

Adsorption characteristics of noble metals on the strongly basic anion exchanger Purolite A-400TL

A. Wołowicz · Z. Hubicki

Received: 14 March 2014 / Accepted: 16 May 2014 / Published online: 12 June 2014
© The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract Ion exchange is an alternative process for uptake of noble metals from aqueous solutions. In the present study, the sorption of Pd(II), Pt(IV), and Au(III) ions from aqueous solution was investigated by using Purolite A-400TL (strongly basic anion exchanger, gel, type I) in a batch adsorption system as a function of time (1 min–4 h). Initial Pd(II) concentration (100–1000 mg/L), beads size (0.425–0.85 mm), rate of phases mixing (0–180 rpm), and temperatures (ambient, 313 K) were taken into account during the Pd(II) sorption process. Moreover, the column flow adsorption study was carried out, and the breakthrough curves were obtained for Pd(II) ions. The equilibrium, kinetic, desorption, and ion-exchange resin reuse studies were carried out. The experimental results showed that Purolite A-400TL—the strongly basic anion-exchange resin could be used effectively for the removal of noble metal ions from the aqueous medium. The kinetics of sorption process is fast and the resin could be reused without reduction of capacity (three cycles of sorption–desorption, the reduction of capacity is smaller than 1 %). The column studies indicated that in the dilute acidic solution (0.1 M HCl) the working anion exchange capacity is high (0.0685 mg/cm³) in comparison with the other SBA resins examined under the same experimental conditions, e.g., Amberlite IRA-458 (0.0510 mg/cm³), Amberlyst A-29 (0.0490 mg/cm³), Dowex MSA-1 (0.0616 mg/cm³), Dowex MSA-2 (0.0563 mg/cm³), Varion ADM (0.0480 mg/cm³), and Varion ATM (0.0490 mg/cm³)

etc. The highest % of Pd(II) desorption was obtained using thiourea, acidic thiourea, sodium hydroxide, and ammonium hydroxide as eluting agents (%D1 was in the range of 23.9–46.9 mg/g).

Introduction

Ion-exchange resins have played a very significant role in many branches of industry. As was reported by “Global Industry Analysts, Inc.” in 2010, the global market for ion-exchange resins is projected to exceed \$535 million by the year 2015. This tendency results from the growing demand for pure water and its lack in the world, increasing population growth, urbanization, industrialization, and pollution, etc. [1]. At present, the main ion-exchange resins manufacturing companies such as Dow Corporation, Rohm and Hass Company, Purolite Corporation, Lanxess, etc., produce a wide selection of ion-exchange resin types [2]. Among the ion-exchange resins available on market strongly basic anion-exchange resins play a significant role. Many examples of the commercial ion-exchange resins of different types for recovery of precious metals from solutions of different composition can be found in [1–6].

Among the recovery methods of valuable metal ions, the hydrometallurgical method is one of the most effective, whereas ion-exchange methods (sorption on ion-exchange resins) are the only economical methods for removal of gold and Platinum Group Metals from the diluted solution obtained after leaching the scrap materials containing the above mentioned metals. The advantage of the hydrometallurgical processes using the ion-exchange resins and ion-exchange method applied for recovery of noble metal ions is their possible recovery even from solutions in which noble metal ions are in trace concentration. There are no

A. Wołowicz (✉) · Z. Hubicki
Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie-Skłodowska University, Maria Curie-Skłodowska
Square 2, 20-031 Lublin, Poland
e-mail: annamyrt@poczta.onet.pl

Z. Hubicki
Fertilizer Research Institute, 24-100 Puławy, Poland

other methods which can be so effective as ion exchange used for such application. Based on the above facts, the ion-exchange method was applied for noble metal ions recovery from the diluted solutions using Purolite A-400TL. Moreover, a lack of consistent knowledge related to the behavior of noble and base metals on Purolite A-400TL has lead us to cope with the resin for more complete understanding of their sorption and desorption properties. The SBA resin of similar matrix (PS–DVB) and structure-type (gel) Lewatite MonoPlus M-600 but type 2 was applied previously by us in Pd(II) recovery both in the batch and column studies [7].

This article reported the efficiency of the commercially available strongly basic anion-exchange resin of type 1 [8] Purolite A-400 TL for noble (Pd(II), Pt(IV), Au(III)) metal ions removal from acidic solutions of different composition (HCl; HCl–HNO₃). Various parameters such as effect of phases contact time, initial metal ions concentration, agitation speed, temperature, and beads size distribution were considered in the batch mode to optimize conditions for the effective removal of these metal ions. Additionally, to characterize the loading processes of Pd(II) onto the SBA resin, a column system was applied. Equilibrium, kinetic, desorption, and SBA resin reuse studies were also carried out.

Experimental

Reagents and solutions

The single stock solutions containing metal ions such as Pd(II), Pt(IV), and Au(III) were prepared from solids: PdCl₂ or liquid: H₂PtCl₆, HAuCl₄ in 0.1 M HCl. In the case of palladium stock solution, a weighed amount of salt was dissolved in 1.0 M HCl solutions (temperature: 333 K, microwaves (Inter Sonic, type IS-1 with a thermoregulator), digestion time = 1 h). The concentration and composition of acidic solutions containing selected metal ions were following: 0.1–6.0 M HCl—100 mg/L M(II), M(III) or M(IV) and 0.1–0.9 M HCl—0.9–0.1 M HNO₃—100 mg/L M(II), M(III) or M(IV).

All the reagents were of analytical purification grade (POCh, Poland).

Purolite A-400TL characteristics

Purolite A-400TL is a strongly basic polystyrene-divinylbenzene anion-exchange resin of –N⁺(CH₃)₃ (type 1) functional groups. It has a gel structure; the total exchange capacity is 1.3 eq/L (in the Cl[–] form). Harmonic mean sizes are equal to 0.425–0.85 mm (uniform coefficient max. 1.3). The maximum operating temperature is 373 K

(in the Cl[–] form) and 333 K (in the OH[–] form). The pH limits are following: 0–14 (stability) and 1–10 (operating; the OH[–] form). Moisture retentions and reversible swelling are equal to 48–54 and 20 % (Cl[–] to OH[–]), respectively. Purolite A-400TL has excellent physical stability which permits a long life without the development of excessive pressure drop, even when operating at high flow rates. It also shows good kinetics of exchange. Purolite A-400TL is advisable for the demineralization of water and silica removal.

From the physical structure point of view, gel-type ion-exchange resin beads are homogeneous, whereas in the case of macroporous (macroreticular) one of the resin beads are heterogeneous and consist of interconnected macrospores surrounded by gel-type microbeads agglomerated together. The macrospores have sizes ranging from several angströms up to many hundreds of angström, while microbeads give the resin a large internal surface area which depends on the size of these microbeads.

