U.P.B. Sci. Bull., Series B, Vol. 81, Iss. 4, 2019 ISSN 1454-2331

PLATINUM GROUP METALS REMOVAL USING POLYMERIC RESINS: A PERFORMANCE COMPARISON BETWEEN A PHOSPHINE AND THIOUREA-FUNCTIONALISED RESIN AND AN ION-EXCHANGE RESIN

Ancuta MUSINA[1], Vasile LAVRIC[2]

The removal of platinum group metals from synthetic aqueous solutions using a phosphine and thiourea – functionalized resin, MPX-317, and an anionic resin, SQD, was investigated. The batch methodology was used throughout the studies. The affinity and sorption capacity of selected metal ions Pd(II), Pt(II), Rh(III), Ir(III) were evaluated. The addition of sodium chloride as well as the effect of HCl concentration on platinum group metals sorption were considered. When the sorption mechanism consists of ion-exchange interactions, sodium chloride addition and high concentrations of hydrochloric acid will determine a decrease of both recovery degree and sorption capacity. The sorption mechanism of MPX-317 is by coordinate covalent bonds for all metals, although for Rh and Ir, these bonds seem more difficult to form, due to the metals' complicated chemistry in solution.

Keywords: chelating resin, ion-exchange resin, platinum group metals (PGMs), chloride species, coordinate covalent bonds, ionic interactions

1. Introduction

Platinum group metals (PGMs) are used in many applications due to their remarkable physical properties (high conductivity, thermal stability) and their rich chemistry. They are used in electronic devices, glass and ceramics, medical applications and pharmaceuticals, but their main usage is as catalysts in chemical process industries and in catalytic converters in order to minimize cars and trucks exhaust emissions [1].

In comparison with other precious metals (Au and Ag), the PGMs supply is very limited not only because of their low natural abundance, but also due to the complex processes required for their extraction and refining [2]. The concentration of PGMs in different waste water streams (from mining, refining, plating, etc.) is usually low [3], often between 2 to 100 mg/L [4], yet the high volumes of effluents will lead to high monetary losses, due to the high prices of these metals. Therefore, their recovery is of great interest.

---

[1] PhD Student, Doctoral School "Applied Chemistry and Materials Science", University POLITEHNICA of Bucharest

[2] Professor, Chemical and Biochemical Engineering Department, University POLITEHNICA of Bucharest, e-mail: vasile.lavric@upb.ro

Separation and refining of PGMs are based predominantly on the subtle difference between their anionic chloro-complexes because the aqueous chloride solution is the only cost-effective medium in which all the PGMs can be solvated and concentrated [2]. Moreover, the leaching process with acidic sodium chloride solutions of spent catalysts containing Pd is one of the most effective methods for secondary raw materials treatment [5]. Ru and Os are generally separated by means of oxidative distillation [6] and therefore they were not considered in this study.

In order to recover the last traces of PGMs from waste streams, a significant number of methods are used in different settings: precipitation, liquid-liquid extraction, electrochemical treatment, membrane processes, adsorption, and ion exchange [7]. Some of the important criteria in choosing the separation process are high efficiency and minimum losses of precious metals, but ecological considerations are often essential as they can have a considerable effect on production costs [8]. Among these methods, the ion-exchange processes have been particularly attractive due to their simplicity [9]. Most of the resins are non-toxic, non-volatile, non-flammable, while the equipment is simple, easy to use [10], therefore the method presents fewer environmental hazards than solvent extraction and/or precipitation techniques [11].

Usually, the commercially used ion exchangers are weak or strong base anion exchangers, able to capture the PGMs chloro-complexes that are formed in the hydrochloric acid media, via unselective electrostatic interactions [12]. The trend for the metal(M)-chloro complexes to form ion pairs with anion-exchangers is: $[MCl_6]^{2-}$ > $[MCl_4]^{2-}$>> $[MCl_6]^{3-}$ > aquo-species [2]. Due to the increasing competition at high concentrations of common metals and chloride in the waste streams, more selective exchangers are needed in order to efficiently capture the PGMs. Materials bearing functionalities that can form coordinate covalent bonds with PGMs, such as amines, thiols, thiourea/isothiourea or phosphine sulphides, showed better efficiency and selectivity than classic ion-exchange materials. These resins, known as chelating resins, can be neutral, positively charged or negatively charged and they will inevitably present, to some extent, a mixed mechanism of adsorption, including both chelation and ion exchange interactions, which take place simultaneously or step-wise. Their relative strengths could be different, depending on the nature of the solvated metal ion [13]. The electrostatic interactions can be strongly suppressed by the addition of an electrolyte in the solution, typically an alkali metal salt. Among the known resins, chelating resins containing thiourea functional groups exhibit particularly high selectivity to PGMs [14].

As PGMs can form different species in chloride media, depending on the solution composition, the adsorption mechanism involved can differ, i.e. chelation rather than ion exchange, as well as the affinity of the metal species for sorption sites on the adsorbents [15].

In this paper, two resins were investigated: MPX-317, produced by Italmatch - Magpie (formerly Magpie Polymers, France), and SQD, produced by Suqing (China). MPX-317 is a macroporous resin material with a polyacrylic backbone containing phosphine and thiourea functionalities (capacity: minimum 1.0 eq/kg) while SQD is a commercial high capacity weak anionic resin containing primary (–NH2) and secondary (=NH) amines functionalities (capacity: higher than 7.0 eq/kg). The density of both resins is between 0.65 and 0.75 g/mL. It has been shown before that phosphine-functionalized polymers have very good affinity towards Pd [16] while phosphine-oxide resins have been used successfully for PGMs recovery [11,15,16]. For this study the most important four PGMs were considered: palladium, platinum, rhodium, and iridium. Because the separation and purification of the PGMs are largely carried out by exploiting differences in the stability of their anionic chloro-complexes [8], chloride media was chosen for the studies.

The influences of acidity, given by hydrochloric acid, as well as the ionic strength, controlled by sodium chloride addition, on the degree of recovery of PGM complexes were evaluated. At the same time, the performance of the chelating resin MPX-317 was compared with the one of the ion-exchange resin, SQD, highlighting the differences in the adsorption behavior.

2. Materials and methods

2.1. General

The solutions containing metals were prepared using commercially available salts purchased from Strem: palladium (II) chloride (59.91% Pd, metal purity 99.9%), $PdCl_2$, platinum (II) chloride (73.63% Pt, metal purity 99.9%), $PtCl_2$, rhodium (III) chloride hydrate (38 % Rh), $RhCl_3*xH_2O$, and iridium (III) chloride hydrate (54.29% Ir, metal purity 99.99%), $IrCl_3*xH_2O$. Rhodium and iridium chloride salts are usually sold in hydrated form, where the degree of hydration can vary. Hydrochloric acid 37% and sodium chloride, reagent grade, were bought from Chem-Lab.

