exchange zone, t_m were calculated.

The time required for the formation of exchange zone can be deduced according to the following equation:

$$t_f = \frac{V_z}{U_r} \times S \tag{7}$$

where $V_z = V_t - V_p$; distinction between the total volume of effluent, V_t, and the volume collected to break point appearance, V_p (cm^3); U_r – the flow rate (cm^3/min), S – the total column cross-section area and $S = \prod r^2$ (cm^2); r – the radius of column = 0.5 cm).

The time required for moving exchange zone, t_m, was also obtained from Eq. (8):

$$t_m = \frac{V_t}{U_r} \times S \tag{8}$$

where V_t – the total effluent volume [4].

2.6. Adsorption isotherms

Among the weakly basic anion exchange resins under discussion, Amberlyst A-23 was chosen (the most efficient for Pd(II) sorption) in order to determine the sorption isotherm. The isotherm was obtained by means of the batch method (analogous for that described in Section 2.4.1). The concentrations of Pd(II) in the solutions (0.1 M HCl–1.0 M NaCl–x mg/dm^3 Pd(II)) were variable and included in the range 100–2400 mg/dm^3. The phases contact time was equal to 240 min, temperature (295 ± 2 K).

The adsorption data were analyzed in terms of Langmuir (Eq. (9)), Freundlich (Eq. (10)), and Temkin–Pyzhev (Eq. (11)) isotherm models. The characterization of the adsorption models is presented in Table 1 [23–26].

2.7. Analytical procedure – the iodide method

The iodide method was used to determine the concentration of Pd(II) during the sorption process [27,28]. In the acidic medium (HCl, H_2SO_4) containing excess of iodide (e.g. KI) palladium(II) forms a brown–red complex $[PdI_4]^{2-}$ ($[PdCl_4]^{2-} + 4KI \rightarrow [PdI_4]^{2-} + 4KCl$), which provides the basis for a moderately sensitive spectrophotometric method of determining

Table 1
Characteristics of the adsorption models.

Equilibrium adsorption models	Lineal form	Plot	Calculated coefficient
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$ (9)	C_e/q_e vs. C_e	$Q_0 = 1/\text{slope}$ $b = \text{slope}/\text{intercept}$
Freundlich	$\log q_e = \log k_F + \frac{1}{n}\log C_e$ (10)	$\log q_e$ vs. $\log C_e$	$1/n = \text{slope}$ $k_f = 10^{\text{intercept}}$
Tempkin	$q_e = \left(\frac{RT}{b_T}\right)\ln A + \left(\frac{RT}{b_T}\right)\ln C_e$(11)	q_e vs. $\ln C_e$	$b_T = (RT/\text{slope})$ $A = \exp(\text{intercept}/\text{slope})$

C_e – equilibrium concentration of palladium ions (mg/dm^3); Q_0 – Langmuir constant related to monolayer capacity (mg/g); b – Langmuir constant (L/g); q_e – sorption capacity (mg/g); k_F – Freundlich constant (mg/g); $1/n$ – Freundlich constant; R – gas constant (8.314 J/mol K); T – temperature (K); b_T – Temkin constant related to heat of sorption (J/mol); A – Temkin constant (dm^3/g).

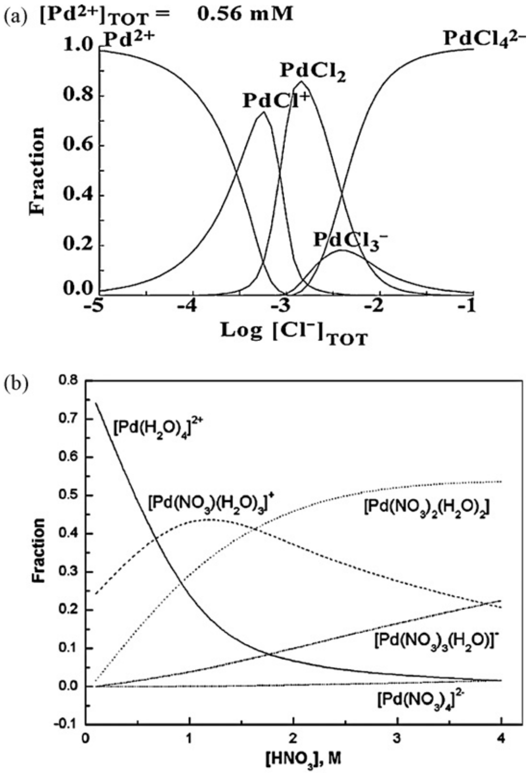

Fig. 3. Distribution graph of Pd species depending on the composition of the solutions: (a) chloride; (b) nitrate solutions.

Pd(II). The colour of the complex does not depend on the concentration of hydrochloric and sulfuric acids up to 10 M. Ascorbic acid is added usually as a reductant to reduce the iodine liberated by atmospheric oxygen. The solution containing unknown concentration of palladium(II) ions was put into a 50 cm^3 flask, then 5 cm^3 of 6 M HCl, 10 cm^3 of 20% KI solutions and 2 or 6 cm^3 of 1% (newly prepared) ascorbic acid solution depending of the solutions under investigation were added. Absorbance was measured at the analytical wavelength, $\lambda_{max} = 407$ nm in the 1-cm cell against blank test as the reference.

3. Results and discussion

3.1. Species of palladium(II) complexes

Depending on the concentration of chloride and nitrate ions palladium can form different chloride, nitrate and chloride–nitrate complexes. Due to the fact that palladium has a large tendency to undergo hydrolysis, hydrolytic species of Pd(II) complexes (aqua-complexes) occur, too.