Methods and measurements

The sorption, equilibrium, kinetic, desorption, and reuse studies were carried out by means of the batch method using a thermostated shaker (Elpin⁺, 358S, Lubawa, Poland). Sorption studies: The sorption studies were conducted in Erlenmeyer 100 mL flasks by adding 0.5 (±0.0005) g of Purolite A-400TL to 50 mL of metal solutions of 100 mg/L concentration (0.1–6.0 M HCl—100 mg/L M(II), M(III) or M(IV) and 0.1–0.9 M HCl—0.9–0.1 M HNO₃—100 mg/L M(II), M(III) or M(IV)). After shaking the flasks at 180 rpm and ambient temperature and time interval from 1 min to 4 h, the SBA resin was separated from aqueous solution by filtration. The final concentration of metal ions in the solution after sorption processes was determined using The Fast Sequential Atomic Absorption Spectrometer, VarianAA240FS, equipped with the appropriate hollow cathode lamps and SIPS autosampler and then calculated using the following equation:

$$q_e = (C_o - C_e)V/W \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of M(II), M(III), or M(IV), respectively (in mg/L); V (in L) is the volume of M(II), M(III), or M(IV) contacting solution; W (in g) is the SBA resin mass.

Kinetic studies

Kinetic experiments were identical to those of the sorption test, but some experimental conditions were changed to examine the influences of Pd(II) initial metal concentration, temperature, beads size distribution, and agitation speed on the sorption processes. The experimental

conditions were following (mass of the ion exchanger, m_j ; volume of the solution, V ; initial Pd(II) concentration, C_o ; amplitude, A ; agitation speed, V_{as} ; temperature T ; phases contact time, t ; beads size distribution, bs):

- $m_j = 0.5$ g, $V = 50$ mL, $C_o = 100, 500, 1000$ mg Pd(II)/L, $A = 8$, $V_{as} = 180$ rpm, T —ambient, $t = 1$ min to 4 h, bs—0.425–0.85 mm—effect of the initial Pd(II) concentration,
- $m_j = 0.5$ g, $V = 50$ mL, $C_o = 500$ mg Pd(II)/L, $A = 8$, $V_{as} = 120, 150, 180$ rpm, T —ambient, $t = 1$ min to 4 h, bs—0.425–0.85 mm—effect of agitation speed,
- $m_j = 0.5$ g, $V = 50$ mL, $C_o = 500$ mg Pd(II)/L, $A = 8$, $V_{as} = 180$ rpm, T —ambient, 313, 333 K, $t = 1$ min to 4 h, bs—0.425–0.85 mm—effect of temperature,
- $m_j = 0.5$ g, $V = 50$ mL, $C_o = 500$ mg Pd(II)/L, $A = 8$, $V_{as} = 180$ rpm, T —ambient, $t = 1$ min to 4, beads size— f_1, f_2, f_3, f_4 ($0.85 > f_1 \geq 0.6$ mm; $0.6 > f_2 \geq 0.5$ mm; $0.5 > f_3 \geq 0.43$ mm, $0.43 > f_4 \geq 0.425$ mm)—effect of beads size distribution.

The kinetic studies were carried out from the solutions containing Pd(II) ions (single solutions) of the following composition: 0.1 M HCl—100, 500 or 1000 mg Pd(II)/L and 0.1 M HCl—0.9 M HNO₃—100, 500 or 1000 mg Pd(II)/L (effect of initial Pd(II) concentration) and 0.1 M HCl—500 mg Pd(II)/L and 0.1 M HCl—0.9 M HNO₃—500 mg Pd(II)/L (effect of agitation speed, effect of temperature, and effect of beads size distribution).

The saturation degree (or fractional attainment of equilibrium) (F) is calculated from Eq. 2:

$$F = q_t/q_e \quad (2)$$

where q_t and q_e are the amount of Pd(II) sorbed (in mg/g) at time t and equilibrium, respectively. Based on the kinetic curves (plot of F vs t) the half-exchange times, $t_{1/2}$ (in s), were determined at $F = 0.5$ [9].

Equilibrium studies

The equilibrium studies were carried out under the experimental conditions: $m_j = 0.5$ g, $V = 50$ mL, $C_o = 100$ –6000 mg/L in 0.1 M HCl, $A = 8$, $V_{as} = 180$ rpm, T —ambient, $t = 24$ h, bs—0.425–0.85 mm, and the procedure was identical to those applied during the sorption studies.

Desorption studies

Different eluting agents were prepared by dilution of concentrated hydrochloric acid (0.1–6.0 M HCl), nitric acid (0.1–4.0 M HNO₃), sulfuric acid (0.5–4.0 M H₂SO₄), ammonia (0.5–2.0 M NH₄OH), sodium hydroxide (0.1–3.0 M

NaOH), 1.0 M TU (thiourea), 1.0 M TU—1.0 M HCl; 1.0 M TU—1.0 M HNO₃ in order to elute the retained noble metal ions from Purolite A-400TL. The desorption experimental conditions were: $m_j = 0.5$ g, $V = 50$ mL, $A = 8$, $V_{as} = 180$ rpm, T —ambient, $t = 2$ h and changeable concentration and types of eluting agents. The sorption–desorption cycle was repeated three times to obtain information about Purolite A-400TL reuse possibility.

Breakthrough capacities

In characterization of SBA resin applicability for metal sorption purposes, loading capacity is one of the main parameters commonly used. It is defined as a number of metal ion equivalent per mass of resin that can be removed from the solution containing the ion (in equilibrium state) [2, 7].

The dynamic procedures were applied to obtain the breakthrough curves and capacity. The one-centimeter diameter columns were filled with swollen Purolite A-400TL in the amount of 10 mL. Then, the solution of 100 mg/L was passed through the anion-exchange resin bed at the rate of 0.4 mL/min. The eluate was collected in the fractions, and the metal concentrations were determined.

Analytical procedure

The concentration in the solution after the sorption, desorption, kinetic, equilibrium, and reuse studies was obtained by the AAS method. Standard solutions were prepared by dilution of the standard stock solutions (1000 mg/dm³ in 0.1 M HNO₃) with acids and distilled water. The concentration of the standard solutions was changeable depending on the metal ions concentration determination. An oxidizing air-acetylene flame was used for atomization. The other parameters were following: lamp current 10 mA—Pd(II); 4.0 mA—Au(III); 7 mA—Pt(IV), slight width 0.2 nm—Pd(II), Pt(IV); 1.0 nm—Au(III), acetylene flow 2 dm³/min, air flow 13.5 dm³/min, and the analytical wavelength 247.6 nm—Pd(II); 242.8 nm—Au(III); 265.9 nm—Pt(IV).

Results and discussion

Sorption capacity—effect of experimental conditions

The complexation chemistry and ionic state of Platinum Group Metals and gold in the chloride solutions with varying chloride ion concentration have been described by other researchers [2, 10, 11]. In the chloride solutions the palladium(II), platinum(IV), and gold(III) metal ions can exist in different forms of their complexes. Depending on the solution pH and total concentration of chloride anions, these metals form cationic, non-anionic, and anionic

complexes. More information about the Pd(II), Pt(IV), and Au(III) complexes species can be found in [2, 12, 13].