Six types of solutions were prepared for each metal, tagged **S0** to **S5**, thus a total of 30 solutions. These solutions were prepared by dissolving weighed quantities of solid salts in hydrochloric acid solutions. The concentration of the PGM in these solutions was approximately 1 mM. This concentration was chosen according to values commonly found in industrial effluents [4] and, also, since it is used often in scientific research [10,19]. Although Rh and Ir are usually less concentrated, in this study similar concentrations were considered for all PGMs in order to compare the affinity of resins towards them in similar conditions. Sodium chloride was added in some of these solutions to increase the ionic strength. The concentrations of metals, HCl, and NaCl are listed in Table 1. For Rh and Ir solutions, a relatively important deviation between the calculated and measured concentrations was observed, probably due to a poorer dissolution of the salts in the given conditions, combined with the solvation peculiarities.

Table 1

Solutions used in the thermodynamic studies

Solution	HCl, M	NaCl, M	Concentration, mM			
			Pd	Pt	Rh	Ir
S0	0.3	0	1.0	1.0	0.8	0.7
S1	1	0	1.0	0.7	0.7	0.8
S2	5	0	1.0	0.9	0.8	0.9
S3	0.3	0.7	1.0	0.9	0.8	0.9
S4	0.3	4.7	0.9	0.9	0.7	0.7
S5	1	4	1.0	0.9	0.7	0.7

2.2. Equipment

Quantitative analysis of the residual metals in the solutions were determined with a Varian 720-ES (Australia) inductively coupled plasma optical emission spectrometer (ICP-OES) using an external calibration method.

In order to assure a good contact between the resin and the solutions, the tubes containing the mixture resin and solution were shaken in an IKA KS-130 (Germany) shaker.

A microwave digestion system Milestone MLS-1200 Mega (USA) was used to extract the metal-loaded resins.

2.3. Experimental

Metal capture in batch mode was carried out by contacting different amounts of resin with 15 mL aqueous metal solution with known initial concentration. The used resins are produced and stored wet. To be more accurate in comparing resins loading per mass unit (each resin has different properties: density, percentage of water), the resins were dried in an oven at 50 °C for about 12 hours and weighted as dry resins. Before each test, after the weighing, the resins were converted to the chloride form with 1M HCl solution using a standard conditioning procedure described in the Supporting Info document.

The tubes were sealed and mechanically agitated on the shaker at 400 rpm at room temperature (20 - 22°C). After reaching the equilibrium (preliminary experiments proved that 48 hours are enough to reach equilibrium), the solution was decanted, and the resin rinsed with water. Replicates were systematically set for some of the experiments (about 25% of the total performed test) to verify that the results are repeatable. The relative standard deviation was lower that 5% and therefore only the average values will be presented further. The solutions were analysed at several dilutions by ICP-OES.

Screening tests were performed bringing in contact 100 mg of each resin with 15 mL of each solution and stirring for 48 hours at room temperature. The efficiency of PGMs sorption from the chloride solutions was estimated by means of the recovery degree (***R***, %):

$$\boldsymbol{R} = \frac{C_0 - C_{eq}}{C_0} \cdot \mathbf{100} \tag{1}$$

where C_0 is the initial concentration of the metal of interest in solution, in mM, and C_{eq} is the equilibrium concentration of the metal in solution, in mM.

Thermodynamic equilibrium studies were performed putting in contact different amounts of resin (25 mg, 50 mg, 100 mg, 200 mg, and 500 mg) with 15 mL of each solution for 48 hours at ambient temperature. After the test, the resins beads were filtered off and the solutions were analyzed. The metal uptake ***q*** (the amount of metal adsorbed, mmol, per unit of sorbent mass, g) was determined by mass balance:

$$\boldsymbol{q} = \frac{(C_0 - C_{eq}) \cdot V}{m} \tag{2}$$

where C_{eq} is the concentration of the metal of interest after adsorption in solution, in mM, V is the volume of solution used, in L, and m is the mass of the resin used for the experiment, in g.

Determination of metal content was performed using a microwave digestion procedure. Some of the resins were extracted (100 mg resin used for thermodynamic equilibrium test) with freshly prepared *aqua regia* using the procedure described in the Supporting Info document. The obtained extracts were analyzed by ICP-OES and the metals concentrations were determined.

3. Results and discussions

In hydrochloric acid solutions, PGMs are present mainly as anionic species; therefore conventional anion exchange materials should be considered for their bulk recovery from low-grade streams [20]. However, the equilibrium ionic state of PGMs in solutions varies according to the parameters of the contacting medium, such as, acidity, concentration of chloride ions and other competing ions present within solutions [19].

In aqueous solution containing chloride anions, the PGM metal cations tendency is to form stable and kinetically inert octahedral $[MCl_6]^{n-}$ or square-planar $[MCl_4]^{2-}$ complexes [21].

The most common oxidation state of Rh and Ir is +3, whereas Pt and Pd can occur in either +2 or +4 valence state in aqueous solution. The divalent state largely predominates over the tetravalent state at 25°C, except under extremely oxidizing conditions [22]. Thus Pt(IV), Rh(III), and Ir(III) exist mainly as $[PtCl_6]^{2-}$ $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ in hydrochloric acid solution, while Pt(II), and Pd(II) form $[PtCl_4]^{2-}$, and $[PdCl_4]^{2-}$ species [23].

The reactivity of the chloro complexes with other ligands is in the order $[PdCl_4]^{2-}$ >> $[PtCl_4]^{2-}$ > $[RhCl_6]^{3-}$ > $[IrCl_6]^{3-}$>> $[(Pt, Ir)Cl_6]^{2-}$ [24].

It was observed that, in the stored ("aged") PGM solutions, aqua-complexes can predominate, resulting in much lower recovery of PGMs, especially for Rh [25], therefore only fresh solutions were used for this study. In order to design an industrial adsorption unit, information about equilibrium properties, namely adsorption isotherms, are required. Although industrial adsorption processes are most of the time carried on in fixed-bed columns, batch studies are a prerequisite to evaluate the adsorbent capacity in laboratory experiments. There are two common methods to perform equilibrium batch studies: *the volume varying method* – mixing equal masses of adsorbent with a constant volume of various concentrations of the metal of interest or *the mass varying method* – mixing of various masses of adsorbent with a constant volume of effluent containing a constant metal concentration.

Millar *et al.* [26] suggested that the variation of the metal concentration means dilution of the solutions, and that could introduce some errors. Therefore, in this study, batch equilibrium studies were conducted using the mass varying method, described also in the Dow's standard procedure for equilibrium isotherm testing [27].

Palladium

In the chloride solution, Pd(II) can form stable chloride complexes, such as $[PdCl]^{+}$, $[PdCl]_2$, $[PdCl_3]^{-}$, $[PdCl_4]^{2-}$, $[PdCl_5]^{3-}$, $[PdCl_6]^{4-}$ [5]. However, in the acidic solution containing 0.1M and higher chloride concentration, the major complex is $[PdCl_4]^{2-}$ [10]. The Pd(II) sorption from the chloride solutions by the two resins under discussion was investigated. The recovery degree from the six different solutions is depicted in Fig. 1, for both resins.