Palladium in the chloride solutions can form stable chloride-complexes such as $[PdCl]^+$, $[PdCl_2]$, $[PdCl_3]^-$ and $[PdCl_4]^{2-}$: $Pd^{2+} + Cl^- \rightarrow [PdCl]^+$, $\log K = 6.1$; $Pd^{2+} + 2Cl^- \rightarrow [PdCl_2]$, $\log K = 10.7$; $Pd^{2+} + 3Cl^- \rightarrow [PdCl_3]^-$, $\log K = 13$; $Pd^{2+} + 4Cl^- \rightarrow [PdCl_4]^{2-}$, $\log K = 16$; $Pd^{2+} + 5Cl^- \rightarrow [PdCl_5]^{3-}$, $\log K = 14$; $Pd^{2+} + 6Cl^- \rightarrow [PdCl_6]^{4-}$, $\log K = 12$ (Fig. 3). The most stable palladium(II) chloride-complex is $[PdCl_4]^{2-}$ due to the highest value of the stability constant. 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 $[PdCl_3(OH)]^{2-}$, $[PdCl_2(OH)_2]^{2-}$, $[PdCl(OH)_3]^{2-}$ and $[Pd(OH)]^+$, $[Pd(OH)_2]$, $[Pd(OH)_3]^-$, $[Pd(OH)_4]^{2-}$. The reaction schemes of hydroxide complexes of palladium(II) are following: $Pd^{2+} + 2H_2O \rightarrow [Pd(OH)]^+ + H_3O^+$, $K = 10^{-2.3}$; $Pd^{2+} + 4H_2O \rightarrow [Pd(OH)_2] + 2H_3O^+$, $K = 10^{-4.2}$, $Pd^{2+} + 6H_2O \rightarrow [Pd(OH)_3]^- + 3H_3O^+$, $K = 10^{-12}$; $Pd^{2+} + 8H_2O \rightarrow [Pd(OH)_4]^{2-} + 4H_3O^+$, $K = 10^{-14}$ [29,30].

In the chloride–nitrate solutions containing Cl^- and NO_3^- ions, chloropalladium(II), nitratepalladium(II) and chloride–nitratepalladium(II) appear but the chemical morphology of the chloride–nitratepalladium(II) complexes is more complicated and not described in literature. In aqueous nitrate solutions palladium(II) may form a series of anionic complexes with nitrate ions: $Pd^{2+} + NO_3^- \Leftrightarrow [Pd(NO_3)]^+$; $Pd^{2+} + 2NO_3^- \Leftrightarrow [Pd(NO_3)_2]$; $Pd^{2+} + 3NO_3^- \Leftrightarrow [Pd(NO_3)_3]^-$; $Pd^{2+} + 4NO_3^- \Leftrightarrow [Pd(NO_3)_4]^{2-}$. Moreover, free palladium(II) ion $[Pd(H_2O)_4]^{2+}$ can form nitrate–hydroxide complexes of palladium(II): $[Pd(H_2O)_3(NO_3)]^+$; $[Pd(H_2O)_2(NO_3)_2]$; $[Pd(H_2O)(NO_3)_3]^-$; $Pd(NO_3)_4{}^{2-}$. In 0.1 M nitric acid medium majority of palladium exists as the free ion $[Pd(H_2O)_4]^{2+}$. Its concentration decreases with the nitric acid concentration increase. The maximum of the $[Pd(NO_3)(H_2O)_3]^+$ complex is at 1.0 M HNO_3. With the nitric acid concentration increase the portion of $[Pd(NO_3)_2(H_2O)_2]$ species increases [31–33].

3.2. ATR–FT-IR analysis

The FT-IR spectra for the weakly basic anion exchange resins Amberlyst A-23, Amberlyst A-24 and Dowex-WGR-2 before and

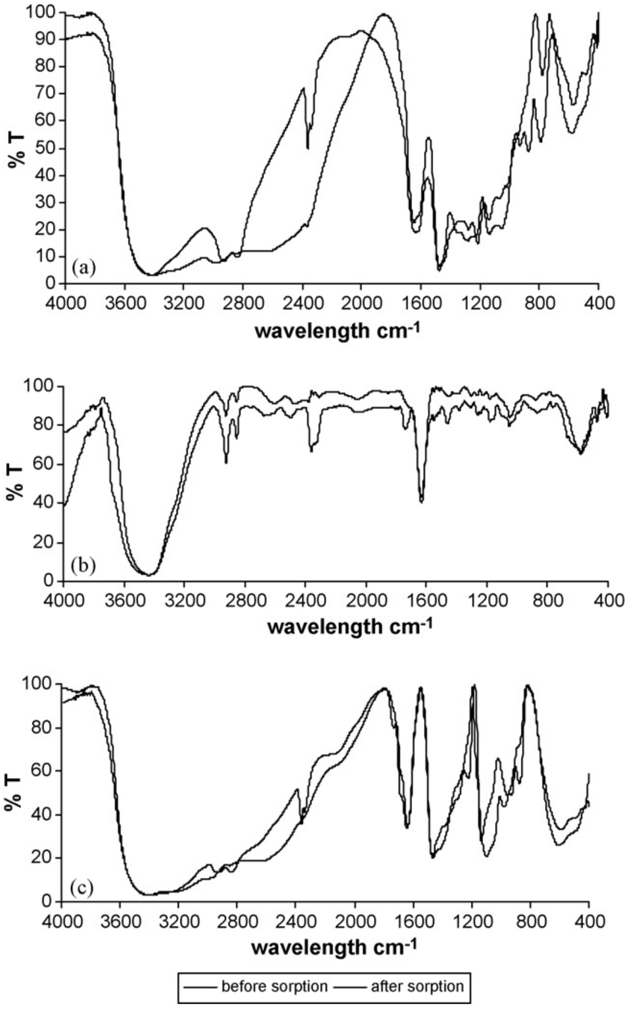

Fig. 4. ATR–FT-IR spectra before and after the sorption process of Pd(II) on (a) Amberlyst A-23; (b) Amberlyst A-24; (c) Dowex-WGR-2.

after modification by means of palladium(II) ions (after the sorption process) were recorded from 4000 to 400 cm^{-1} in order to predict the mechanism of Pd(II) sorption. The spectra of the anion exchange resins mentioned above are shown in Fig. 4.

