Equilibrium and kinetic studies of palladium(II) ions sorption onto Dowex resins

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Palladium(II) sorption was studied in hydrochloric acid solutions with sodium chloride addition onto Dowex MSA-1 and Dowex MSA-2 resins by means of the static method. The dependence between the amount of palladium(II) ions sorbed at time t in a disequilibrium state (q_t) as well as the sorption capacities (q_e) and phases contact time were obtained. The results were applied in kinetic studies using the pseudo-first (Lagergren equation) and pseudo-second order kinetic equations (linear form of Blanchard equation proposed by Ho, PSO). Moreover, the equilibrium studies were caried out at ambient temperature and fitted to the Langmuir and Freundlich isotherms. The AFM pictures of the surface of anion exchange resins before and after the loading process were also recorded. Both resins exhibit high selectivity towards palladium(II) ions. The sorption capacities are in the range 7–10 mg/g for both resins under discussion in all examined solutions. The pseudo-second order kinetic equation and the Langmuir isotherm show the best fit with the experimental data.

Keywords and phrases: palladium, sorption, pseudo-first order kinetic equation, pseudo-second order kinetic equation, isotherms.

Introduction

Anion exchange resins are well estabilished materials for the separation of metal ions e.g. platinum metal ions (PGMs). The rate of the anion exchange process is very important due to the practical, economical and industrial points of view. Due to the fact that the exchange-rate can be one of the factors limiting applicability of anion exchange resins, a lot of attention is also paid to kinetic and equilibrium studies of sorption systems. Various kinetic equations based on the concentration of solute [1, 2] and also those based on the concentration of sorbent [3–7] are used to describe the sorption processess on different types of sorbents. Among these models, the Lagergren [3] as well as Blanchard [6] equations are frequently used to describe the sorption system. The Lagergren equation was for the first time proposed in 1898 in order to describe the adsorption of carboxylic acids on wood carbon. In the literature concerning kinetics of adsorption process from solutions the name Lagergren equation is used as frequently as the pseudo-first order equation. Different theoretical interpretation of the above mentioned equation is well known e.g. by

Boyd [8], Azizian [9], Liu [10] and McKay, Allen [11]. Boyd and coworkers provided the pseudo-first order kinetic equation based on the mechanism of the ion exchanger on the boundary aqueous solution/zeolite layer with the following assumptions: (1) rate of the adsorption is expressed as the differences between the exchange rate reactions of A ion to B and B ion to A, (2) reaction stoichiometry is 1 to 1, (3) concentration of ions in solution is independent of time. Based on the classical kinetic theory of Langmuir adopted for the solid/solutions system and the assumptions that (1) adsorption rate is proportional to the concentration of adsorbate and the amount of unoccupied sites, (2) concentration of adsorbate is independent of time, the kinetic model of the Langmuir equation is reduced to the pseudo-first one. This interpretation proposed by Azizian related only to the homogenous surface. Liu's interpretation of the pseudo-first order kinetic equation related also to the adsorption process onto the homogeneous structure. The adsorption rate is proportional to the concentration of adsorbate in solutions whereas the desorption of adsorbate to the amount of the occupied adsorption sites. The total

adsorption rate can be controlled by the diffusion rate of adsorbate through "liquid film" surrounding the particle of adsorbate and the equilibrium state can be described by the Henry equation. When the above mentioned conditions are satisfied McKay and Allen obtained the expression which is in accordance with the pseudo-first order kinetic equation from the mathematical point of view.

The pseudo-second order kinetic equation (PSO) was proposed by Blanchard [6] in 1984 for the exchange reaction of divalent metallic ions onto NH_4^+ ions fixed zeolite particles and is one of the most frequently used kinetic equation to describe the entire period for most of the sorption systems solution/solid. More information about applicability of the Ho's pseudo-second order kinetic equation to various sorption systems is included in [12].

Experimental

Characteristics of strongly basic anion exchange resins

Characteristics of strongly basic anion exchange resins: The two strongly basic anion exchange resins Dowex MSA-1 and Dowex MSA-2 were used in the equilibrium and kinetic studies of sorption of palladium(II) ions from the chloride solutions with the macrocomponent addition. The basic properties of resins under discussion are presented in Table 1.