In our studies (metal ions sorption from the chloride solutions: 0.1–6.0 M HCl—100 mg/L M(II), M(III), or M(IV)) Pd(II), Pt(IV), and Au(III) metal ions exist in the forms of anionic complexes of different ionic structure and properties (see Table 1) [10, 11]. The effect of acids concentrations (chloride concentrations) and phases contact time on the metal ions sorption on Purolite A-400TL is presented in Fig. 1a–c for the chloride and Fig. 1d chloride–nitrate solutions (in this case only the equilibrium sorption capacities for Pd(II), Pt(IV), and Au(III) were compared). In the dilute chloride solutions such as 0.1 M HCl, the equilibrium sorption capacities achieved the highest possible values for Pd(II) and Pt(IV) (removal is quantitative) 10 mg/g and 9.99 mg/g for Au(III). With the hydrochloric acid concentration increase, the equilibrium sorption capacities decrease. The reduction of sorption capacity is the highest for Pd(II) and is equal to 29 %. The sorption capacities drop from 10 mg/g (0.1 M HCl) to 7.10 mg/g (6.0 M HCl); from 10 mg/g (0.1 M HCl) to 9.31 mg/g (6.0 M HCl), and from 9.99 mg/g (0.1 M HCl) to 9.72 mg/g (6.0 M HCl) for Pd(II), Pt(IV), and Au(III), respectively. These sorption capacities changes indicate only 6.9 and 2.7 % reduction of their values for Pt(IV) and Au(III). Phases contact time also influences on the sorption capacities. The amount of the metal ions uptake increased with the increasing phases contact time. At the beginning of the sorption process (for short phases contact time), the q_t values increase is high and they decrease with

the phases contact time increase. When the system reached equilibrium, further increase of the phases contact time does not result in the increase of q_t values because they remain unchanged. The rapid sorption observed during the first 30 min is probably due to the abundant availability of active sites on the anion exchanger surface (the solute concentration gradient was relatively high) and with the gradual occupancy of these sites, the sorption becomes less efficient. With the hydrochloric acid concentrations increase, the time necessary to attain equilibrium is longer. In 0.1 M HCl solution quantitative removal of Pd(II) is obtained after only 15 min, whereas for Pt(IV) and Au(III) longer time is needed. Compared to other studies this time is very short and similar to that obtained for the Dowex MSA-1 [14], Lewatite TP-220 [12], and Purolite A-830 [15] ion exchange resins.

For the chloride–nitrate(V) solutions, the changes of q_t values are different. With the hydrochloric acid concentration increase and nitric acid concentration decrease the equilibrium sorption capacities for Pd(II) also increased by about 8 %, whereas for Pt(IV) and Au(III) noble metal ions, the changes of q_t values with acids concentrations are negligible (0.4 % for Au(III) and about 1 % for Pt(IV) increase was observed). Time required to reach equilibrium is longer for the HCl–HNO₃ solutions compared to the HCl solutions. More information about changes of Pd(II) solutions in the nitrate solution can be found in [16].

Not only the acids concentrations and phases contact time were taken into account during the recovery process but also the agitating speed, beads size distribution, initial

Table 1 Noble metals oxidation and chloro-complexes [10, 11]

Metal	Electron configuration	LK	Ionic structure		Complexes formed low—[Cl ⁻]-high	Redox stability	Kinetic stability	Thermal stability
Pd(II)	d ⁸	4	Square planar		PdCl ₄ ²⁻	Stable	Very stable	—
Pd(IV)	d ⁶	6	Octahedral		PdCl ₆ ²⁻	Unstable	Stable	Unstable
Pt(II)	d ⁸	4	Square planar		PtCl ₄ ²⁻	Unstable	Unstable	—
Pt(IV)	d ⁶	6	Octahedral		PtCl ₆ ²⁻	Stable	Very stable	Very stable
Au(III)	d ⁸	4	Square planar		AuCl ₄ ⁻	—	—	—

LK coordination number, — data not available

concentration, and temperature. The rate of recovery process (kinetic studies) was also determined and expressed by the saturation degree (fractional attainment of equilibrium, F) and the half-exchange times, $t_{1/2}$ (in s). The effects of the experimental condition on the sorption process and its kinetics are presented in Table 2.

Effect of initial Pd(II) concentration: The influence of initial Pd(II) concentration on loading was studied by adding 0.5 g Purolite A-400TL to 50 mL solution containing 100, 500, and 1000 mg/L Pd(II) and 0.1 M HCl at ambient temperature, with the results showing that the sorption rate was very fast at the initial stage: after 1 min of sorption 71, 81, and 91 % of Pd(II) were removed from the solutions containing 100, 500, and 1000 mg/L Pd(II), respectively. F reached very high values after 1 min (higher than 0.5), therefore, $t_{1/2}$ cannot be determined with high quality (for $F = 0.5$). Half-exchange time is smaller than 60 s for all presented cases. After 10 min (100 mg Pd(II)/L) and 15 min (500 and 1000 mg Pd(II)/L), F reached the constant values.

Similar observation was also made for the HCl–HNO₃ solutions (F reached 0.55–0.76 values after 1 min). As expected, increasing the initial concentration caused an increase in equilibrium sorption capacity. As was pointed out previously [16, 17], the rate of ion exchange is affected by the initial metal concentration when the controlling step is film diffusion, whereas the system is governed by intraparticle diffusion, the sorption rate is not influenced by metal concentration. In our cases at the beginning of the sorption process, an insignificant effect of metal ion concentrations on the Pd(II) sorption is observed. For the solutions of 500 and 1000 mg Pd(II)/L concentration, the metal recovery is not quantitative, the sorption capacities are 49.97 mg/g (max. 50 mg/L) and 94.95 mg/g (max. 100 mg/L). This is explained by the fact that as the concentration of metal ion increases, more and more surface sites are covered, and hence at higher concentration of metal ions, the capacity of the anion-exchange resin is exhausted due to non-availability of the surface sites. It is, therefore, evident