The FT-IR spectrum of Amberlyst A-23 showed the absorption of –OH group (stretching vibration of –OH group, strong, broad peak) in the region of wavelength from 3414 to 3360 cm^{-1} (3400 cm^{-1}) (in the parenthesis the literature data of the wavenumber where the peaks of the earlier mentioned groups should occur are given). Moreover, the peaks related to stretching vibration of $-CH_2$ (alkane) at 2912 cm^{-1} (2925 cm^{-1}), vibration of C=C aromatic ring at 1612 cm^{-1} (1610 cm^{-1}), deformation vibration of $-CH_2$ group at 1462 cm^{-1} (1460 cm^{-1}), vibration of –OH group in plane at 1336 cm^{-1} (1390 cm^{-1}) are observed. The asymmetric stretching vibration of phenolic C–C–OH, vibration of C–O–C aliphatic ether and stretching vibration of $-CH_2OH$ groups occurred at 1256 cm^{-1} (1237 cm^{-1}), 1120 cm^{-1} (1100 cm^{-1}) and 1040 cm^{-1} (1045 cm^{-1}) wavenumbers, respectively. The peaks related to the substituted benzene, vibration of CH out-of plane, vibration of CH in plane, ortho-substituted and adjacent 5H at 922 cm^{-1} (976 cm^{-1}), 864 cm^{-1} (885 cm^{-1}), 780 cm^{-1} (760 cm^{-1}) and 656 cm^{-1} (694 cm^{-1}) are observed, respectively. The lack of the band related to the stretching vibration of N–H in the region from 3500 to 3200 cm^{-1} suggests that Amberlyst A-23 contains tertiary-amine functional groups [34]. In the region: 1980–2770 cm^{-1}, 2380–2270 cm^{-1} and 1000–860 cm^{-1} after the sorption process some peaks disappeared as the effect of palladium(II) complexes binding with resin. The same changes in the first two regions are also observed in the case of Dowex-WGR-2 [35,36].

The spectra for Amberlyst A-24 before and after the sorption process are similar. The peaks related to the vibration of the acrylic matrix and functional groups of resin appear at the same wavelength but their intensities are different. This fact can be explained by the fact that Pd(II) sorption process on Amberlyst A-24 is not satisfactory enough (low values of the capacities) therefore the spectra after the sorption process do not show differences compared with those before the sorption (commercial anion exchange resin is modified to a small extent). The results indicated that the sorption could be carried out by ion exchange between Pd(II) ions and hydrogen atoms of –OH, $-NH_2$ groups of anionic resins.

3.3. *Effect of phases contact time*

The influence of phases contact time on palladium(II) sorption from the chloride and chloride–nitrate solutions by the weakly basic anion exchange resins under discussion was investigated and the plots presenting the changes of the amount of Pd(II) adsorbed versus time, q_t (mg/g) vs. t (min) for Amberlyst A-23 are depicted in Fig. 5. The kinetic curve showed that the sorption of Pd(II) was rapid for the first 30 min and then slowed considerably till saturation was attained. The experimental results suggest that the amount of Pd(II) adsorbed (mg/g) increases with the increasing contact time. This tendency is observed in the case of all examined resins. This can be explained by the fact, that at the initial stage of sorption a large number of surface sites is available for palladium(II) and after a lapse of time the number of sites decreases and additionally, repulsion between the solute molecules of solid and the bulk phases occurs causing hindrance to the remaining surface sites occupied by palladium(II). Smooth, simple and continuous time variation curves indicate the monolayer coverage on the surface of anionic resins [37]. The time 250 min is enough to achieve equilibrium for