Table 1. Characteristics of Dowex resins [13].

Description	Dowex MSA 1	Dowex MSA 2
Structure	Macroporous	
Type	Strongly basic, type 1	Strongly basic, type 2
Functional groups	Trimethyloammonium -N⁺(CH₃)₃	Dimethyl-hydroxyethyl- quaternary ammonium -N⁺(CH₃)₂C₂H₄OH
Maximum operating temperature [K]	342	350
Matrix	Polystyrene-divinylbenzene	
Water retention [%]	56–64	48–56
Operating pH range	0–14	0–14
Total exchange capacity [eq/dm³]	1.0	1.1

Batch method — palladium(II) sorption

The batch method was applied in the studies of palladium(II) sorption from the chloride solutions with the macrocomponent addition (0.1–2.0 M HCl — 1 M NaCl — 100 μg/cm³, 0.1–2.0 M HCl — 2 M NaCl —

100 μg/cm³). The procedure of Pd(II) sorption was following: drying of resin, preparation of solutions, weighing resin (0.5 g), shaking mechanically (0.5 g resin + 0.05 dm³ solution, speed = 180 rpm, time 1–720 min), separation of phases (filtration), determination of Pd(II) concentration using the iodide method and calculation of sorption parameters such as: the amount of palladium(II) ions sorbed at time t (q_t) and the sorption capacities (q_e) using the following equations:

$$q_t = (C_o — C_t)V/W \qquad (1)$$

$$q_e = (C_o — C_e)V/W \qquad (2)$$

where: C_o — the initial concentration of palladium(II) ions (mg/dm³),

C_e — the equilibrium concentration of palladium(II) ions (mg/dm³),

V — volume of solutions (0.05 dm³),

W — weight of dry anion exchanger (0.5 g).

Equilibrium and kinetic studies

The obtained results were analyzed using the linear form of the pseudo-first and pseudo-second order kinetic equations (Table 2). Equation (4) was reported by Ho to explain the sorption kinetics of divalent metal ions onto peat particles assuming chemisorption. Moreover, the equilibrium studies were carried out by means of static method. The procedure was analogous for the batch method (subchapter 1.2) but the concentration of palladium(II) ions in the chloride solutions was changeable in the range 100–2800 μg/cm³. The Langmuir and Freundlich isotherm equations are presented in Table 2.
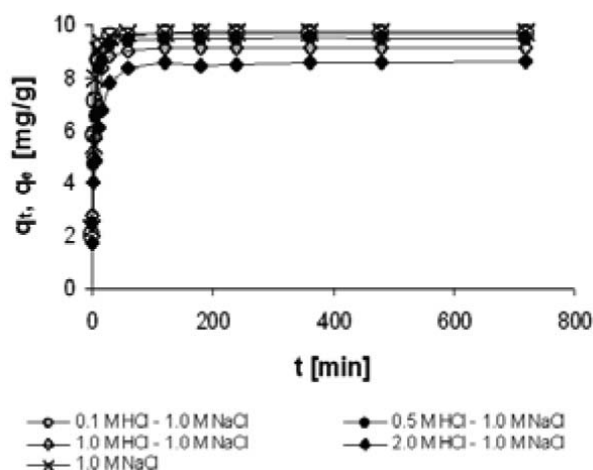
Results and discussion