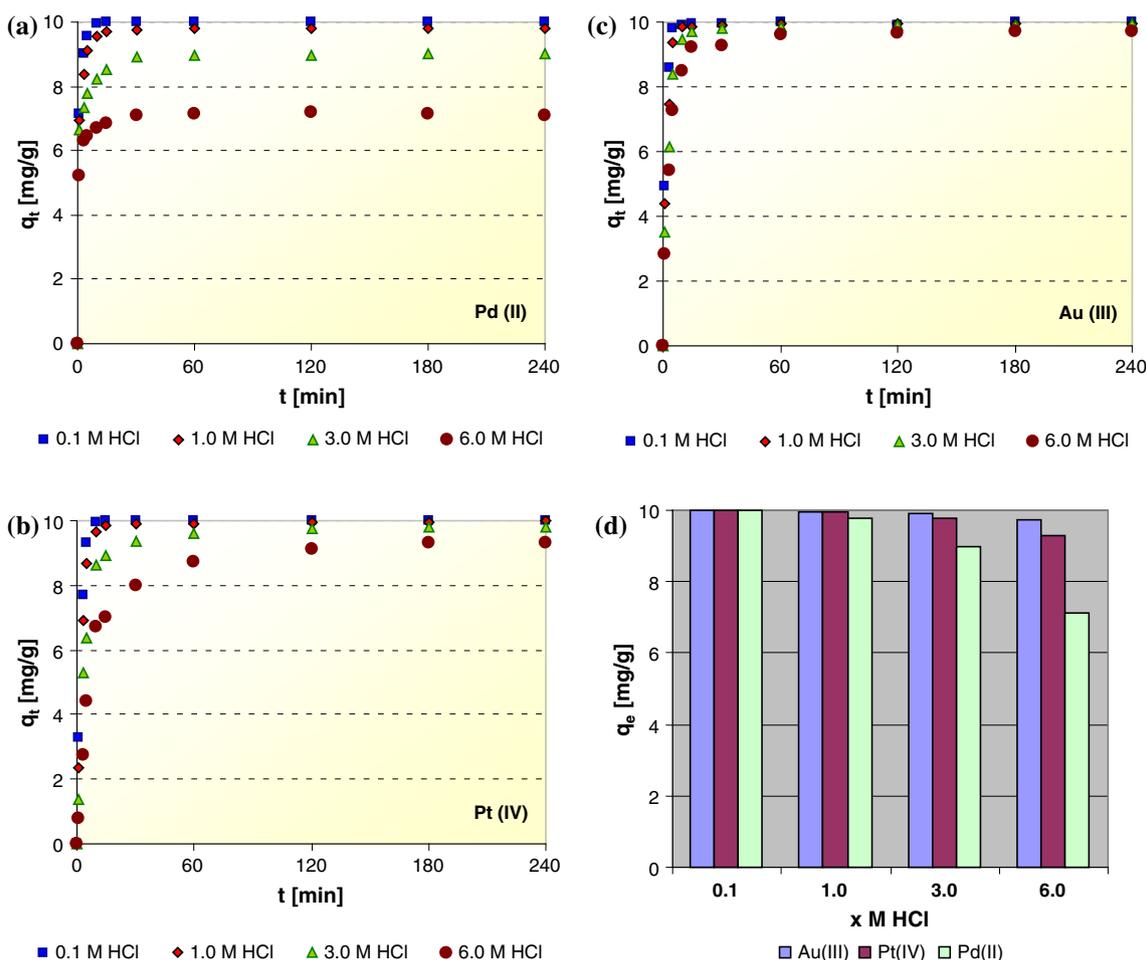
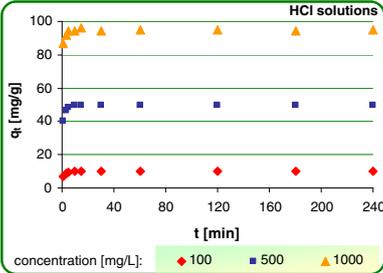
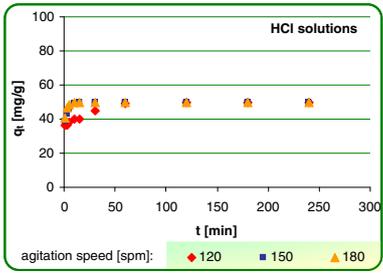
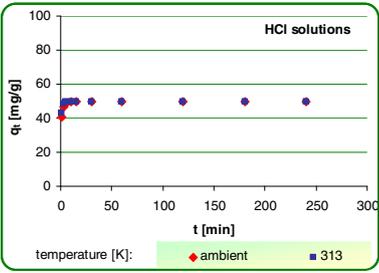
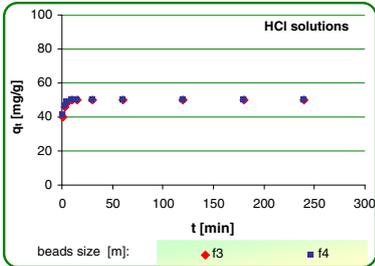


Fig. 1 Changes of the equilibrium sorption capacities in **a–c** HCl and **d** HCl–HNO₃ systems obtained during the **a, d** Pd(II), **b, d** Pt(IV), **c, d** Au(III) metal ions sorption on Purolite A-400TL (experimental

conditions: $m_j = 0.5$ g, $V = 50$ mL, $C_o = 100$ mg/L in 0.1 M HCl, $A = 8$, $V_{as} = 180$ rpm, T —ambient, $t = 1$ min to 4 h, $bs = 0.425$ – 0.85 mm)

Table 2 Comparison of F values depending of the experimental conditions applied

Time	F						Plot q_t versus t	Experimental conditions
	Effect of initial Pd(II) concentration (mg/L)							
	HCl system			HCl–HNO ₃ system			$t_{1/2}$ (s)	
t (min)	100	500	1000	100	500	1000		
1	0.71	0.81	0.91	0.68	0.55	0.76	<60 s	 <p>$m_j = 0.5$ g, $V = 50$ mL, $C_o = 100, 500, 1000$ mg/L in 0.1 M HCl, $A = 8, V_{as} = 180$ rpm, T—ambient, $t = 1$ min to 4 h, $bs = 0.425\text{--}0.85$ mm</p>
3	0.90	0.93	0.97	0.85	0.77	0.78		
5	0.95	0.97	0.99	0.93	0.88	0.85		
10	1.00	0.99	0.99	0.98	0.99	0.88		
15	1.00	1.00	1.00	0.99	0.99	1.00		
30	1.00	1.00	0.99	1.00	1.00	1.00		
60	1.00	1.00	1.00	1.00	1.00	1.00		
120	1.00	1.00	1.00	1.00	1.00	1.00		
180	1.00	1.00	0.99	1.00	1.00	1.00		
240	1.00	1.00	1.00	1.00	1.00	1.00		
Time	Effect of agitation speed (rpm)						Plot q_t versus t	Experimental conditions
	HCl system			HCl–HNO ₃ system			$t_{1/2}$ (s)	
t (min)	120	150	180	120	150	180		
1	0.72	0.77	0.81	0.71	0.56	0.55	<60 s	 <p>$m_j = 0.5$ g, $V = 50$ cm³, $C_o = 500$ mg/L, $A = 8$, $V_{as} = 120, 150, 180$ rpm, T—ambient, $t = 1$ min to 4 h, $bs = 0.425\text{--}0.85$ mm</p>
3	0.73	0.87	0.93	0.76	0.64	0.77		
5	0.76	0.92	0.97	0.72	0.78	0.88		
10	0.80	0.98	0.99	0.82	0.95	0.99		
15	0.80	1.00	1.00	0.83	0.95	0.99		
30	0.89	1.00	1.00	0.94	1.00	1.00		
60	0.99	1.00	1.00	0.98	1.00	1.00		
120	1.00	1.00	1.00	1.00	1.00	1.00		
180	1.00	1.00	1.00	1.00	1.00	1.00		
240	1.00	1.00	1.00	1.00	1.00	1.00		
Time	Effect of temperature (K)						Plot q_t versus t	Experimental conditions
	HCl system			HCl–HNO ₃ system			$t_{1/2}$ (s)	
t (min)	298	313	333	298	313	333		
1	0.81	0.86	*	0.55	0.83	*	<60 s	 <p>$m_j = 0.5$ g, $V = 50$ cm³, $C_o = 500$ mg/L, $A = 8, V_{as} = 180$ rpm, T—ambient (about 298), 313 K. $t = 1$ min to 4 h, $bs = 0.425\text{--}0.85$ mm</p>
3	0.93	0.98		0.77	0.94			
5	0.97	0.99		0.88	0.97			
10	0.99	1.00		0.82	0.95			
15	1.00	1.00		0.83	0.95			
30	1.00	1.00		0.94	1.00			
60	1.00	1.00		0.98	1.00			
120	1.00	1.00		1.00	1.00			
180	1.00	1.00		1.00	1.00			
240	1.00	1.00		1.00	1.00			