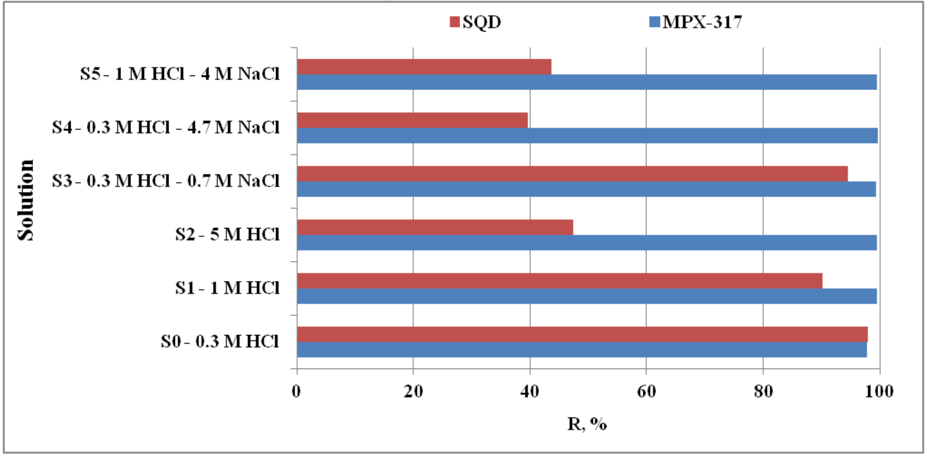

Fig. 1 Comparison of Pd recovery from Pd chloride solutions using MPX-317 and SQD resins; Conditions: 100 mg resin, 15 mL solution, 1mM Pd

Analyzing Fig. 1, it was observed that MPX-317 presents almost the same performance, regardless the acid and the sodium chloride concentrations, indicating that the Pd capture goes through a coordination mechanism. On the other hand, the SQD affinity of Pd decreases drastically with the increase in chloride concentration. The decrease in the SQD sorption yield of $[PdCl_4]^{2-}$ with the increase in chloride concentration is caused by competitive sorption of Cl^- and HCl_2^- type ions. The plot presenting the amount of Pd adsorbed on the resin versus the Pd concentration left in the solution at equilibrium, q_e (mmol/g) vs. C_e (mM), is presented in Fig. 2.

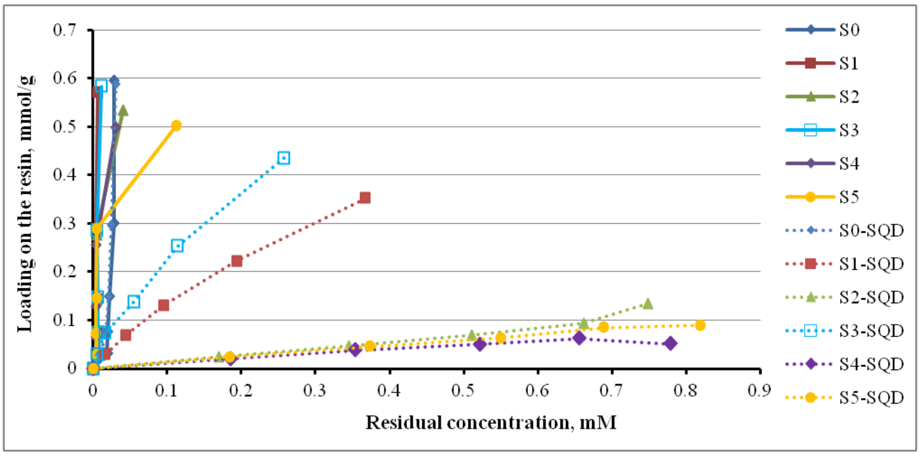

Fig. 2 Pd loading on the MPX-317 and SQD resins. S0: 0.3 M HCl, S1: 1 M HCl, S2: 5 M HCl, S3: 0.3 M HCl & 0.7 M NaCl, S4: 0.3 M HCl & 4.7 M NaCl, S5: 1 M HCl & 4 M NaCl. Conditions: 25, 50, 100, 200 or 500 mg resin, 15 mL solution, 1mM Pd

It can be observed from Fig. 2 that MPX-317 has a very good affinity towards Pd together with a high chemisorption capacity. Even when the solution composition is changed dramatically, the behavior remains very similar. SQD shows a good performance in S0 case, but with the increase in acid or sodium chloride concentration, the loadings are decreasing significantly. The ratio of Pd to resin mass employed in this study was not low enough to generate an isotherm with a distinct plateau region where maximum Pd loading had occurred, for both resins in S0. However, the results emphasized the main objective of this study, namely, the distinct behavior of the two resins when the ionic strength and/or the acid concentration is varied. The loadings of Pd from chloride solutions, obtained in thermodynamic equilibrium studies, are listed in Table 2.

From Table 2, it can be observed that, in the S0 solution, both resins show very good and similar performances, achieving a loading of 0.6 mmol/g (corresponding to 1.2 meq/g) at a recovery degree of more than 97% for all the experimental conditions. MPX-317 shows a slightly lower performance in the case of S5 solution, with a recovery of about 88% when 25 mg of resin are used, probably because the high ionic strength decreases the dissociation Pd chloride complexes.

Table 2

Pd loading on the studied resins

Resin mass, mg	Loading, mmol/g											
	$S0\cdot10^2$		$S1\cdot10^2$		$S2\cdot10^2$		$S3\cdot10^2$		$S4\cdot10^2$		$S5\cdot10^2$	
	MPX-317	SQD	MPX-317	SQD	MPX-317	SQD	MPX-317	SQD	MPX-317	SQD	MPX-317	SQD
25	60	59	57	35	53	13	58	44	50	5	50	9
50	30	30	29	22	28	9	29	25	26	6	29	8
100	15	15	14	13	14	7	14.5	14	13	5	14.5	6
200	7.5	7.5	7	7	7	5	7	7	6	4	7	5
500	3	3	3	3	3	2	3	3	3	2	3	2

Accordingly, in the same conditions, SQD captures only 16% of the Pd present in the solution, since it is anionic in nature. These results show that the sorption mechanism for the two resins is very different: MPX-317 forms coordination bonds with Pd, therefore the sorption process is almost not affected by the presence of the competing agents, such as HCl and NaCl, while SQD forms non-selective ionic bonds, therefore the Pd loading on the resin will decrease with the increase in concentration of other competing anions. To verify the loading of the metals on the resins, 100 mg resin was extracted using *aqua regia*, according to the procedure described in the Supporting Info document. This type of procedure destroys the chemical functionality of the resin; however, it is the most reliable procedure to remove the adsorbed metal from the resin. The amount of the precious metals adsorbed on the resin was determined by analyzing the extract solutions. A difference of less than 5% was observed when this extraction method was compared with the calculated results, validating the obtained results.