The strongly basic anion exchange resins Dowex MSA-1 and Dowex MSA-2 can be applied in the sorption, recovery or preconcentration processes of palladium(II) ions due to the high selectivity of both resins towards these ions. Dowex MSA-1 shows slightly higher sorption capacities than the other one. The selectivity series obtained based on the q_e values are following: Dowex MSA-1 > Dowex MSA-2. The values of sorption capacities drop with the hydrochloric acid increase in the range from 0.1 to 2.0 M and with the sodium chloride addition. Moreover, the amount of palladium(II) complexes increases with the phases contact time increase [13]. The changes of the values of q_e and q_t depending on the phases contact time and concentration of hydrochloric acid and sodium chloride are depicted in Figs. 1–2.
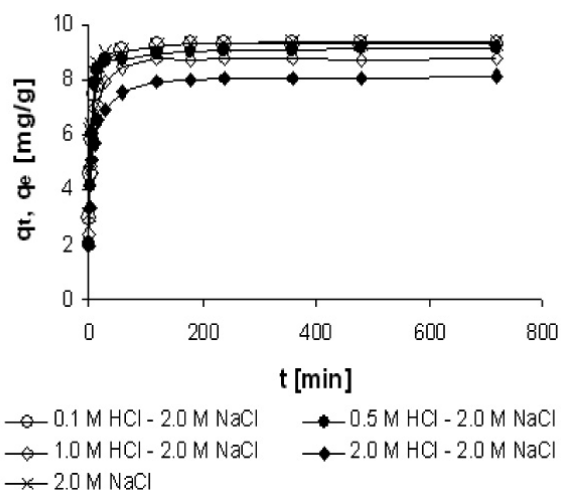
Table 2. Characteristics of the kinetic and isotherm equations [14].

Adsorption models	Linear form	Plot	Calculated parameters	Eq. no
Reaction-base kinetic models				
Lagergren	$log(q_e - q_t) = log\ q_e - (k_1/2.303)\ t$	$log(q_e-q_t)$ vs. t	$k_1 = -2.303 \times slope$ $q_e = 10^{intercept}$	(3)
Ho	$t/q_t = 1/k_2q_e^2 + (1/q_e)\ t$	t/q_t vs. t	$q_e = 1/slope$ $k_2 = slope^2/intercept$ $h = k_2q_e^2$	(4) (5)
Equilibrium isotherm models				
Langmuir	$C_e/q_e = 1/Q_ob + C_e/Q_o$	C_e/q_e vs. C_e	$Q_o = 1/slope$ $b = slope/intercept$	(6)
Freundlich	$log\ q_e = log\ k_F + 1/n\ log\ C_e$	$log\ q_e$ vs. $log\ C_e$	$1/n = slope$ $k_F = 10^{intercept}$	(7)

where: q_e, q_t — sorption capacity of Pd(II) complexes at equilibrium and at time t (mg/g); k_1 — rate constant of Lagergren equation (1/min) k_2 — rate constant of Ho equation (g/mg min); h — initial sorption rate, (mg/g min); C_e — equilibrium concentration of palladium ions (mg/dm^3) ; Q_o — Langmuir constant related to the monolayer capacity (mg/g) ; b — equilibrium constant of Langmuir (L/g) ; k_F — Freundlich constant (mg/g); 1/n — Freundlich constant.

a)

Fig. 2. Comparison of palladium(II) complexes sorption capacities for the solutions with 1.0 M NaCl and 2.0 M NaCl for Dowex MSA-1.

b)

Fig.1. Effect of phases contact time and composition of solutions on the sorption process of palladium(II) complexes from chloride solutions with a) 1.0 M NaCl and b) 2.0 M NaCl addition onto Dowex MSA-1.
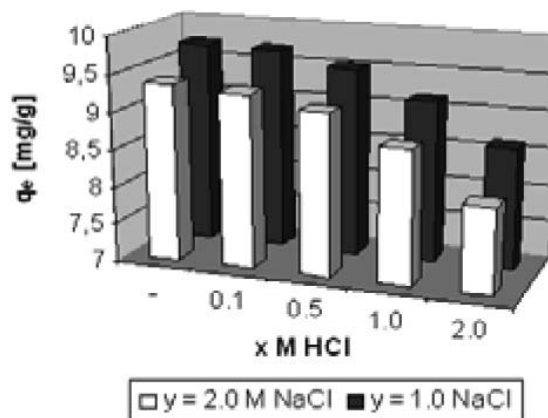
Effectiveness of the Pd(II) sorption process was confirmed by the AFM pictures of both resins before and after the sorption process. As follows from Fig. 3 morphology of the surface of resin beads is slightly different for the resins after the sorption process. After sorption of Pd(II) the structure of the resins is less porous than that before sorption. The comparing the commercially Dowex resins it can be stated that the difference between their structures before sorption is really small available.