Time <i>t</i> (min)	Effect of beads size						Plot q_t versus t	Experimental conditions
	HCl system			HCl–HNO ₃ system				
	f_3	f_4	f_1, f_2	f_3	f_4	f_1, f_2		
							$t_{1/2}$ (s)	
1	0.80	0.82	**	0.78	0.80	**	<60 s	
3	0.92	0.93		0.87	0.89			
5	0.96	0.98		0.90	0.91			
10	1.00	1.00		0.96	0.96			
15	1.00	1.00		0.99	0.97			
30	1.00	1.00		0.99	0.99			
60	1.00	1.00		0.99	0.95			
120	1.00	1.00		0.99	0.99			
180	1.00	1.00		0.99	0.99			
240	1.00	1.00		1.00	1.00			

$m_j = 0.5$ g,
 $V = 50$ cm³, $C_o = 500$ mg/L,
 $A = 8$, $V_{as} = 180$ rpm,
 T —ambient,
 $t = 1$ min to 4,
 beads size— f_1, f_2, f_3, f_4
 $0.85 > f_1 \geq 0.6$ mm,
 $0.6 > f_2 \geq 0.5$ mm,
 $0.5 > f_3 \geq 0.43$ mm,
 $0.43 > f_4 \geq 0.425$ mm

* 333 K was the maximum PuroliteA-400TL temperature, therefore, to avoid possible anion-exchange resin decomposition this temperature was not applied

** Mass of the beads from this population was not enough to carry out the batch sorption for all phases contact time

that in low concentration ranges the percentage of sorption is high (usually quantitative) because of availability of more active sites on the surface of sorbent.

Effect of agitation speed

The kinetic profiles obtained for different agitation speeds are similar after 60–120 min of phase contact time (in all cases the applied speed was 120, 150, and 180 rpm). This time is enough to reach equilibrium by the system even for the cases of 120 rpm. When the agitation speed increases, the time required to reach equilibrium decreases. For 180 rpm agitation speed, this time is reduced to 30 min (HCl and HCl–HNO₃ systems). As expected, the sorption capacities at equilibrium are very close (varying by less than 0.5 % for HCl and 3 % for the HCl–HNO₃ systems). The effect of agitation speed on the sorption process is observed at the beginning of the process. With the agitation speed increase from 120 to 180 rpm, the F values also increase and exceed 0.5 after 1 min ($F = 0.72$ –120 rpm; $F = 0.77$ –150 rpm; $F = 0.81$ –180 rpm—HCl system, $F = 0.71$ –120 rpm; $F = 0.56$ –150 rpm; $F = 0.55$ –180 rpm for HCl–HNO₃ system). Exception to the rule are the F values for 1 and 3 min phases contact time for the HCl–HNO₃ system where the values decrease or change in some way. Faster phases mixing assure that all the surface binding sites are made readily available for metal uptake. Additionally, changes of agitation speed cause changes of the external boundary film surrounding the resin beads (lower mixing—the external boundary film is thicker). A similar effect of sorption capacities changes with the agitation speed was observed by other researchers e.g. Sepideh et al. [18] half-exchange time is smaller than 60 s for all presented cases and it decreases with the agitation speed increase (the HCl

system). As was pointed out previously [16, 17] when the rate of ion exchange increases with the agitation speed, the process is controlled by resistance to film diffusion, otherwise if the agitation speed does not influence on the rate of sorption the process is controlled by intraparticle diffusion.

Effect of temperature

The purpose of this research is to study the effect of temperature on the sorption of Pd(II) ions by Purolite A-400TL. The effect of temperature on the removal of Pd(II) in the acidic solution by Purolite A-400TL was studied at ambient temperature and 313 K. Due to the fact that 333 K is the maximum temperature of thermal stability of anion-exchange resin, the temperature study was neglected to avoid anion-exchange resin decomposition. The data are presented in Table 2 which shows that sorption of Pd(II) ions by Purolite A-400TL negligibly increased with the increase in temperature (HCl system; q_t values increased from 40.5 mg/g (298 K) to 43.0 mg/g (333 K)—1 min phases contact time, from 46.5 mg/g (298 K) to 48.7 mg/g (333 K)—3 min phases contact time, from 48.5 mg/g (298 K) to 49.7 mg/g (333 K)—5 min phases contact time, from 49.7 mg/g (298 K) to 49.9 mg/g (333 K)—10 min phases contact time). A similar temperature effect is observed for 1–3 min phases contact time for the HCl–HNO₃ system (HCl–HNO₃ system; q_t values increased from 27.1 mg/g (298 K) to 40.1 mg/g (333 K)—1 min phases contact time, from 38.4 mg/g (298 K) to 45.3 mg/g (333 K)—3 min phases contact time, from 43.6 mg/g (298 K) to 46.6 mg/g (333 K)—5 min phases contact time). After 10 min of phases contact time for the HCl–HNO₃ system, the obtained q_t values are higher at ambient temperature than at 333 K. The F values increased with the phases contact time

significantly and also negligibly with the increase of temperature. Usually after 15 min of phases contact time, the F values remain unchanged. At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ions to escape from the anion-exchange resin surface to the solution phase, which results in a decrease in sorption as temperature increases.

Effect of bead size distribution

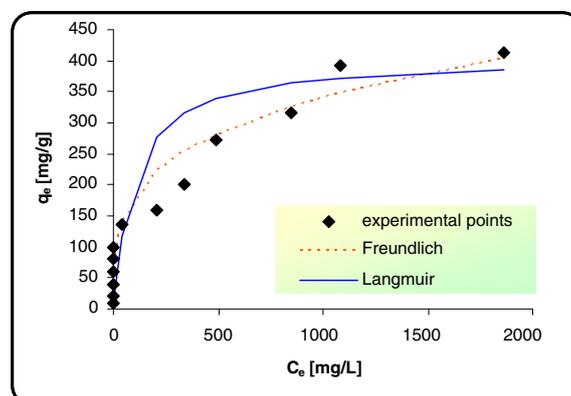
200 g of the anion-exchange resin was divided into fractions of different beads size by the classical sieve analysis. The fractions were following: $0.85 > f_1 \geq 0.6$ mm; $0.6 > f_2 \geq 0.5$ mm; $0.5 > f_3 \geq 0.43$ mm, and $0.43 > f_4 \geq 0.425$ mm. Due to the fact that the most of the beads belong to f_3 and f_4 fractions and the first and second ones were not enough abundant in this case the sorption of Pd(II) was checked only at equilibrium time for comparison. Based on the values of the equilibrium sorption capacities, the effect of beads size distributions on the sorption process of Pd(II) on Purolite A-400TL is not marked. The differences of the sorption capacity values at equilibrium time are so small that they can

