Comparison of Varion resins selectivity towards palladium(II) ions in hydrochloric acid solutions with sodium chloride addition

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Ion exchange is Ion exchange is found more and more significant importance in metal processing, and hydrometallurgy in general, not only for the removal of impurities but also for the preconcentration process of metal ions. The ion exchange method (dynamic method) was applied in the preconcentration of palladium(II) ions from the chloride solutions with sodium chloride addition. Varion resins such as the strongly basic anion exchange resins: Varion ADM and Varion ATM and the weakly basic anion exchange resin Varion ADAM were taken into account during the sorption process. The selectivity series were obtained based on the breakthrough curves of palladium(II) ions determined by means of dynamic method. Moreover, the distribution coefficients: weight and bed as well as the working anion exchange capacities were calculated. From the Varion resins — Varion ADAM is the most promising in the preconcentration of Pd(II).

Keywords and phrases: palladium(II), sorption, Varion resin, strongly and weakly basic anion exchange resins.

Introduction

Ion exchangers is the name given to insoluble electrolytes containing labile ions that easily exchange with other ions from the surrounding solutions. During the exchange reaction no major physical change in the electrolytes' own structure occurs. Ion exchange chromatography has become a valuable and sometimes irreplacable method of metal ions separation, purification and recovery from waste materials in chemical technology. This is possible owing to the common use of ion--exchange resins available on market. Today there are many different industrial applications of ion exchangers, mostly for water purification and waste treatment e.g. softening (removal of hardness), silica removal, demineralizing and deionizing of water, alkalinity reduction, treatment of trade effluents, separation of ion mixtures [1].

Strongly and weakly basic anion exchange resins found many applications among others, in the recovery and preconcentration process of noble metal ions. The aim of this paper was to study the possibilities of palladium(II) recovery using the strongly basic anion exchange resins such Varion ADM, ATM and the weakly basic one Varion ADAM. The sorption process of palladium(II) ions from the chloride (0.1–3.0 M HCl) [2] and chloride-nitrate(V) [3] solutions on the above mentioned Varion resins was considered previously. The continuation of the studies was also examining the sorption behaviour of Pd(II) on Varion resins in the chloride solutions with sodium chloride addition. The choice of solution was connected with the fact that before determination of low concentration of noble metals in different types of samples, decomposition and dissolution steps are indispensable. One of these methods is the chlorination method. The procedure of the chlorination method consist in heating samples with sodium chloride in a current of chlorine at 850 K. Then Platinum Group Metals (PGMs) can be readily converted to water-soluble sodium salts which are dissolved in weak acid or water and thus separated from the chlorination--resistant and water-insoluble constituents. Due to this fact PGM metals usually exist in the chloride solutions [4].

Experimental

In the studies of palladium(II) ions sorption from the chloride solutions with sodium chloride addition onto Varion resins the dynamic method was used. The

Table 1. Characteristics of the dynamic method and parameters obtained based on the breakthrough curves of Pd(II).

Description	Parameters	Symbol	Equation
— anion exchanger preparation (transformed OH^- form into the Cl^- form) — column packing (amount of resin-10 cm^3) — solutions passing through the resin bed (flow speed 0.4 cm^3/min) — collecting the eluate into fractions — determination of Pd(II) content — determination of breakthrough curves — calculation of sorption parameters	Working ion exchange capacity	C_r (g/cm^3)	$C_r = (V_p \cdot C_o)/V_j$ (1)
	Mass distribution coefficient	D_m	$D_m = (U - U_o - V_v)/m_j$ (2)
	Bed distribution coefficient	D_v	$D_v = D_m d_z$ (3)

C_o — initial concentration of Pd(II) ions (mg/dm^3); V_p — collected volume of effluent between the first fraction and that to the breakthrough point (cm^3), V_j — volume of the anion exchanger bed put into the columns (10 cm^3), U — effluent volume at C = 0.5 C/C_o (cm^3), U_o — dead volume in the column (cm^3), V_v — void (inter-particle) anion exchanger bed volume, m_j — dry anion exchanger weight (g), d_z — anion exchanger bed density.

Table 2. Characteristics of Varion resins [2–3].

Description	Varion ATM	Varion ADM	Varion ADAM
Structure	Macroporous	Macroporous	Macroporous
Type	Strongly basic	Strongly basic	Weakly basic
Functional groups	- $N^+(CH_3)_3$	- $N^+(CH_3)_2C_2H_4OH$	- $N(CH_3)_2$
Ionic form as shipped	Cl^-	Cl^-	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/cm^3]	1.2	1.2	1.2

breakthrough curves were obtained and the following parameters were calculated: working anion exchange capacities, weight and bed distribution coefficients. The description of the applied method with characterization of parameters is shown in Table 1 whereas the physicochemical properties of anion exchange resin are used in Table 2.