The pseudo-first and pseudo-second order kinetic equations were applied to fit the experimental results. The corresponding parameters (Table 3) of these kinetic models were determined by linear regression of the plots. The correlation coefficients, R^2 of the plots t/q_t vs. t indicate that the pseudo-second order kinetic equation well describe the sorption process of Pd(II) complexes whereas the pseudo-first order kinetic equation can not be applied in the Pd(II) sorption system kinetic description. Moreover, the experimental sorption
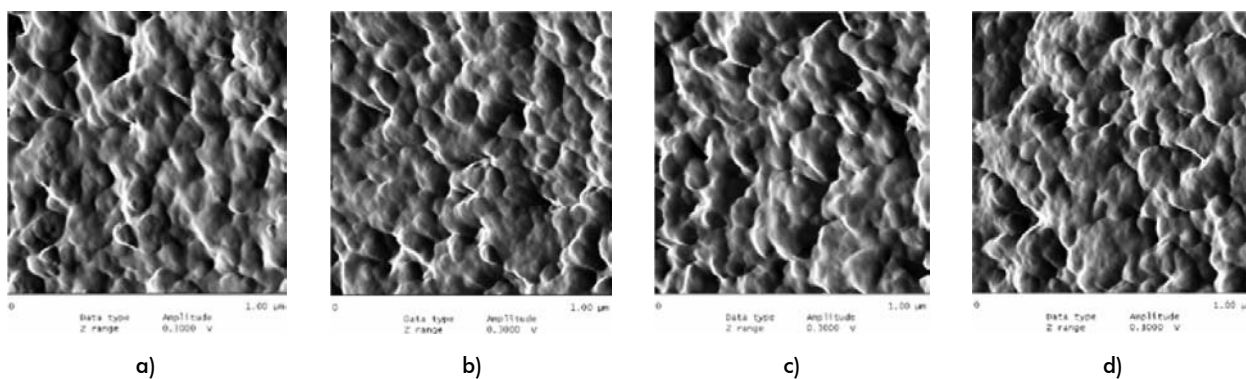
Fig. 3. AFM pictures of a-b) Dowex MSA-1 and c-d) Dowex MSA-2 resins a, c) before and b, d) after the sorption process of Pd(II) ions.

Table 3. Kinetic parameters obtained for the pseudo-first and pseudo-second order kinetic equations.