be neglected: $q_t = 49.95$ mg/L (f_1), $q_t = 49.95$ mg/L (f_2), $q_t = 49.96$ mg/L (f_3), $q_t = 49.96$ mg/L (f_4)—HCl system; $q_t = 48.53$ mg/L (f_1), $q_t = 48.49$ mg/L (f_2), $q_t = 48.52$ mg/L (f_3), $q_t = 48.66$ mg/L (f_4)—HCl–HNO₃ system. At the beginning of the sorption process, this effect is also not marked enough compared to the other experimental parameters described above for which at the beginning the changes of q_t values were more marked. As expected, the sorption rate and the time required to reach equilibrium do not change with the beds size increase. Our previous studies of the effect of beads size distribution on the Pd(II) sorption process indicated that the sorption process can be effected by ion-exchange resin beads size much more than in this paper (Purolite A-400TL—polystyrene-divinylbenzene, gel) [15]. Kinetic studies of Purolite A-830 (polyacrylic, macroporous) [15] indicated that the equilibrium sorption capacities are not changed but the rate of sorption increases with the beads size decrease. Similar observation was made by Wawrzekiewicz [19] who applied Amberlite IRA-458 and Amberlite IRA-67 (polyacrylic, gel) for Direct Red 75 sorption. This change of rate sorption was explained by the fact that for the small beads the diffusion path lengths of the exchanging

Table 3 Equilibrium results—parameters and fitting plot

Isotherm model applied					Parameters	
	Equation	No.	Plot	Symbols		
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	(3)	C_e/q_e vs C_e	Q_0 —the Langmuir monolayer sorption capacity (mg/g), b —the Langmuir constant related to the free energy of sorption (dm ³ /mg), R_L —separation factor or equilibrium parameter,	Q_0 (mg/g)	404.15
				k_F —the Freundlich adsorption capacity (mg/g), $1/n$ —the Freundlich constant related to the surface heterogeneity	b (dm ³ /mg)	0.0106
					R_L	0.4868
					R^2	0.9448
Freundlich	$\log q_e = \log k_F + \frac{1}{n} \log C_e$	(4)	$\log q_e$ vs $\log C_e$		k_F (mg/g)	51.25
					$1/n$	0.2745
					R^2	0.9266

Fitting



ions to and from the active sites are shorter [19]. The fast Pd(II) sorption in this case is confirmed also by the F values close to 1 after 5–10 min of phases contact time and by small values of $t_{1/2}$. Due to the fact that the bead size effect can be neglected, it can be stated that in this case the diffusion path lengths of the exchanging ions did not play a significant role. Based also on the other experimental parameters examined here (agitation speed, temperature, and initial concentration), it can be concluded that the film diffusion plays a more significant role in the sorption process of Pd(II) on Puroite A-400TL.

Equilibrium studies

The equilibrium isotherm equations are used to describe the experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent.

Equilibrium studies were carried out using the batch method. The initial Pd(II) concentrations were in the range from 100 to 6000 mg/L (in 0.1 M HCl). The Langmuir and Freundlich isotherms described in [12, 15] were applied. The Langmuir and Freundlich parameters were obtained by plotting C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$, respectively, and the data are provided in Table 3. Table 3 shows that the Langmuir model is more suitable than the Freundlich adsorption isotherm.

The Freundlich isotherm plot of Pd(II) ions sorption provides a correlation coefficient of 0.9266, the values of k_F and $1/n$ obtained from the plot were 51.25 mg/g and 0.2745, respectively. The values of R^2 are smaller than 0.99 which indicate that the relationship C_e/q_e versus C_e is not linear. The Langmuir plot gives a better correlation coefficient than the Freundlich one, and the correlation coefficient is equal to 0.9448 but it is still not satisfactory. The sorption capacity value calculated from the Langmuir isotherm equation is equal to 404.15 mg/g, whereas the experimental q_e is higher by about 3 % (413.93 mg/g). The difference between the calculated and the experimental sorption capacity values is not high. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or the equilibrium parameter, R_L ($R_L = 1/(1 + bC_0)$). The parameter indicates the isotherm shape as follows: $R_L > 1$ —unfavorable, $R_L = 1$ —linear, $0 < R_L < 1$ —favorable, $R_L = 0$ —irreversible. The R_L values are 0.4868, and it is a typical behavior of the favorable isotherm.

Column experiment

Column experiments were conducted using a glass tube of 1 cm diameter by passing the initial solution concentration of 100 mg Pd(II)/L through the Puroite A-400TL beads.

The breakthrough curve (plot C/C_0 vs V) and the working ion exchange capacities (Eq. 5), the weight (Eq. 6) and bed (Eq. 7) distribution coefficients were calculated using the following equations:

$$C_r = (V_p \cdot C_0)/V_j \tag{5}$$

$$D_w = (U - U_0 - V)/m_j \tag{6}$$

$$D_v = D_w d_z \tag{7}$$

where C_r is the working ion exchange capacity, V_p is the collected volume of effluent between the first fraction and that to the breakthrough point (mL), C_0 is the initial Pd(II) concentration, V_j is the volume of ion exchanger bed put

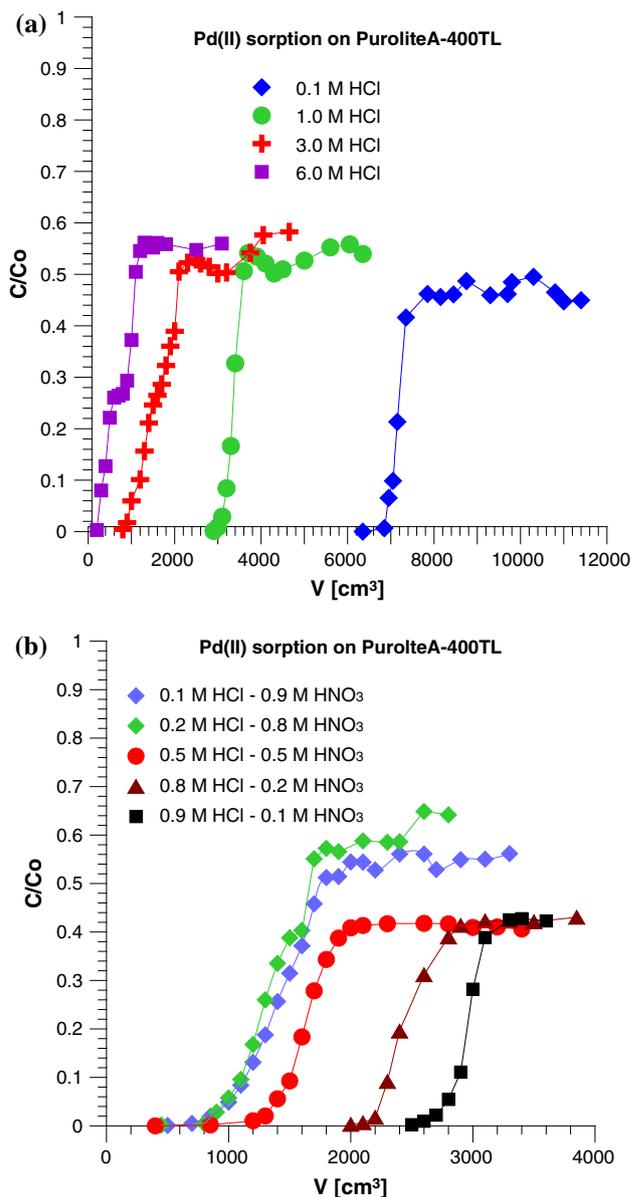
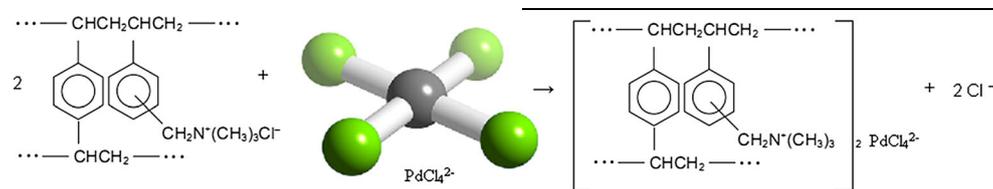