The composition of chloride solutions with sodium chloride addition was following: 0.1–2.0 M HCl — 1.0 M NaCl — 100 μg/cm^3, 0.1–2.0 M HCl — 2.0 M NaCl — 100 μg/cm^3. The content of palladium(II) ions in the eluate was determined by means of the iodide method.

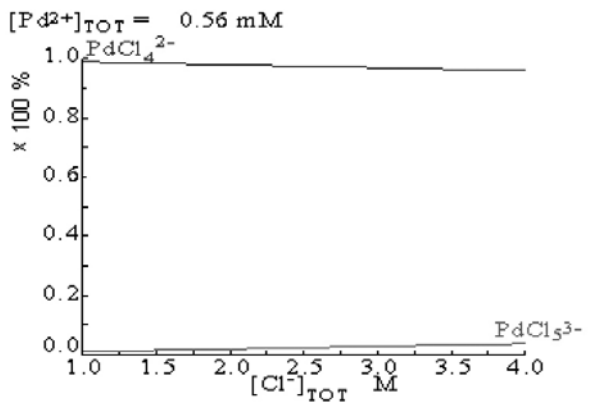


Fig. 1. Distribution graph of Pd(II) species in the HCl — NaCl — Pd(II) solution (based on the program Hydra Medusa: Make Equilibrium Diagrams Using Sophisticated Algorithms).

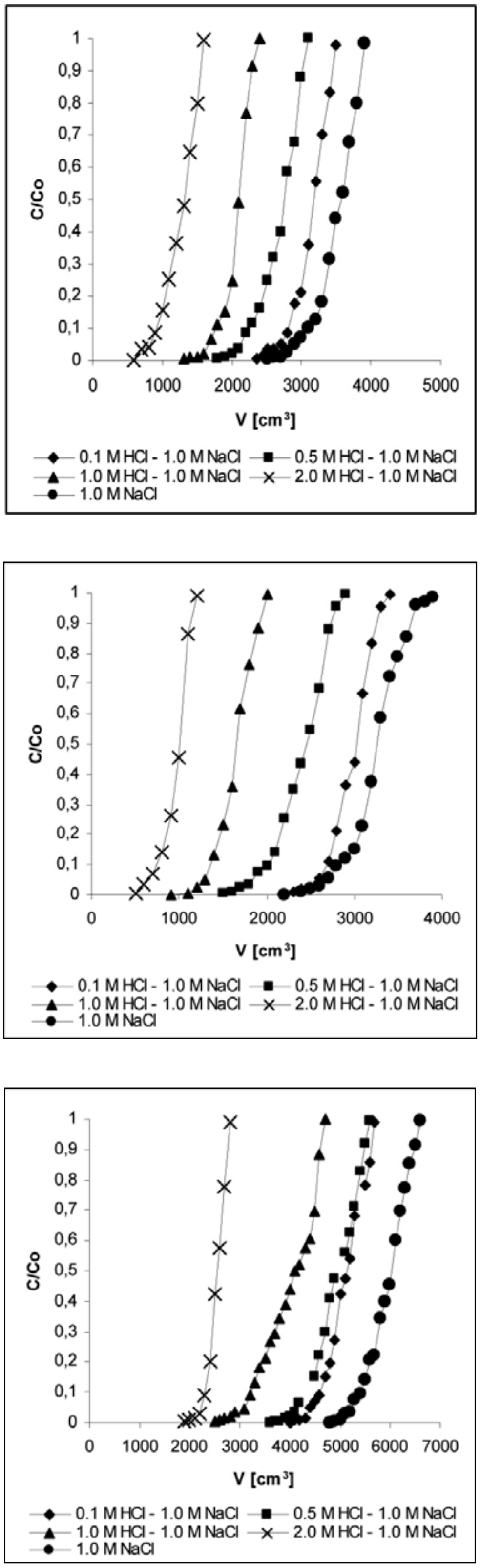
Results and discussion

Palladium in chloride solutions with NaCl addition occurs in the form of anionic chloro complexes type $PdCl_4^{2-}$ (Fig. 1). Due to this fact anion exchange resins are suitable for the recovery process of Pd(II).

Fig. 2. presented the breakthrough curves of palladium(II) ions sorption onto Varion resins from the solutions with 1.0 M NaCl addition. Based on these breakthrough curves the sorption parameters were calculated and presented in Table 3. As follows from the Fig. 2 and Table 3 palladium(II) sorption depends on the concentration of hydrochloric acid and sodium chloride addition. The capacities and distribution coefficients decrease with an increase of the HCl and NaCl concentration. D_m and D_v start at a maximum and drop with the increasing hydrochloric acid strength due to the increasing competition between Cl^- and metal-complex anions. These competitions lead to a reduced capacity, too.