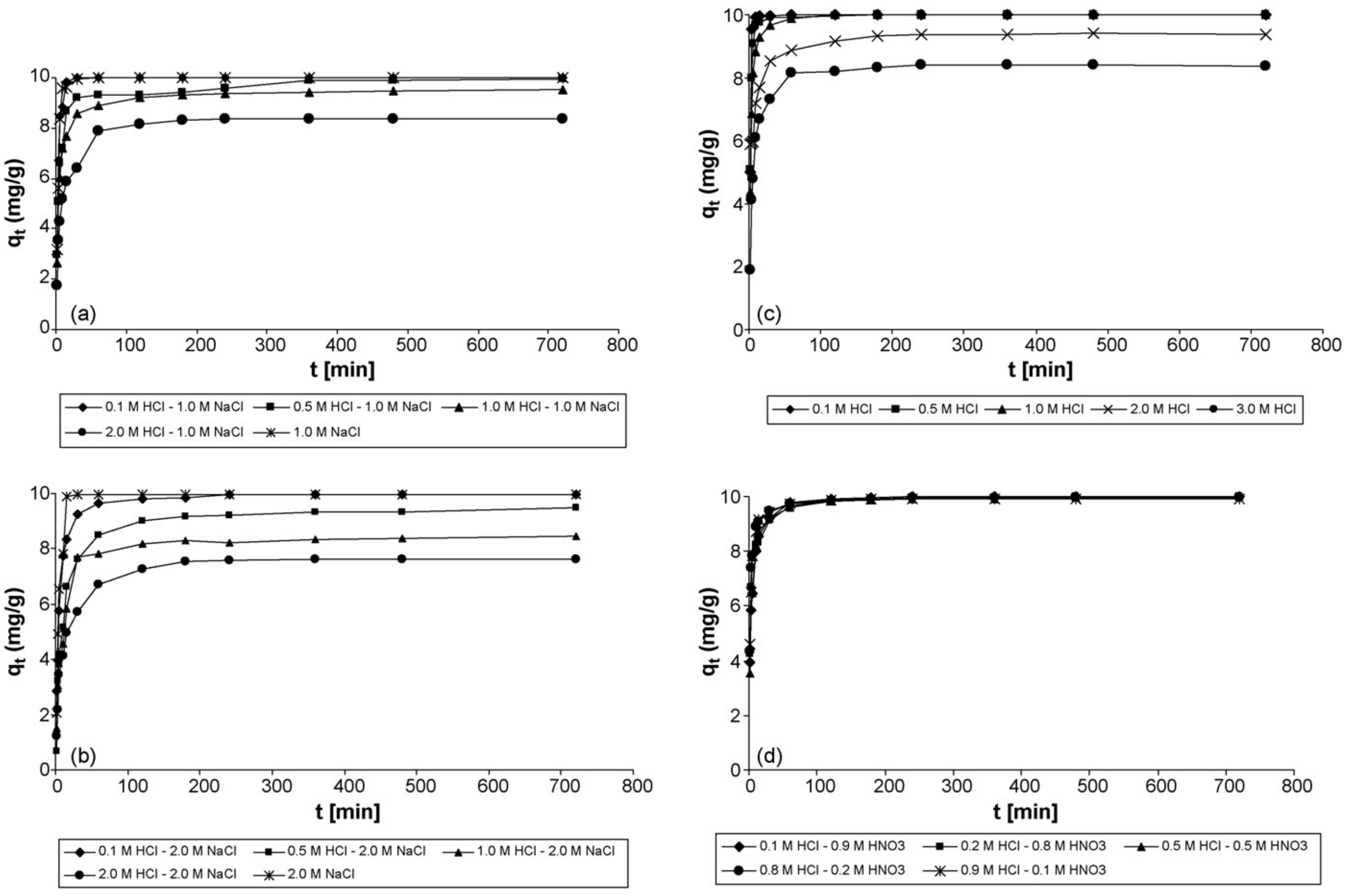

Fig. 5. Effect of phases contact time on Pd(II) sorption on Amberlyst A-23 in (a) x M HCl–1.0 M HCl; (b) x M HCl–2.0 M NaCl; (c) x M HCl; (d) x M HCl–y M HNO_3.

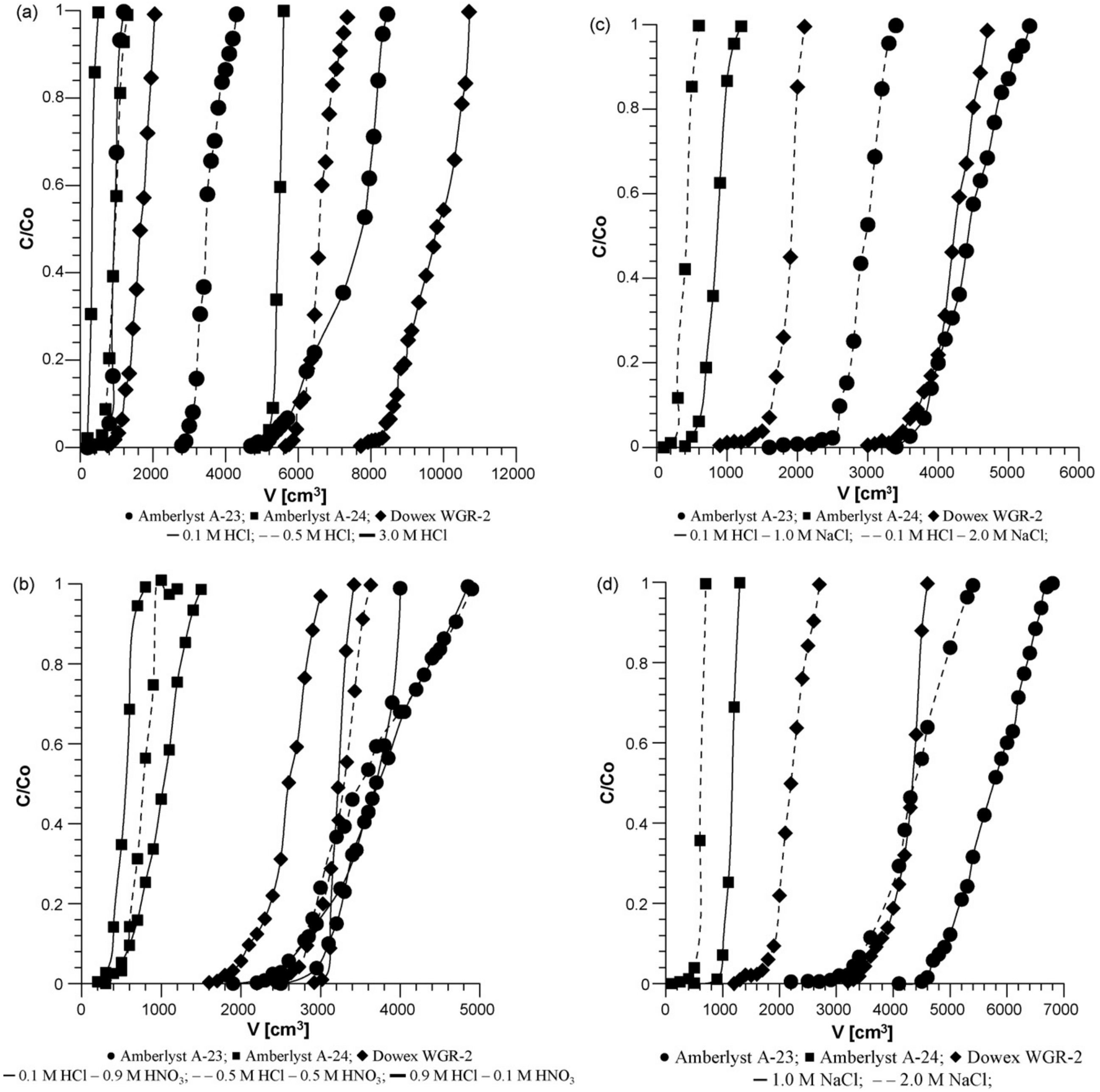

Fig. 6. Breakthrough curves of palladium(II) for (a) chloride; (b) chloride–nitrate; (c and d) chloride with sodium chloride addition solutions.