Platinum

The platinum (II) recovery degree from six different chloride solutions using MPX-317 and SQD resins was investigated and is presented in Fig. 3.

The two resins present a similar behavior as observed for Pd capture (Fig. 1), with MPX-317 capture performance being slightly influenced and SQD being considerably affected by the presence of the competing agents (Fig. 3). Although the total concentration of chloride is the same (5M) for solutions S2, S4, and S5, the presence of NaCl in a higher concentration is more detrimental for SQD capture performance.

The Pt removal investigation was continued with equilibrium thermodynamic studies. The plot presenting the amount of Pt adsorbed on the resin versus the Pt concentration left in the solution at equilibrium is shown in Fig. 4.

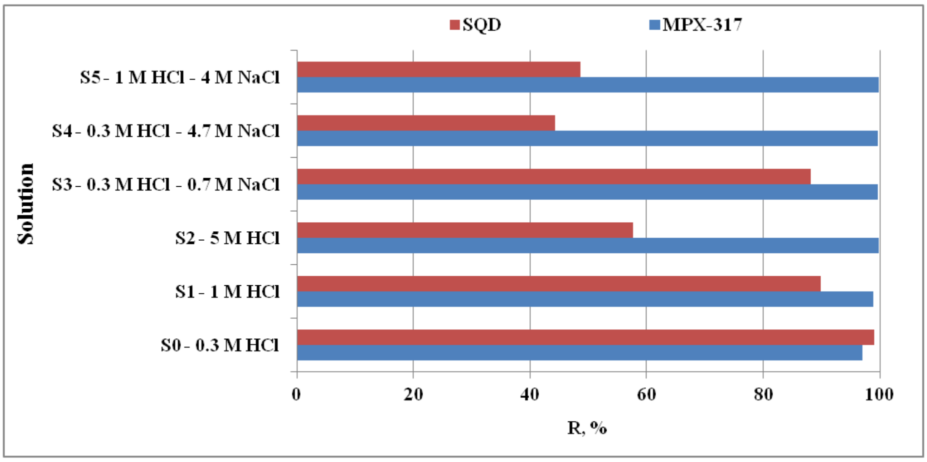

Fig. 3 Comparison of Pt recovery from Pt chloride solutions using MPX-317 and SQD resins; Conditions: 100 mg resin, 15 mL solution, 1mM Pt

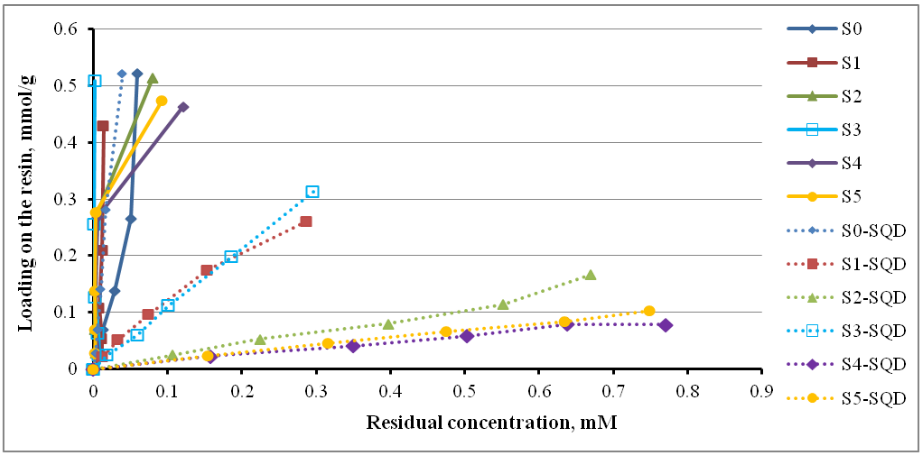

Fig. 4 Comparison of Pt loading on the MPX-317 and SQD resins. S0: 0.3 M HCl, S1: 1 M HCl, S2: 5 M HCl, S3: 0.3 M HCl & 0.7 M NaCl, S4: 0.3 M HCl & 4.7 M NaCl, S5: 1 M HCl & 4 M NaCl. Conditions: 25, 50, 100, 200 or 500 mg resin, 15 mL solution, 1mM Pt

As in the case of Pd capture, MPX-317 shows a great affinity for Pt, regardless the changes in the composition of the solution, showing that this resin is very efficient for Pt and Pd adsorption, even in very low quantities. Even in the case of the lowest mass, MPX-317 resin chemisorbs all the Pt from solution, due to its high capacity. On the contrary, SQD is heavily affected by the presence of hydrochloric acid and sodium chloride and the loadings on the resins are decreasing considerably (Fig. 4). The tested conditions (Pt initial concentration and mass of resin) did not allow to emphasize the maximum adsorption capacity of the MPX-317 resin.

Table 3

Pt loading on the studied resins

Resin mass, mg	Loading, mmol/g											
	$S0\cdot10^2$		$S1\cdot10^2$		$S2\cdot10^2$		$S3\cdot10^2$		$S4\cdot10^2$		$S5\cdot10^2$	
	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD
25	52	52	43	26	51	17	51	31	46	8	47	10
50	27	28	21	17	28	11	26	20	27	8	28	8
100	14	14	11	10	14	8	13	11	13	6	14	7
200	7	7	5	5	7	5	6	6	7	4	7	5
500	3	3	2	2	3	2	3	3	3	2	3	2

The results obtained in Pt adsorption thermodynamic equilibrium studies from chloride solutions are listed in Table 3.

MPX-317 and SQD present similar behavior in the S0 solution (Table 3), achieving a maximum loading of 0.52 mmol/g (corresponding to 1.04 meq/g). With the increase in chloride concentration, the performance starts to decrease. If, for MPX-317, the lowest recovery degree is 87% in S4 (25 mg resin), for SQD is as low as 15%, for the same conditions. This shows clearly that the resins adsorb this metal by different mechanisms. Anion exchange resins are not selective; therefore, with the increase in competing anions concentration, the loading of the metal of interest will be lower due to the lower availability of free sorption sites on the resin. Moreover, the electrostatic interactions are strongly suppressed by the presence of an electrolyte, NaCl in this study. In the case of MPX-317, the sorption mechanism might include a step driven by electrostatic interactions, the step where the metal complexes are attracted to the active sites prior to the coordination bonds forming between the metal and the resin functionality. Also, the negatively charged platinum complex cation might form with sodium a salt which dissociates much slowly, thus keeping the former in solution. This might explain the slightly lower capture performance at higher ionic strength. The extraction of the charged resins confirmed the calculated loadings.