The selectivity series of Varion resins in solutions under discussion can be presented in the following order:

Varion ADAM > Varion ADM > Varion ATM.



a)

b)

c)

Fig. 2. Breakthrough curves of palladium(II) ions sorption onto a) Varion ADM, b) Varion ATM, c) Varion ADAM.

The calculated values of the working capacities for Varion ADAM are higher if compared to Varion ADM, ATM. The differences in the values of the working ion-exchange capacities 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.

In the case of the strongly basic anion exchange resins palladium(II) mechanism binding can be presented as follows [5]:

$$2\ R\text{-}N(CH_3)_3^{+}Cl^{-} + [PdCl_4]^{2-} \rightarrow RN(CH_3)_3^{+}]_2[PdCl_4]^{2-} + 2\ Cl^{-} \qquad (1)$$

whereas for Varion ADAM protonation of amine functional groups occurred and the electrostatic interaction taking place:

$$R - NH_2 + H^{+},Cl^{-} \rightarrow RNH_3^{+}Cl^{-} \qquad (2)$$

$$2RNH_3^{+}Cl^{-} + [PdCl_4]^{2-} \rightarrow [RNH_3^{+}]_2[PdCl_4^{2-}] + 2Cl^{-} \qquad (3)$$

The morphology of the surface of resins beads before and after sorption of Pd(II) are shown in Fig. 3. The heterogeneity and porous structure are different for the Varion ADAM resin before and after sorption process. Surface of resin after sorption process is more smoothing than before sorption — effect of Pd(II) binding with resin, the pores of the resins are "stopping".

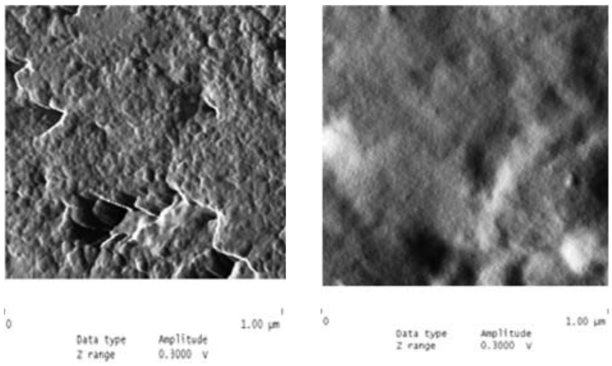


Fig. 3. AFM pictures of resin Varion ADAM before and after sorption process of Pd(II).

Summing up the Varion resin are suitable for palladium(II) metal recovery, and the highest selectivity towards Pd(II) showed Varion ADAM.

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Table 3. Sorption parameters for Varion resins.

Solutions	Anion exchanger	Mass distribution coefficient, D_m		Bed distribution coefficient, D_v		Working ion exchange capacity, C_w [g/cm³]	
		x = 1	x = 2	x = 1	x = 2	x = 1	x = 2
x M NaCl	Varion ADM	1099.3	698.5	356.6	226.6	0.0250	0.0130
0.1 M HCl — x M NaCl		976.0	665.5	316.6	215.9	0.0235	0.0130
0.5 M HCl — x M NaCl		841.9	559.8	273.1	181.6	0.0180	0.0100
1.0 M HCl — x M NaCl		646.1	450.1	209.6	146.0	0.0130	0.0075
2.0 M HCl — x M NaCl		402.6	299.9	130.6	97.3	0.0050	0.0040
x M NaCl	Varion ATM	1027.1	1027.1	325.4	325.4	0.0230	0.0156
0.1 M HCl — x M NaCl		953.9	953.9	302.2	302.2	0.0220	0.0100
0.5 M HCl — x M NaCl		774.6	774.6	245.4	245.4	0.0150	0.0110
1.0 M HCl — x M NaCl		519.9	519.9	164.7	164.7	0.0110	0.0075
2.0 M HCl — x M NaCl		317.2	348.8	100.5	110.5	0.0050	0.0040
x M NaCl	Varion ADAM	1480.1	1030.5	602.4	419.4	0.0490	0.0290
0.1 M HCl — x M NaCl		1260.9	974.0	513.2	396.4	0.0400	0.0290
0.5 M HCl — x M NaCl		1216.7	856.5	495.2	348.6	0.0380	0.0240
1.0 M HCl — x M NaCl		1013.3	722.9	412.4	294.2	0.0250	0.0175
2.0 M HCl — x M NaCl		625.1	532.7	254.4	216.8	0.0190	0.0100

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