all systems and resins, therefore this equilibrium time was chosen in adsorption studies. The highest values of sorption capacities are usually observed for Amberlyst A-23 (7.61–9.99 mg/g), lower for Dowex-WGR-2 (8.70–9.99 mg/g) and much lower in the case of Amberlyst A-24; from 2.03 to 9.96 mg/g. The differences of the sorption capacities are caused by different matrix and structure of the resins. Those two factors (matrix: phenol-formaldehyde, acrylic, epoxy-amine and structure: gel or macroporous) have an effect on palladium(II) behaviour in the examined systems. All weakly basic anion exchange resins examined here possess amino groups which are helpful in the sorption process (HSAB theory, N as a donor atom). Moreover, those groups can act as a hydrogen bonding donator. The amino group on the matrix of Amberlyst A-23 and Dowex-WGR-2 can form hydrogen bonds with the hydrogen atom of the hydroxyl group. In the case of Amberlyst A-24 with the matrix without hydroxyl group hydrogen bonding interaction is negligible [15].

3.4. *Breakthrough curves of Pd(II)*

Isoplanes of palladium(II) were determined for anionic resins under discussion in order to observe progress of Pd(II) sorption process, how efficient are Pd(II) ions retained on resins. Fig. 6 depicts the comparison of a few (not all) Pd(II) isoplanes for Amberlyst A-23, Amberlyst A-24 and Dowex-WGR-2. Based on those isoplanes and Eqs. (3)–(8) the working and total anion exchange capacities, C_r, C_t, mass and bed distribution coefficients, K_d, K'_d as well as the time required for the moving and formation of the exchange zone, t_m, t_f were calculated. Table 2 present the collected values of the above mentioned parameters. Making comparison between the total and the working anion exchange capacities the total capacities possess higher values than the working anion exchange capacities. Moreover, anionic resins possess different values of capacities. This fact indicates that those resins possess different selectivity towards palladium(II) ions. Based on the working anion exchange capacities

Table 2
Comparison of sorption capacity, the mass, bed distribution coefficients and the time required for formation and moving of exchange zone.

Solution	C_r ($\times 10^{-2}$ g/cm^3)			C_t ($\times 10^{-2}$ g/cm^3)			$K_d \times 10^2$			$K'_d \times 10^2$			$t_f \times 10^3$			$t_m \times 10^3$		
	A-23	WGR-2	A-24	A-23	WGR-2	A-24	A-23	WGR-2	A-24	A-23	WGR-2	A-24	A-23	WGR-2	A-24	A-23	WGR-2	A-24
0.1 M HCl	4.7	7.7	4.8	7.8	9.8	5.5	21.88	30.04	20.16	7.76	9.80	5.46	13.35	21.00	10.99	7.36	5.85	1.57
0.5 M HCl	4.3	5.7	1.4	5.9	6.6	2.1	16.79	20.16	7.81	5.87	6.58	2.11	10.40	14.42	4.61	4.71	3.34	1.86
1.0 M HCl	2.8	3.2	0.3	3.5	4.4	1.0	10.72	13.42	3.52	3.46	4.38	0.95	7.07	9.56	2.55	2.95	3.34	1.96
2.0 M HCl	0.8	1.5	–	1.7	2.4	0.5	7.72	7.38	1.73	1.65	2.41	0.47	5.50	5.50	1.37	2.51	2.55	1.37
3.0 M HCl	0.2	0.8	–	1.0	1.7	0.3	3.41	5.03	1.18	0.95	1.64	0.32	2.16	4.02	0.98	1.96	2.55	0.98
0.1 M HCl–0.9 M HNO_3	1.9	1.6	0.1	3.7	2.6	0.6	16.58	7.95	2.01	3.72	2.59	0.55	10.60	5.89	1.57	5.79	2.75	1.37
0.2 M HCl–0.8 M HNO_3	2.1	1.7	0.2	3.8	2.6	0.7	11.26	7.96	2.48	3.74	2.60	0.67	6.67	6.02	1.96	5.31	2.75	1.57
0.5 M HCl–0.5 M HNO_3	2.2	2.3	0.3	3.5	3.3	0.8	5.96	10.08	2.84	3.50	3.29	0.77	4.32	7.12	2.16	5.30	2.55	1.57
0.8 M HCl–0.2 M HNO_3	2.8	2.9	0.3	3.5	4.1	1.0	4.00	12.46	3.51	3.46	4.06	0.95	3.14	8.42	2.26	2.17	2.75	1.67
0.9 M HCl–0.1 M HNO_3	3	2.9	0.3	3.7	3.2	1.0	2.38	9.86	3.79	3.69	3.22	1.03	1.96	6.71	2.94	2.06	0.98	2.36
1.0 M NaCl	4.5	3.2	0.5	5.8	4.3	1.2	21.88	13.27	4.26	5.76	4.33	1.15	16.59	9.03	2.55	4.51	2.75	1.57
0.1 M HCl–1.0 M NaCl	3.4	3.1	0.4	4.4	4.2	0.9	16.79	12.93	3.15	4.42	4.22	0.85	13.21	9.22	2.36	3.73	3.14	1.57
0.5 M HCl–1.0 M NaCl	2.1	2	0.3	2.8	3.0	0.6	10.72	9.22	2.15	2.82	3.01	0.58	8.44	6.87	1.47	2.94	2.94	0.88
1.0 M HCl–1.0 M NaCl	1.1	1.3	0.1	2.0	2.3	0.4	7.72	6.86	1.61	2.03	2.24	0.44	3.98	5.89	1.37	3.34	3.34	1.18
2.0 M HCl–1.0 M NaCl	0.6	0.8		0.9	1.5	0.3	3.41	4.62	1.24	0.90	1.51	0.34	2.36	4.18	0.98	0.98	2.71	0.98
2.0 M NaCl	2.9	1.3	0.3	4.4	2.2	0.7	16.58	6.73	2.36	4.37	2.20	0.64	9.52	5.30	1.37	4.91	2.75	0.88
0.1 M HCl–2.0 M NaCl	2.2	1	0.2	3.0	1.9	0.4	11.26	5.85	1.52	2.97	1.91	0.41	9.43	4.12	1.18	2.36	2.16	0.79
0.5 M HCl–2.0 M NaCl	0.8	0.8	–	1.6	1.7	0.5	5.96	5.22	1.64	1.57	1.70	0.44	9.62	4.51	1.37	2.75	2.94	1.37
1.0 M HCl–2.0 M NaCl	0.3	0.8	–	1.1	1.5	0.4	4.00	4.65	1.25	1.05	1.52	0.34	7.66	4.22	0.98	2.55	2.75	0.98
2.0 M HCl–2.0 M NaCl	0.2	0.5	–	0.6	1.1	0.3	2.38	3.36	0.99	0.63	1.10	0.27	7.85	2.94	0.98	1.57	1.96	0.98