Rhodium

Many studies reported that, in weakly acidic solutions, rhodium suffers the so called “ageing” process – transformation to kinetically inert complexes [28, 29]. Some authors [28] claim that 24 hours are enough for this process to complete. According to published data [30], complexes based on $[RhCl_6]^{3-}$ are predominant in hydrochloric acid solutions with HCl concentrations higher than 6 M. As the acidity drops, complex transformations occur in solutions, which include aquation, hydrolysis, isomerization, and polymerization.

In these systems, Rh(III) aquachloro complexes of general formula $[RhCl_n(H_2O)^{6-n}]_{3-n}$ (0≤n≤6) and cis- and trans-isomers of components $[Rh(H_2O)_2Cl_4]^-$ and $[Rh(H_2O)_4Cl_2]^+$ are formed. Moreover, bi-nuclear complexes can appear, as $[Rh_2Cl_9]^{3-}$. Furthermore, it was found that relatively large amounts of "highly" aquated $[RhCl_n(H_2O)^{6-n}]_{3-n}$ ($0 \leq n \leq 4$) species persist in up to 2.8 M HCl. In 1 M HCl, the abundance of $[RhCl_5(H_2O)]^{2-}$ species is about 34% of the total [31]. A 95% abundance of $[RhCl_6]^{3-}$ complex anion occurs only when the HCl concentration is above 6 M [6]. In 0.1 M HCl, four differently charged chloro complexes – $[RhCl_4(H_2O)]^{2-}$, $[RhCl_3(OH)(H_2O)]^{2-}$, $[RhCl_3(H_2O)_3]$, and $[RhCl_2(H_2O)]^{4+}$– were separated and identified [30]. It was suggested that the presence of a chloride salt in a freshly-prepared solution will assure the occurrence of rhodium as the hexachloro-complex, which is the most labile form [32]. Due to its complex chemistry in aqueous solutions, Rh is considered, by some authors, as one of the most complicated PGM to adsorb [31, 33]. The removal degree of Rh(III) from the six different chloride solutions, obtained using the two resins under investigation, is presented in Fig. 5.

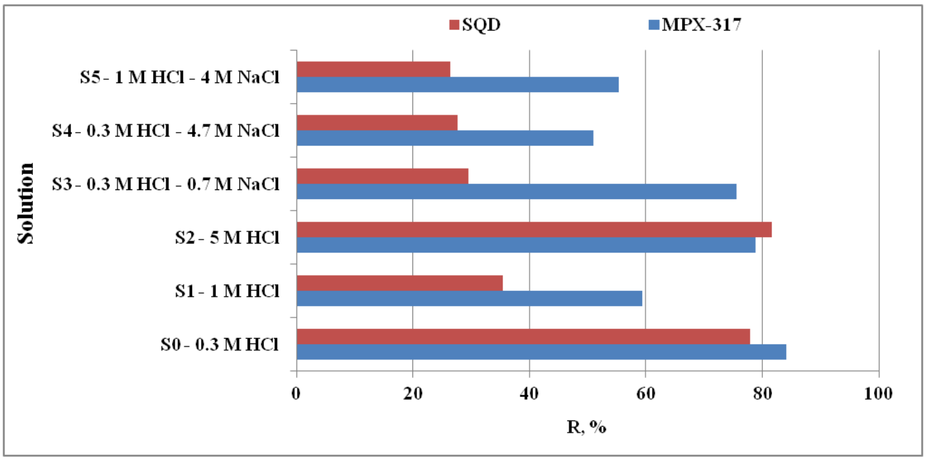

Fig. 5 Comparison of Rh removal from Rh chloride solutions using MPX-317 and SQD resins; Conditions: 100 mg resin, 15 mL solution, 1mM Rh

The screening test shows that the two resins performance is very different compared to the two PGMs previously analyzed, with a maximum removal of about 80% for S0 and S2 solutions (Fig. 5) for both resins. With the ionic strength increase, the performance is decreasing for both resins. In this case the ionic interactions are more important than for the other two PGMs studied before, therefore the presence of NaCl has a detrimental effect on the metal adsorption, when MPX-317 is used as adsorbent material. Fig. 6 shows the Rh capture thermodynamic studies.

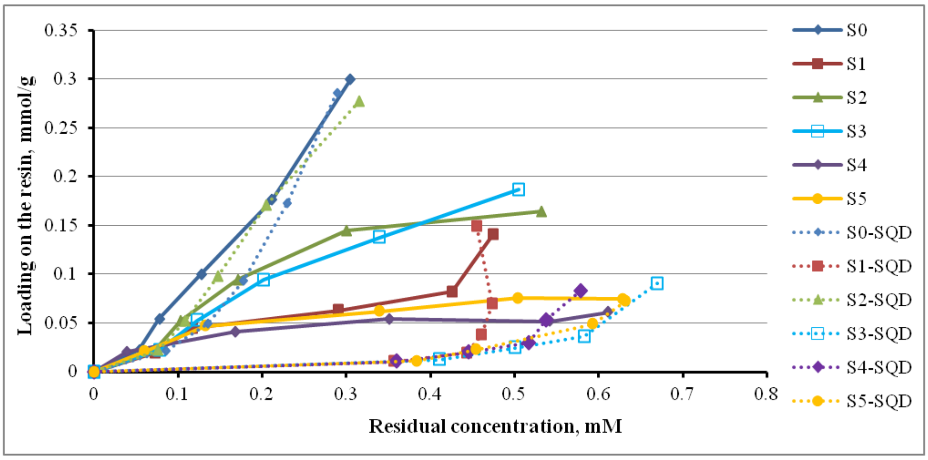

Fig. 6 Comparison of Rh loadings on the MPX-317 and SQD resins. S0: 0.3 M HCl, S1: 1 M HCl, S2: 5 M HCl, S3: 0.3 M HCl & 0.7 M NaCl, S4: 0.3 M HCl & 4.7 M NaCl, S5: 1 M HCl & 4 M NaCl. Conditions: 25, 50, 100, 200 or 500 mg resin, 15 mL solution, 1mM Rh

In the case of Rh, the performance of the two resins resembles more than that observed for Pd and Pt capture. If, for SQD, the behavior is relatively similar with the previous results, for MPX-317, a completely different behavior was observed, compared to the Pd and Pt adsorption on this material, presenting a lower affinity towards Rh and a capture performance that is decreasing with the increase in acid or sodium chloride concentration. Warshawsky *et al.* [34] classified the PGMs in 2 groups: the so-called primary PGM, including Pd and Pt, that form the same complex at all acid concentrations and can be extracted from solution with high binding constants, and the secondary PGMs, Rh, Ir, Ru, and Os, that form true chloro-complexes only in highly concentrated HCl solutions and can be extracted with much lower binding constants [34].