Fig. 2 Breakthrough curves of Pd(II) sorption on Puroite A-400TL from a HCl and b HCl–HNO₃ systems

into the columns, D_w is the weight distribution coefficient, U is the effluent volume at $C = 0.5 C/C_o$ (mL), U_o is the dead volume in the column (mL), V is the void (interparticle) ion exchanger bed volume (which amounts to ca. 0.4), m_j is the dry ion exchanger weight (g), D_v is the bed distribution coefficient, d_z is the ion exchanger bed density. The breakthrough curves are presented in Fig. 2, whereas the calculated parameters in Table 4. As can be seen the breakthrough curves possess at the beginning the S-shape but then the end of the curves is not typical. Figure 2 indicates that the ratio of C to C_o achieved a constant value. This tendency was not observed previously, only for Purolite S-984 the breakthrough curves possess also unusual shape [20]. The explanation of such tendency has not been found yet. Probably, a gel structure as well as the resin capacity can play a main role here. The SBA resin capacities values change with the concentration of acids. For the HCl system, the values of the working ion exchange capacities are much higher for dilute acidic solutions compared to the capacities obtained for the HCl–HNO₃ system. Additionally, typical reduction of C_r values was observed with the increasing HCl acid concentrations. The competitive effect of Cl[−] anion and Pd(II) complexes is marked here [2]. For the HCl–HNO₃ system, the capacities increase with the HCl concentration increase and HNO₃ concentration decreases. Such behavior was observed previously for about 30 examined ion-exchange resins [4, 5, 8, 12, 14, 15, 20] etc. The mechanism of Pd(II) can be presented as follows:



Purolite A-400TL shows high sorption capacity (0.0685 mg/cm³) compared to the other SBA resins such as Amberlite IRA-458, Amberlyst A-29, Dowex MSA-1, Dowex MSA-2, Varion ADM, Varion ATM (capacities for other SBA resins are in the range from 0.048 to 0.0616 mg/cm³) in 0.1 M HCl.

Desorption and reusable properties of purolite A-400TL

The desorption studies and possibilities of Purolite A-400TL reuse were carried out. In the desorption studies, many eluting agents of different concentrations were applied such as 0.1–4.0 M HNO₃, 0.1–6.0 M HCl, 0.5–4.0 M NH₄OH, 0.5–3.0 M NaOH, 0.5–4.0 M H₂SO₄, and 1.0 M TU (thiourea) or acidic TU (1.0 M TU—1.0 M

HCl; 1.0 M TU—1.0 M HNO₃). The desorption results are shown in Table 5. Based on Table 5 the following observations can be made:

- *sorption* SBA resin capacities are high and even after three cycles of sorption–desorption these values remain almost unchanged—the capacity reduction is smaller than 1 %. The advantage of this resin is the fact that it can be used many times without significant reduction of capacity.
- *desorption* effectiveness of desorption studies is not satisfactory enough. Application of acids gives desorption yield in the range from 0.1 to 30.5 % (D₁), from 0 to 20.3 % (D₂), and from 0.1 to 18.5 % (D₃). Better % of desorption was obtained by using basic solution but the desorption yield did not exceed 47 %. Acidic solutions of TU and those without acid in this case did not give satisfactory results either. The % of desorption usually decreases with the next cycle of sorption–desorption. In the calculation of % D, e.g., in the second step, the amount of Pd(II) not desorbed in the first cycle was taken into account and added to the amount of Pd(II) retained in the second step of sorption.

The comparison of eluting agents applied in Pd(II) desorption from other (bio)sorbents and the effectiveness of ion-exchange resin regeneration was presented previously in Table S7 in [15]. As follows from the table acids, bases and TU solutions were usually applied as eluting agents. The effectiveness of % D is different but acidic

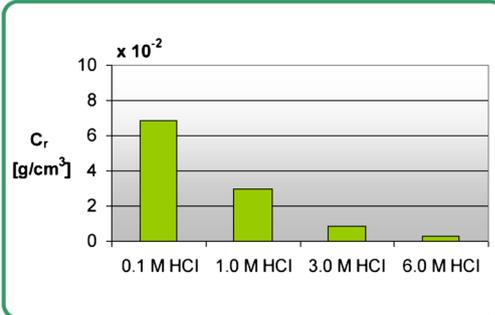
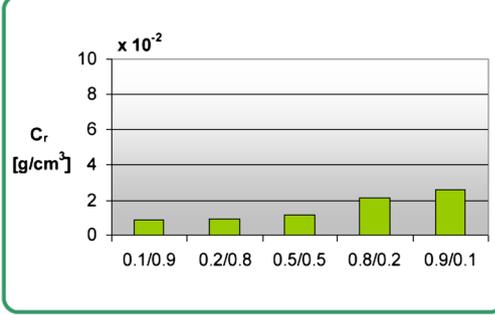
thiourea solution seems to be the most appropriate for this purpose but in many cases the use of such solutions did not give a quantitative Pd(II) recovery. Sometimes changes of volume of the eluting agents, concentrations, and temperature make the elution more quantitative.