the selectivity series are following: Dowex-WGR-2 > Amberlyst A-23 > Amberlyst A-24 (0.1–3.0 M HCl); Dowex-WGR-2 ≈ Amberlyst A-23 > Amberlyst A-24 (0.1–0.9 M HCl–0.9–0.1 M HNO_3). In the case of solution with sodium chloride addition, the series are following: Amberlyst A-23 > Dowex-WGR-2 > Amberlyst A-24 (1.0 M NaCl, 2.0 M NaCl; 0.1 M HCl–2.0 M NaCl) and Dowex-WGR-2 ≈ Amberlyst A-23 > Amberlyst A-24 for residual solutions. Amberlyst A-24 possesses the smallest values of sorption parameters. In some cases the break point of column is observed just after the sorption process starts therefore the values of working anion exchange capacities for Amberlyst A-24 cannot be determined. Differences in the capacity values come from various physicochemical properties of resins and also from different mechanism of palladium(II) binding. In the case of Amberlyst A-24 high value of capacities are observed in dilute solution such as 0.1 M HCl, and then the capacities drastically drop with increasing of hydrochloric acid concentration. This fact can be explained by the sieve effect and palladium complexes exclusion due to small sizes of micropores. Moreover, high values of capacities in the case of Amberlyst A-21 in 0.1 M HCl solutions can be caused by binding of palladium(II) complexes by amine groups of the resin in the not only superficial layer of anion exchanger but also inside resin matrix.

The nature of palladium(II) mechanism depends on such parameters as pH, anion exchange properties as well as palladium(II) metal ion properties. The pH effect on the sorption mechanism can be explained by the values of the point of zero charge (pH_{ZPC}). pH values can be lower or higher than the point of zero charge (pH_{ZPC}). In the first case at $pH < pH_{ZPC}$ the surface of resin is positively charged, whereas in the opposite situation $pH < pH_{ZPC}$ the surface of resin is negatively charged causing the attraction between resin and palladium complexes (e.g. chloro-anionic complexes of Pd) resulting in greater capacities at low pH values. Additionally, matrices of the resins under discussion with the hydroxyl groups such as phenol-formaldehyde, epoxy-amine contain a donor atom of oxygen which has also influence on efficient Pd(II) sorption.

In the acidic solutions containing hydrochloric acid and palladium ions in form of anionic chloro-complexes the sorption of hydrochloric acid as well as the sorption of above mention palladium complexes can be observed. The sorption of acid on weakly basic anion exchange resin follows a two-step mechanism. Firstly, the free ionogenic groups of the resin are protonated by H^+ ions of the acid (Eq. (12)) and in the second step the anion association (resin-salt dissociation) occurs (Eq. (13)). This mechanism can be presented by using the following equation:

$$\text{Step 1}: \quad R\text{–}NH_2 + H^+Cl^- \rightarrow RNH_3{}^+Cl^- \tag{12}$$

Protonation of the above mentioned groups results into the formation of positively charged surface due to the presence of protonated species on the surface of pore walls of resins:

$$\text{Step 2}: \quad RNH_3{}^+Cl^- + [PdCl_4{}^{2-}] \rightarrow [RNH_3{}^+PdCl_4{}^{2-}] + Cl^- \tag{13}$$

The second step – anion association is a result of electrostatic interaction between the positively charged functional groups and the negatively charged anion of the acid [15,38–41]. Bhandari et al. [38,39] believed that specific adsorption of anions of acid in the region close to the pore walls can be occurred. Minor part of the amine groups in free base form of all kinds are protonated due to the reaction with water molecules. Because of the poor dissociation of the free base form, a substantial exchange of hydroxyl ions for anions of strong acid occurs only in acidic media [42]:

$$R_1\text{–}NH_2{}^- - OH^- + H^+ + Cl^- \leftrightarrow R_1\text{–}NH_2{}^- - Cl^- + H_2O \tag{14}$$

The chloride ions can be sorbed also by pure amine group without considering its ammonia-like dissociation:

$$R_1\text{–}NH_2 + H^+ + Cl^- \leftrightarrow R_1\text{–}NH_2{}^+ - Cl^- \tag{15}$$