It can be observed that none of the resins presents favorable isotherms, the residual Rh concentration being significantly high (Fig. 6). The results obtained in sorption removal of Rh(III) from chloride solutions with various HCl concentrations are listed in Table 4. In S0 case, the two resins show similar behavior, achieving a loading of about 0.3 mmol/g (corresponding to 0.9 meq/g) at a removal degree of 62%, for 25 mg resin (Table 4). The ability of MPX-317 to capture Rh species is declining with the increase in chloride concentration, suggesting that the ionic interactions are more important than coordinate bonds, or that the Rh complexes are blocked in association-dissociation processes with the supplemental Na^+ ions. Also, it has been observed that the highly charged octahedral complexes, such as $[RhCl_6]^{3-}$, are particularly difficult to extract due to steric effects [35].

In S2 and S3 cases, the MPX-317 capturing performance is the same, indicating that 0.7 M NaCl has a similar effect as 4.7 M HCl on the capture ability. Moreover, the maximum loading is almost halved compared to S0, showing that the solution composition has a great influence on the Rh capture.

Table 4

Rh loading on the studied resins

Resin mass, mg	Loading, mmol/g											
	$S0 \cdot 10^2$		$S1 \cdot 10^2$		$S2 \cdot 10^2$		$S3 \cdot 10^2$		$S4 \cdot 10^2$		$S5 \cdot 10^2$	
	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD
25	30	29	14	15	16	28	19	9	6	8	7	7
50	18	17	8	7	14	17	14	6	5	5	8	5
100	10	9	6	4	9	10	9	4	5	3	6	3
200	5	5	4	2	5	5	5	2	4	2	5	2
500	2	2	2	1	2	2	2	1	2	1	2	1

Loadings are decreasing even more when the ionic strength is increased, as observed in S4 or S5 cases. In these solutions, the trends for both resins are very similar. SQD shows the best performance in the S0 and S2 cases. For these solutions, SQD shows a similar behavior, probably due to a low chloride competition in S0 case and due to the $[RhCl_6]^{3-}$ species present in the S2 solution that are more attracted to the resin's active sites.

In S3, S4, and S5 cases, the behavior of SQD is very similar, namely a very low capability to recover Rh, as observed for MPX-317 as well. If for S0 and S1 by doubling the mass of resin the loadings will roughly get halved, not the same trend is observed for the other solutions. In these solutions, various species, presenting higher volumes might be present. With the increase in the resin mass more active sites will be available and the steric effects are slightly less pronounced, leading to higher loadings. Although S0 contains the lowest HCl concentration and thus it's very likely to have several Rh species present in the solution, as well, the solution contains more than 3 times less chloride than S1 and therefore the competition is less pronounced in this case. One of the widely accepted explanations of the relatively small extraction of Rh is the high kinetic inertness of Rh chloride complexes [19]. The calculated loadings were confirmed by extraction.

Iridium

In the oxidation state +3, iridium will form with chloride the octahedral complex $[IrCl_6]^{3-}$. At low chloride concentration, it can form the aquo-complex $[Ir(H_2O)_3Cl_3]$ [24]. The Ir(III) sorption from the chloride solutions on the two resins under investigation is presented in Fig. 7, as the removal degree from the six different solutions.

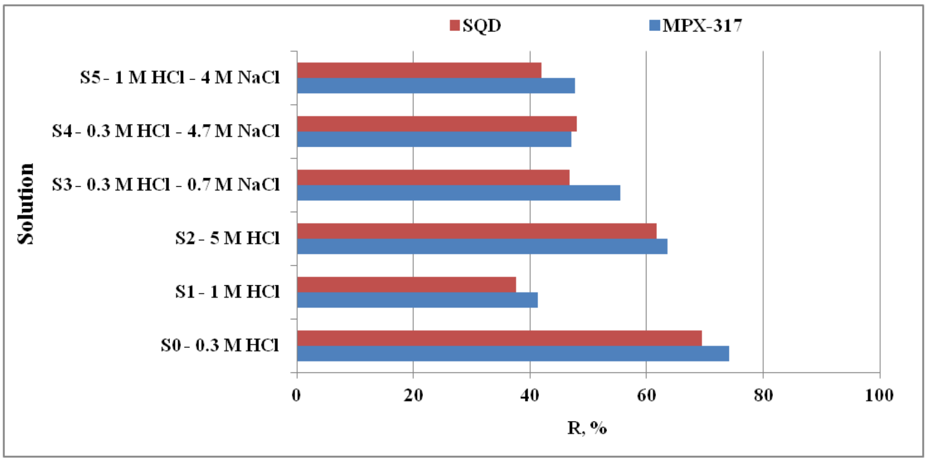

Fig. 7 Comparison of Ir removal from Ir chloride solutions using MPX-317 and SQD resins; Conditions: 100 mg resin, 15 mL solution 1mM Ir

From the screening test, it was observed that the studied resins have similar Ir capture performance, with SQD showing slightly lower removal degree values. The highest values are close to 75% (Fig. 7). The lowest performance is seen in the S1 solution. The study of the Ir capture by the two resins was continued with the thermodynamic experiments. Fig. 8 presents the Ir loadings on the two resins as a function of the Ir concentration left in the solution at equilibrium.

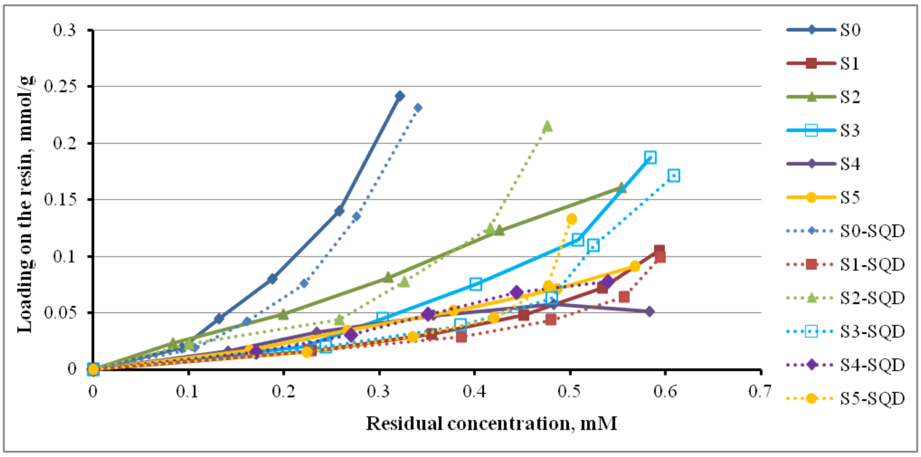

Fig. 8 Comparison of Ir loadings on the MPX-317 and SQD resins. S0: 0.3 M HCl, S1: 1 M HCl, S2: 5 M HCl, S3: 0.3 M HCl & 0.7 M NaCl, S4: 0.3 M HCl & 4.7 M NaCl, S5: 1 M HCl & 4 M NaCl. Conditions: 25, 50, 100, 200 or 500 mg resin, 15 mL solution, 1mM Ir

In the Ir adsorption case, MPX-317 and SQD behave the same, showing the best performance for the S0 solution and presenting lower loadings in more complex solutions. In the latter cases, the loading on the resin is depending greatly upon the composition of the solution. As observed for Rh as well (Fig. 6), both resins present unfavorable isotherms. The Ir adsorption process on the two studies materials is like the Rh adsorption process. Both metals present similar complexes in chloride effluents and these complexes have higher charge density than Pd and Pt, leading to a lower affinity towards the adsorbent.