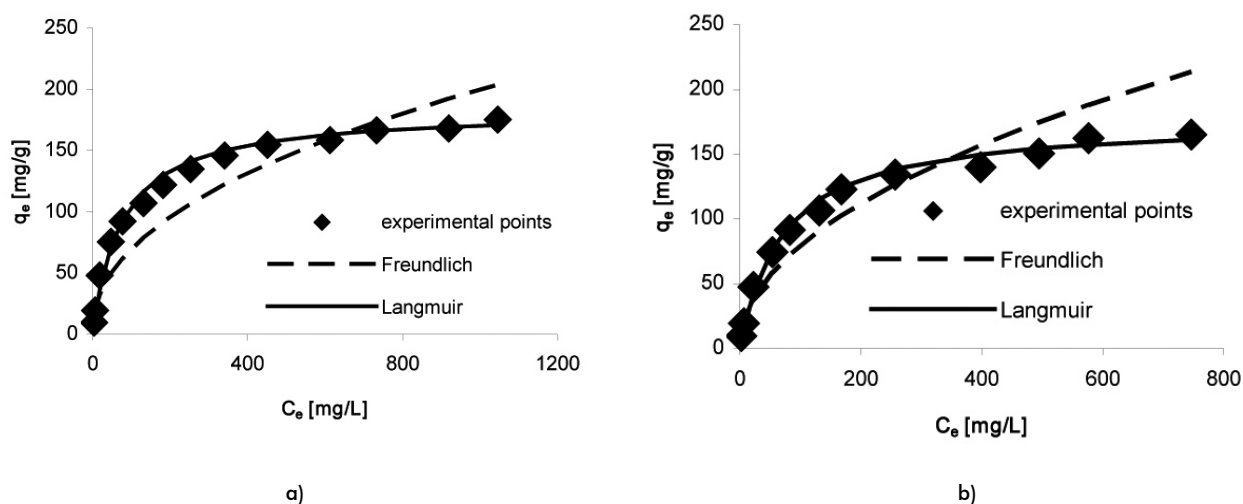| Systems		$q_{e\cdot exp}$	Pseudo-first kinetic order equation			Pseudo-second kinetic order equation				$q_{e\cdot exp}$	Pseudo-first kinetic order equation			Pseudo-second kinetic order equation			
			$q_{e.cal}$	k_1	R^2	$q_{e.cal}$	$q_{e.cal}$	$q_{e.cal}$	R^2		$q_{e.cal}$	k_1	R^2	$q_{e.cal}$	$q_{e.cal}$	$q_{e.cal}$	R^2
x M HCl — 1.0 M NaCl	x / 0.1	9.70	0.61	0.03	0.790	9.72	0.08	7.55	1.000	9.77	0.74	0.01	0.844	9.79	0.06	6.02	1.000
	0.5	9.51	0.52	0.03	0.798	9.54	0.07	6.30	1.000	9.58	0.69	0.02	0.922	9.60	0.09	8.64	1.000
	1.0	9.16	0.89	0.02	0.754	9.19	0.06	5.19	1.000	9.26	0.82	0.01	0.731	9.28	0.05	4.51	1.000
	2.0	8.63	0.94	0.01	0.662	8.65	0.03	2.51	1.000	8.70	0.94	0.01	0.5818	8.70	0.04	2.82	0.999
	-	9.71	0.60	0.04	0.734	9.73	0.09	8.93	1.000	9.76	1.91	0.01	0.581	9.77	0.11	10.86	1.000
x M HCl — 2.0 M NaCl	x / 0.1	9.32	0.66	0.01	0.703	9.34	0.05	3.99	1.000	9.25	0.83	0.01	0.644	9.28	0.05	4.22	1.000
	0.5	9.16	0.61	0.01	0.821	9.19	0.04	3.52	1.000	9.12	0.70	0.01	0.789	9.16	0.05	4.03	1.000
	1.0	8.80	0.77	0.01	0.560	8.82	0.04	3.37	1.000	8.74	0.68	0.01	0.809	8.77	0.05	4.05	1.000
	2.0	8.15	0.91	0.01	0.760	8.17	0.03	2.09	1.000	7.99	0.90	0.01	0.656	8.01	0.04	2.47	1.000
	-	9.37	0.76	0.01	0.775	9.39	0.06	5.40	1.000	9.40	0.87	0.01	0.695	9.42	0.06	5.74	1.000

Fig. 4. Fitting of Langmuir and Freundlich isotherm models to the experimental data obtained for the Dowex a) MSA-1, b) MSA-2 resins.

capacity values, $q_{e'exp}$ are similar to the predicted values of sorption capacities from the pseudo-second order kinetic equation, $q_{e'cal}$ (see Fig. 4).

The Langmuir and Freundlich isotherms were also obtained and the corresponding parameters were calculated. A higher correlation coefficient was obtained in the case of the Langmuir ($R^2 = 0.9978$ — MSA-1; $R^2 = 0.9953$ — MSA-2) than for the Freundlich isotherms ($R^2 = 0.9186$ — MSA-1; $R^2 = 0.9453$ — MSA-2). The fitting of isotherm models to the experimental data are presented in Fig. 4.

Conclusions

Both resins show high selectivity towards palladium(II) ions and can be applied in their recovery and preconcentration process. The selectivity series are following Dowex MSA-1 > Dowex MSA-2.

Kinetic evaluation of the experimental data showed that the sorption of Pd(II) on the Dowex resins followed well the pseudo-second order kinetic equation

The sorption capacities obtained from the Langmuir isotherms — monolayer capacities are equal to 182.75 mg/g and 176.44 mg/g for Dowex MSA-1 and Dowex MSA-2, respectively.

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