Based on the hard and soft acids and bases theory (HSAB), the ion exchangers of the functional groups containing one or more donor atoms such as nitrogen atoms, oxygen or sulfur atoms interact strongly with soft acids. Ions of soft metal such as palladium(II) show affinity for soft bases with the donor atoms: O < N < S. The resins examined here as those with the amine functional groups with N donor atoms can be protonated to a larger or smaller extent in the acidic solution. Amine groups may contribute to palladium chelation, but their ability to react with palladium is reduced by amino groups protonation. Therefore palladium(II) sorption mechanism can be ion exchange and electrostatic attraction of anionic palladium(II) complexes by protonated amine groups can take place. At higher pH the electrostatic repulsion between the surface sites and palladium(II) ions causes the decrease in the sorption yield of Pd(II) [25,43,44].

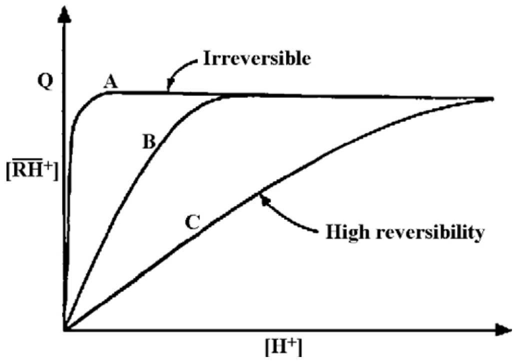

Fig. 7. Reversibility of sorption (A – typical rectangular isotherm, which depicts case of irreversible sorption; B and C – represent the medium and strong reversibility in sorption).

The differences in the selectivity of weakly basic anion exchange resins under consideration towards Pd(II) ions can be explained by different basicity of the resins and different extent of reversibility of sorption (Fig. 7) which increases with the decrease in the resin basicity and decrease in the acid concentration. Dowex-WGR-2 as anionic resin with weak basicity possess the higher extent of reversibility of protonation step according to the reversible sorption theory based on the electrical double layer than the other resins under discussion. Due to this fact this resin shows the highest values of working anion exchange capacities [15].

3.5. Effect of acids and sodium chloride concentration

Concentration of acids and sodium chloride affects Pd(II) sorption uptake. Fig. 8 shows the changes of the sorption capacities determined by means of the batch method. Different concentrations of acids and sodium chloride result in different ionic strengths of solutions and different total concentrations of chloride ions. The presented results (Fig. 8) show that sorption capacities decrease with the increase of chloride ion concentration. This fact can be explained by strong interaction taking places between the chloride ions and palladium ions to form chloro-complexes. The sodium chloride addition causes that the chloride ion concentration increase results in stronger interaction mentioned above. The same tendency: decrease of the capacities (batch method) with the increase of chloride ions is observed in the case of total and working anion exchange capacities and distribution coefficients. The values of those parameters decrease, too. In the case of chloride–nitrate solutions, the sorption parameters increase with the increasing ratio of hydrochloric acid to nitric acid. Decrease of chemical yield at higher nitric acid concentration can be caused by competitive sorption between NO_3^- and $H(NO_3)_2^-$. Summing up, in the chloride–nitrate solution competitive sorption mentioned earlier can take place concurrently [25,39].

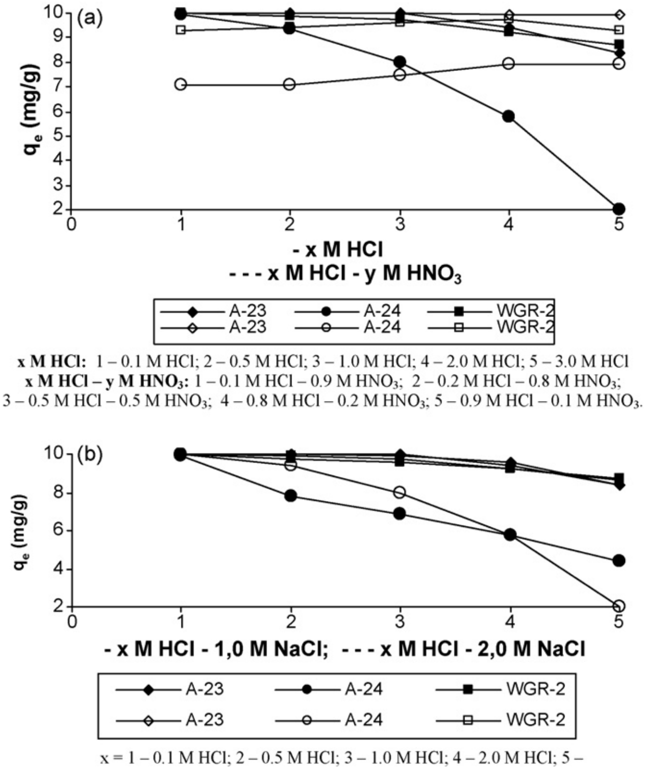

Fig. 8. Influences of (a) acids concentration; (b) sodium chloride concentration on Pd(II) sorption.

3.6. Equilibrium and adsorption studies

The sorption equilibrium data were fitted for the linear Langmuir, Freundlich and Tempkin–Pyzhev isotherms (Fig. 9). The Langmuir isotherms suggest that uptake occurs on a homogeneous surface by monolayer sorption without interaction between the sorbed molecules. The coefficient of determination (R^2) was found to be 0.9926, indicating that the sorption process of Pd(II) ions on Amberlyst A-23 fitted well with the Langmuir model. In other words, the sorption of Pd(II) took place at the functional groups/binding sites on the surface of the weakly basic anion exchange resin which is regarded as the monolayer sorption. The maximum sorption capacity of Pd(II) in the case of Langmuir isotherm is found to be 173.4 mg/g, whereas the Langmuir constant – b parameter is equal to 0.034 dm^3/mg. Additionally, the important parameter, R_L, called the equilibrium parameter was calculated to identify whether sorption system is favourable or unfavourable:

$$R_L = \frac{1}{1 + bC_0} \tag{16}$$

The R_L values between 0 and 1 indicate a favourable sorption process. In the case of Pd(II) sorption on Amberlyst A-23 the R_L value is equal to 0.226 which means that the sorption is favourable.