The results obtained in Ir thermodynamic equilibrium studies from chloride solutions are listed in Table 5.

Table 5

Ir loading on the studied resins

Resin mass, mg	Loading, mmol/g											
	$S0 \cdot 10^2$		$S1 \cdot 10^2$		$S2 \cdot 10^2$		$S3 \cdot 10^2$		$S4 \cdot 10^2$		$S5 \cdot 10^2$	
	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD	MPX -317	SQD
25	24	23	10	10	16	22	19	17	5	8	9	13
50	14	13	7	6	12	12	11	11	6	7	7	7
100	8	8	5	4	8	8	8	6	5	5	5	5
200	4	4	3	3	5	4	4	4	3	3	3	3
500	2	2	2	2	2	2	2	2	2	2	2	1

The performed studies showed that MPX-317 and SQD follow the same capture trends (Table 5), with a maximum loading of 0.23 mmol/g (corresponding to 0.69 meq/g). Iridium sorption mechanism seems to be very similar for both resins. Although the resins present different functionalities, it is very likely that the chelation mechanism observed for MPX-317 involves a preliminary ion interaction step that, in this case, is the determining step, leading to similar results as seen for the ion exchange resin, SQD. The sorption ability of resins is reduced in solutions with higher chloride concentrations. The best results are obtained in the solution with low acidity and with small ionic strength (in solutions without sodium chloride – S0). At the same time, the concentration of the competing chloride ions is limited compared to the other solutions that were tested.

Surprisingly, almost the worst performance is observed in the 1 M HCl solution (S1, Table 5), close to the one obtained in the S4 and S5 solutions. If the low performance for the last two solutions was predictable because of the very high ionic strength that inhibits the ion exchange, for the S1 it was unexpected. The second-best results are for the 5 M HCl (S2). It was expected that the performance decreases with the higher acidity, but, in this case, the performance is much better than in S1 case (1 M HCl). This might be the result of a combined effect between the species that are formed in different solutions and the anions competition. In S2, $[IrCl_6]^{3-}$ species are expected to predominate, species that are more attracted to ion exchange resins than the aqua complexes.

However, because of the high concentration of chloride and the limited selectivity between the Ir chloride species and the chloride, the loadings are not very high. In the S0 case, Ir might not be in most favorable complexes, but as the chloride concentration is not very high, the loadings are much better than in S2. In the S1 case, the non-favorable Ir complexes are associated with a relatively high chloride concentration; therefore, the observed loadings are drastically reduced.

6. Conclusions

The sorption removal of Pd(II), Pt(II), Rh(III), and Ir(III) from freshly prepared chloride solutions on the MPX-317 and SQD resins was investigated. The model solutions parameters (acidity, metal and chloride concentrations) were chosen to simulate the industrial solutions composition.

The study shows that these resins exhibit high sorption capacity of PGMs. MPX-317 has a similar trend for Pd and Pt sorption, forming coordinate covalent bonds with Pd and Pt species; therefore, an increase in acidity or ionic strength of the solution has a very limited effect on its capture performance. On the other hand, as expected, the anionic resin SQD losses drastically its ability to capture Pd or Pt when the acidity or/and the ionic strength of the solution is increased. Rh and Ir chemistry in chloride solutions is more complex and their removal from solutions highly concentrated in chloride is more challenging. These two metals have the tendency to form different complexes that will bind differently to the resins. Moreover, the triple charged species are known to be weakly bound to resins. Also, the complexes have higher volume making extraction even more complicated due to steric effects. At the same time, it was observed that MPX-317 and SQD present relatively similar behavior towards them, indicating that the Rh and Ir sorption mechanism is strongly influenced by the ionic interactions for both resins, although for MPX-317 the latter being seen as a preliminary step. SQD shows slightly higher loading due to the higher concentration of active sites.

The calculated loadings for all four metals were confirmed by the extraction of the charged resins. The best loadings were obtained for Pd, followed closely by Pt, with more than 0.5 mmol/g. The maximum loadings for MPX-317 are very close to the announced theoretical capacity. Although SQD has a higher theoretical capacity, the maximum loadings are very similar to the MPX-317 ones, probably because of the poor selectivity which leads to chloride binding to the active sites. It was demonstrated that the actual amount of the metal sorbed by the studied resins from chloride complexes of PGMs depends on the structure of the resin and on the acidity and the ionic strength of the medium.

MPX-317 proved its capacity to bind all four PGMs, forming coordinate covalent bonds and selectively removing the former from solutions, even at low pH and/or high ionic strengths – the power of this coordinate covalent bond is as such that the metal capture process can be considered irreversible, almost all active sites being occupied, eventually.

Acknowledgments

The authors are grateful to Magpie Polymers, France, where all the experiments were carried out, and especially to Steven van Zutphen who supported this research.

REFERENCES

[1] S. F. Sibley, "Flow Studies for Recycling Metal Commodities in the United States," 2004.

[2] F. L. Bernardis, R. a. Grant, and D. C. Sherrington, "A review of methods of separation of the platinum-group metals through their chloro-complexes," React. Funct. Polym., vol. 65, no. 3, pp. 205–217, Dec. 2005.

[3] B. Godlewska-Żyłkiewicz, "Preconcentration and Separation Procedures for the Spectrochemical Determination of Platinum and Palladium," Microchim. Acta, vol. 147, no. 4, pp. 189–210, Jun. 2004.

[4] O. N. Kononova, A. M. Melnikov, and D. S. Demitrichenko, "Simultaneous Ion Exchange Recovery and Subsequent Separation of Platinum(II, IV), Rhodium(III), and Nickel(II) from Chloride and Sulfate-Chloride Solutions," Solvent Extr. Ion Exch., vol. 31, no. 3, pp. 306–319, 2013.

[5] A. Wołowicz and Z. Hubicki, "Effect of matrix and structure types of ion exchangers on palladium(II) sorption from acidic medium," Chem. Eng. J., vol. 160, no. 2, pp. 660–670, 2010.

[6] W. J. Gerber, K. R. Koch, H. E. Rohwer, E. C. Hosten, and T. E. Geswindt, "Separation and quantification of [RhCln(H2O) 6-n]3-n (n = 0-6) complexes, including stereoisomers, by means of ion-pair HPLC-ICP-MS," Talanta, vol. 82, no. 1, pp. 348–358, 2010.

[7] C. Hagelüken, "Recycling the Platinum Group Metals: A European Perspective," Platin. Met. Rev., vol. 56, no. 1, pp. 29–35, Jan. 2012.