Conclusions

Based on the present study, it is clearly shown that Purolite A-400TL (polystyrene-divinylbenzene anion-exchange resin of $-N^+(CH_3)_3$ (type 1) functional groups and gel-type) is found to be an effective sorbent for removal of Pd(II), Pt(IV), and Au(III) ions from aqueous solution. The experimental sorption capacity of Purolite A-400TL,

Table 4 Comparison of the sorption parameters—column studies of Pd(II) recovery on Purolite A-400TL

System	Dw	Dv
0.1 M HCl	-	-
1.0 M HCl	1057.9	358.4
3.0 M HCl	615.1	208.4
6.0 M HCl	320.8	108.7
0.1 M HCl - 0.9 M HNO ₃	518.9	175.8
0.2 M HCl - 0.8 M HNO ₃	489.7	165.9
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	-	-

– values were not obtained

Table 5 Effectiveness of sorption and desorption processes

0.1 M HCl—100 mg Pd (II)/L							
Eluting agent	S ₁	D ₁	S ₂	D ₂	S ₃	D ₃	
1	0.1 M HNO ₃	100.0	0.5	99.8	0.6	99.8	0.6
2	1.0 M HNO ₃	100.0	10.5	99.8	8.0	99.8	8.2
3	2.0 M HNO ₃	100.0	19.4	99.7	13.1	99.8	12.9
4	3.0 M HNO ₃	100.0	25.9	99.8	16.1	99.8	15.6
5	4.0 M HNO ₃	100.0	30.5	99.8	20.3	99.9	17.4
6	0.1 M HCl	100.0	0.1	99.8	0.0	99.9	0.1
7	1.0 M HCl	100.0	1.9	99.9	2.0	99.8	2.5
8	2.0 M HCl	100.0	5.4	99.9	4.7	99.9	5.8
9	3.0 M HCl	100.0	8.0	99.9	7.4	99.9	8.6
10	6.0 M HCl	100.0	24.3	99.9	19.1	99.9	18.1
11	0.5 M NH ₄ OH	100.0	44.9	99.8	22.4	99.6	19.1
12	1.0 M NH ₄ OH	100.0	42.9	99.8	23.3	99.6	17.5
13	2.0 M NH ₄ OH	100.0	46.9	99.8	23.2	99.8	18.3
14	3.0 M NH ₄ OH	100.0	44.8	99.8	21.4	99.8	17.7
15	4.0 M NH ₄ OH	100.0	43.8	99.7	24.5	99.8	18.9
16	0.5 NaOH	100.0	23.9	99.9	14.3	99.9	5.1
17	1.0 M NaOH	100.0	27.3	99.9	20.6	99.9	16.8
18	2.0 M NaOH	100.0	35.2	99.9	20.8	99.9	17.4
19	3.0 M NaOH	100.0	37.5	99.9	22.4	99.9	18.5
20	0.5 M H ₂ SO ₄	100.0	0.2	99.9	0.2	99.9	0.2

Table 5 continued

0.1 M HCl—100 mg Pd (II)/L							
	Eluting agent	S_1	D_1	S_2	D_2	S_3	D_3
21	2 M H ₂ SO ₄	100.0	3.3	99.9	2.8	99.8	2.6
22	4 M H ₂ SO ₄	100.0	5.2	99.9	3.9	99.8	3.4
23	1.0 M TU	100.0	40.0	99.1	23.3	99.3	14.4
24	1.0 M TU—0.1 HCl	100.0	41.7	99.7	25.0	99.0	16.2
25	1.0 M TU—0.1 HNO ₃	100.0	38.0	99.4	14.1	99.6	15.0

S sorption, D desorption, 1,2,3 number of cycle

strongly basic anion-exchange resin, was found to be 413.93 mg Pd(II)/g, and the calculated one (Langmuir capacity) was equal to 404.15 mg Pd(II)/g. The sorption process is slightly affected by such parameters as agitation rate, bead size distribution, and temperature. The initial Pd(II) concentration and phases contact time play a significant role in Pd(II) recovery. The percentage removal of Pd(II) increased with the increase in contact time. The rate of Pd(II) removal and the kinetics of sorption process are very fast, therefore, the time required to reach equilibrium is very short and the saturation degree (or fractional attainment of equilibrium) reached the constant values after short phases contact time. Half-exchange time is smaller than 60 s for all presented cases. Desorption studies showed that the strongly basic anion-exchange resin can be regenerated (but not quantitative Pd(II) desorption is observed) and reused. Moreover, the reduction of capacity after three cycles of sorption–desorption is negligible (smaller than 1 %). Column studies indicated that in the dilute acidic solution (0.1 M HCl) the working anion exchange capacity is high (0.0685 mg/cm³) in comparison with other SBA resins examined under the same experimental conditions.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Jermakowicz-Bartkowiak D, Kolarz BN (2013) Anionity polimerowe do odzyskiwania metali szlachetnych. *Polimery* 58:524–532 (in Polish)
- Nikolski AN, Ang KL (2014) Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Miner Process Extr Metall Rev* 35:369–389
- Mladenova E, Karadjova I, Tsalev DL (2012) Solid-phase extraction in the determination of gold, palladium, and platinum. *J Sep Sci* 35:1249–1265
- Hubicki Z, Wawrzkiwicz M, Wołowicz A (2008) Application of ion exchange methods in recovery of Pd(II) ions—a review. *Chem Anal* 53:759–784
- Wołowicz A (2011) Zastosowanie włókien i jonitów chelatujących w procesie sorpcji i separacji jonów Pd(II). *Przem Chem* 90:1001–1015
- Syed S (2012) Recovery of gold from secondary sources—a review. *Hydrometallurgy* 30:115–116
- Wołowicz A, Hubicki Z (2011) Comparison of strongly basic anion exchange resins applicability for the removal of palladium(II) ions from acidic solutions. *Chem Eng J* 170:206–215
- Harland CE (1994) Ion exchange: theory and practice, 2nd edn. Royal Society of Chemistry, Cambridge
- Alguail FJ, Adeva P, Alonso M (2005) Processing of residual gold(III) solutions via ion exchange. *Gold Bull* 38:9–13
- Renner H (1997) Platinum Group Metals. In: Habashi F (ed) Handbook of extractive metallurgy. Wiley-VCH, Weinheim, Chichester
- Harris GB (1993) A review of precious metals refining. In: Mishra RK (ed) Precious metals. IPMI, Allentown
- Wołowicz A, Hubicki Z (2012) The use of the chelating resin of a new generation Lewatit MonoPlus TP-220 with the bis-picolyl-amine functional groups in the removal of selected metal ions from acidic solutions. *Chem Eng J* 197:493–508
- Parodi A, Vincent T, Pilsniak M, Trochimczuk AW, Guibal E (2008) Palladium and platinum binding on an amidazol containing resin. *Hydrometallurgy* 92:1–10
- Wołowicz A, Hubicki Z (2011) Investigation of macroporous weakly basic anion exchangers applicability in palladium(II) removal from acidic solutions—batch and column studies. *Chem Eng J* 174:510–521
- Wołowicz A, Hubicki Z (2012) Applicability of new acrylic, weakly basic anion exchanger Purolite A-830 of very high capacity in removal of palladium(II) chloro-complexes. *Ind Eng Chem Res* 51:7223–7230
- Kononova ON, Goryaeva NG, Dychko OV (2009) Ion exchange recovery of palladium(II) from nitrate weak acidic solutions. *Nat Sci* 1:166–175
- Helfferich F (1995) Ion exchange. Dover Publications Inc., Mineola
- Sepideh J, Mahmoud A, Hossein A, Ahmad KD (2012) The effect of kinetics parameters on gold extraction by Lewis cell: comparison between synthetic and leach solutions. *Iran J Chem Eng* 31:59–67
- Wawrzkiwicz M (2011) Comparison of gel anion exchangers of various basicity in direct dye removal from aqueous solutions and wastewaters. *Chem Eng J* 173:773–781
- Wołowicz A, Hubicki Z (2014) Polyacrylate ion exchangers in sorption of noble and base metal ions from single and tertiary component solutions. *Solv Extr Ion Exch* 32:189–205