The Freundlich model assumed heterogenous sorption due to the diversity of the sorption sites or the diverse nature of the metal ions sorbed, free of hydrolyzed species. Additionally, the sorption may be accompanied by interaction between the sorbed molecules. $1/n$ value in the range of 0–1 indicates that the sorption was favourable in the conditions under investigation. The

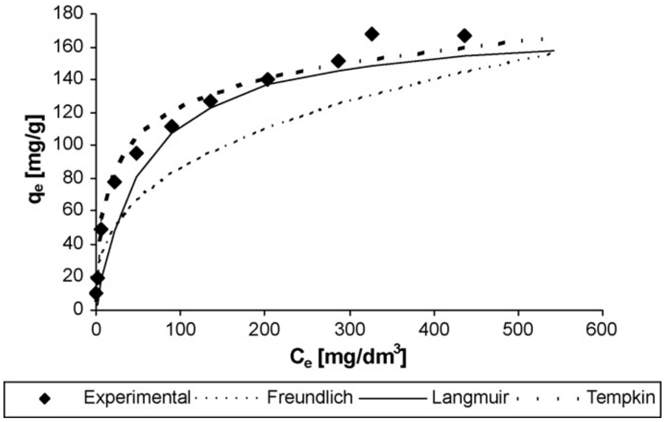

Fig. 9. Adsorption isotherms of Pd(II) ions onto Amberlyst A-23.

Freundlich parameters (see Table 2) are following: $1/n = 0.3912$; $K_F = 17.68$ mg/g. The R^2 value was found to be 0.939. This result indicates that the Freundlich model was not able to describe adequately the relationship between the sorbed amount of Pd(II) and its equilibrium concentration in the solution. However, the Langmuir isotherm model best fitted with the equilibrium data since it presents higher R^2 value.

The Tempkin and Pyzhev model was applied, too. They studied the interaction of the adsorbent and the adsorbate and suggested that the heat of sorption of all molecules in the layer decreased linearly with the coverage. The calculated parameters from the Tempkin and Pyzhev isotherm are following: the correlation coefficient is equal to 0.9817, $b_T = 99.87$ J/mol and $A = 1.44$ dm^3/g.

Summing up the Langmuir isotherm fitted the best experimental and calculated data of the sorption system (Fig. 9).

3.7. Comparison of the obtained results and those included in [11,12,45]

Making comparison between sorption of palladium(II) ions on strongly (Dowex MSA-1, Varion ATM – type 1, Dowex MSA-2, Varion ADM – type 2) and weakly basic (Varion ADAM, Amberlyst A-23, Amberlyst A-24 and Dowex-WGR-2) anion exchange resins from chloride and chloride–nitrate(V) solutions the following conclusion can be made:

- The values of working anion exchange capacities are different for the resins under consideration.
- In the solution of the composition 0.1 M HCl–100 mg/dm^3 Pd(II) the selectivity series is following: Varion ADAM (0.093 g/cm^3) > Dowex-WGR-2 (0.077 g/cm^3) > Dowex MSA-1 (0.062 g/cm^3) > Dowex MSA-2 (0.056 g/cm^3) > Varion ATM (0.049 g/cm^3) ≈ Varion ADM (0.048 g/cm^3) = Amberlyst A-24 (0.048 g/cm^3) ≈ Amberlyst A-23 (0.047 g/cm^3). The similar selectivity is observed for the other solutions.
- The weakly basic anion exchange resins with the epoxy-amine and polyacrylic matrix and the macroporous structure (Varion ADAM and Dowex-WGR-2) possess the best selectivity towards palladium(II) ions.
- Resins with the polyacrylic matrix but a different structure such as Varion ADAM (macroporous) and Amberlyst A-24 (gel) showed extremely different selectivity towards Pd(II) ions. Amberlyst A-24 cannot be used in Pd(II) removal from solution under discussion. This can be due to different sizes of their macro- and micropores and the sieve effect. Adsorption in micropores is usually strong on condition that the molecules are not too big to be able to get into pores. In the case of Pd(II) ions which occur in chloride solutions in the form of big, anionic chloro-complexes, the micropores are too small for the Pd(II) anion get into and the adsorption of Pd(II) ions is strongly affected by the sieve effect causing a significant decrease in capacities.

4. Conclusions

- Weakly basic anion exchange resins exhibit different selectivity towards palladium(II) complexes. Amberlyst A-23 with the phenol-formaldehyde matrix as well as Dowex-WGR-2 with the epoxy-amine matrix can be applied in palladium(II) sorption, recovery from secondary sources or in Pd(II) preconcentration.
- The obtained capacities for Amberlyst A-24 are much lower than for the others under discussion, therefore this resin is not suitable for Pd(II) sorption from the acidic, concentrated solutions. The sieve effect can play a big role here.
- Based on the working anion exchange capacities the selectivity series are following: Dowex-WGR-2 ≈ Amberlyst A-23 > Amberlyst A-24.
- The mechanism of palladium(II) sorption can be ion exchange and ionic interaction is due to protonation of amine groups present in the resins.
- The experimental data was well fit by the Langmuir isotherm model, the monolayer sorption capacity for Amberlyst A-23 is equal to 173.4 mg/g.
- FT-IR analysis confirms that the amine groups participate in palladium binding.

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