[8] R. J. Kriek, W. J. Engelbrecht, and J. J. Cruywagen, "Separation and recovery of some platinum group metals (PGMs) by means of selective photocatalytic reduction," J. South African Inst. Min. Metall., no. April, pp. 75–82, 1995.

[9] F. K. Crundwell, M. S. Moats, T. G. Robinson, and W. G. Davenport, Extractive Metallurgy of Nickel , Cobalt and Platinum-Group Metals. Elsevier Ltd, 2011.

[10] Z. Hubicki and A. Wołowicz, "A comparative study of chelating and cationic ion exchange resins for the removal of palladium(II) complexes from acidic chloride media.," J. Hazard. Mater., vol. 164, no. 2–3, pp. 1414–9, May 2009.

[11] K. F. Lam, C. M. Fong, and K. L. Yeung, "Separation of precious metals using selective mesoporous adsorbents," Gold Bull., vol. 40, no. 3, pp. 192–198, Sep. 2007.

[12] Q. Ricoux, V. Bocokić, J. P. Méricq, D. Bouyer, S. v. Zutphen, and C. Faur, "Selective recovery of palladium using an innovative functional polymer containing phosphine oxide," Chem. Eng. J., vol. 264, pp. 772–779, 2015.

[13] P. N. Nesterenko, P. Jones, and B. Paull, High Performance Chelation Ion Chromatography. The Royal Society of Chemistry, 2011.

[14] N. D. Abovskii, A. A. Blokhin, and Y. V. Murashkin, "Kinetics of platinum(II) and platinum(IV) sorption from hydrochloric acid solutions with a complexing ion exchanger containing thiourea functional groups and with a strongly basic anion exchanger," Russ. J. Appl. Chem., vol. 80, no. 7, pp. 1063–1067, 2007.

[15] M. Can, E. Bulut, A. Örnek, and M. Özacar, "Synthesis and characterization of valonea tannin resin and its interaction with palladium (II), rhodium (III) chloro complexes," Chem. Eng. J., vol. 221, pp. 146–158, 2013.

[16] M. Guinó and K. K. Hii, "Applications of phosphine-functionalised polymers in organic synthesis," Chem. Soc. Rev., vol. 36, no. 4, pp. 608–617, 2007.

[17] A. Muşină, V. Bocokić, V. Lavric, and S. van Zutphen, "Phosphorus-Based Polymers for Selective Capture of Platinum Group Metals", Ind. Eng. Chem. Res., vol. 53, p. 13362 − 13369, Aug. 2014.

[18] Q. Ricoux, J. P. Méricq, D. Bouyer, V. Bocokić, L. C. Hernandez-Juarez, S. van Zutphen, C. Faura, "A selective dynamic sorption-filtration process for separation of Pd(II) ions using an aminophosphine oxide polymer," Sep. Purif. Technol., vol. 174, pp. 159–165, 2017.

[19] A. N. Nikoloski, K.-L. Ang, and D. Li, "Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins," Hydrometallurgy, vol. 152, no. July 2015, pp. 20–32, 2015.

[20] V. Yahorava and M. Kotze, "Ion exchange technology for the efficient recovery of precious metals from waste and low-grade streams," J. South. African Inst. Min. Metall., vol. 114, no. 2, pp. 173–181, 2014.

[21] A. Lienke, G. Klatt, D. J. Robinson, K. R. Koch, and K. J. Naidoo, "Modeling platinum group metal complexes in aqueous solution," Inorg. Chem., vol. 40, no. 10, pp. 2352–2357, 2001.

[22] F. R. Hartley, Ed., Chemistry of the Platinum Group Metals. Elsevier Science Publishers B.V, 1991.

[23] S. A. Cotton, Chemistry of Precious Metals, 1st ed. Chapman & Hall Typeset, 1997.

[24] G. J. Bernfeld, A. J. Bird, R. I. Edwards, H. Köpf, P. Köpf-Maier, C. J. Raub, W. A. M. te Riele, F. Simon, W. Westwood, Pt Platinum, 8th ed. Berlin, Springer, 1985.

[25] A. N. Nikoloski and K.-L. Ang, "Review of the Application of Ion Exchange Resins for the Recovery of Platinum-Group Metals From Hydrochloric Acid Solutions," Miner. Process. Extr. Metall. Rev., vol. 35, no. 6, pp. 369–389, Nov. 2014.

[26] G. J. Millar, S. J. Couperthwaite, and C. W. Leung, "An examination of isotherm generation: Impact of bottle-point method upon potassium ion exchange with strong acid cation resin," Sep. Purif. Technol., vol. 141, pp. 366–377, 2015.

[27] DOW, "Application Information – DOWEX Ion Exchange Resins; Equilibrium Isotherm Testing for Liquid Phase Applications," Midland, 1997.

[28] O. N. Kononova, A. M. Melnikov, T. V. Borisova, and A. S. Krylov, "Simultaneous ion exchange recovery of platinum and rhodium from chloride solutions," Hydrometallurgy, vol. 105, no. 3–4, pp. 341–349, Jan. 2011.

[29] O. N. Kononova, A. S. Glebova, A. M. Mel'Nikov, D. M. Kashirin, and S. G. Konontsev, "Sorption recovery of rhodium(III) from chloride and chloride-sulfide solutions," Russ. J. Appl. Chem., vol. 83, no. 10, pp. 1767–1773, 2010.

[30] S. S. Aleksenko, A. P. Gumenyuk, S. P. Mushtakova, and A. R. Timerbaev, "Speciation studies by capillary electrophoresis - Distribution of rhodium(III) complexed forms in acidic media," Fresenius. J. Anal. Chem., vol. 370, no. 7, pp. 865–871, 2001.

[31] T. E. Geswindt, "Chemical speciation of Rh III complexes in acidic , halide-rich media by means of 103 Rh NMR spectroscopy : The importance of speciation in the selective separation and recovery of rhodium", Ph. D. Thesis, Stellenbosch University, 2013.

[32] S. J. Al-Bazi and A. Chow, "Platinum metals-solution chemistry and separation methods (ion-exchange and solvent extraction)," Talanta, vol. 31, pp. 815–836, 1984.

[33] J. M. Sánchez, M. Hidalgo, J. Havel, and V. Salvadó, "The speciation of rhodium(III) in hydrochloric acid media by capillary zone electrophoresis," Talanta, vol. 56, pp. 1061–1071, 2002.

[34] A. Warshawsky, M. M. B. Fieberg, P. Mihalik, T. G. Murphy, and Y. B, "The Separation of Platinum Group Metals (PGM) in Chloride Media by Isothiouronium Resins," Sep. Purif. Methods, vol. 9, no. 2, pp. 209–265, Jan. 1980.

[35] E. Benguerel, G. P. Demopoulos, and G. B. Harris, "Speciation and separation of rhodium (III) from chloride solutions: a critical review," Hydrometallurgy, vol. 40, no. 1–2, pp. 135–152, Jan. 1996.