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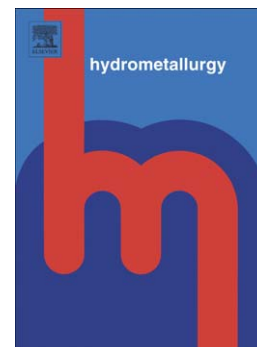
Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins

Aleksandar N. Nikoloski*, Kwang-Loon Ang and Dan Li

Chemical and Metallurgical Engineering and Chemistry,

School of Engineering and Information Technology, Murdoch University, Australia

Abstract

The objective of this study was to investigate the applicability and performance of the selected ion exchangers with different physicochemical characteristics and functional groups to simultaneously recover three different platinum group elements (PGE), platinum(IV), palladium(II) and rhodium(III), present in a chloride solution produced by the leaching of spent automotive catalysts. The tested ion exchangers included a resin with a quaternary ammonium functional group (Lewatit MonoPlus (M+) MP 600), a resin with a polyamine functional group (Purolite S985) and a resin with a thiouronium functional group (XUS 43600.00). The study also focused on the achievable desorption from the loaded resins using different eluent systems. The leach solution was chlorine-saturated and contained 2.35 mol/L hydrochloric acid, platinum and palladium in concentrations of 0.13 mmol/L, and rhodium 0.03 mmol/L. It was found that XUS 43600.00 showed the best adsorption performance for platinum(IV) and palladium(II) chloride complexes among the investigated resins, but weak affinity for rhodium(III) chloride complexes was observed for all three resins. The adsorption kinetics were found to obey the Ho pseudo-second order expression. For Lewatit MonoPlus (M+) MP 600 and Purolite S985 the adsorption was best described by the Freundlich isotherm, while for XUS 43600.00 the Langmuir isotherm was more apt. Desorption of the PGE was examined using four different elution agents: sodium thiocyanate (2 mol/L); hydrochloric acid (2 mol/L); thiourea (1 mol/L) in hydrochloric acid (2 mol/L); and thiourea (1 mol/L) in sodium hydroxide (2 mol/L). The results showed that platinum and palladium can be fully eluted with the acidic thiourea but desorption of rhodium proved difficult with all the eluents.

[*]Corresponding author. Telephone: +61 8 9360 2835; Fax: +61 8 9360 6343.
E-mail address: A.Nikoloski@murdoch.edu.au (A. N. Nikoloski).
Postal address: School of Engineering and Information Technology, Murdoch University, 6150, Western Australia

1 Introduction

In recent years, the recycling of platinum group elements (PGE) has become an increasingly important topic, both as a potential strategy for maintaining the supply of these metals and in terms of converting a previously disposable material into a valuable renewable resource (Anon, 2007; Barakat and Mahmoud, 2004; Bernardis *et al.*, 2005; Faurie, 2011; Gaita and Al-Bazi, 1995; Magilligan *et al.*, 2011; Senthilingam, 2011; Zolotov et al,. 2003). The growing demand for potential secondary sources of PGE has intensified research and development work which aims to recover PGE from wastes or spent materials. These secondary sources can include spent automotive catalysts, catalysts from the chemical industry, electronic scrap, exhausted nuclear fuel, military equipment and even tailings from ore-dressing plants for noble metals-containing deposits (Anon, 2007; Barakat and Mahmoud, 2004; Belyaev, 2003; Matthey, 2011; Rao and Reddi, 2000; Zolotov *et al.*, 2003).

A patented work at Murdoch University was recently published to provide an innovative process for recovering PGE from spent automotive catalysts (Nicol and Nikoloski, 2011). Nicol and Nikoloski (2011) showed that platinum (Pt), palladium (Pd) and rhodium (Rh) can be extracted with effectiveness which compares well to other extraction methods using much more rigorous conditions, *e.g.*, high pressure, high temperature and prolonged reaction times. Subsequently, all three PGE from the leachate solution were successfully recovered by means of precipitation or cementation. Though no comparison was made, the authors suggested that the resulting leachate solution may be subjected to other recovery techniques, *e.g.*, electrowinning, solvent extraction, gas-reduction or adsorption to recover the desired PGE from the leachate solution.

The recovery and separation of PGE in precious metal refineries had been achieved by a series of precipitation processes until the 1970s when other effective and promising techniques, *i.e.*, solvent extraction and ion exchange, were introduced and adopted by the refineries (Bernadies *et al.*, 2005; Edwards *et al.*, 1985, p.2; Renner *et al.*, 2012; Warshawsky, 1987, p.157). These advanced techniques offer a number of advantages which the classical methods were lacking, such that higher selectivity of PGE and higher metal purity can be obtained (Bernadis *et al.*, 2005; Cieszynska and Wiśniewski, 2012; Rengaraj *et al.*, 2001). As a result of these significantly improved features, solvent extraction and ion exchange are recognised by many as potentially more efficient and economically justified, even for application with leachate solutions containing very low PGE concentration. For that

reason, an alternative approach based on ion-exchange (IX) technology was proposed in this study to investigate the recovery of PGE from the chloride leach solution of spent automotive catalyst.

The use of IX for metal recovery and separation is not an unproven technology but is dated back to its unique success achieved in the late 1940s. Early examples include the separation of rare earth elements (Harris and Tompkins, 1947; Ketelle and Boyd, 1947; Marinsky *et al.*, 1947; Spedding *et al.*, 1947a, 1947b), separation of sodium and potassium (Cohn and Kohn, 1948, Schubert, 1949) and amino acids (Cleaver and Cassidy, 1950). Today, IX technology is well established, with modern applications, such as, the recovery of precious metals (*e.g.* gold, silver, PGE), base metals (*e.g.* copper, zinc, nickel and iron) and uranium, removal of trace level impurities from aqueous systems for pollution control, and in pharmaceutical and chemical processing techniques for the production of pure and ultrapure water (Green *et al.*, 1998, 2002; Haines, 1978; Hubicki et al, 2008; Mendes and Berni, 2009; Rousseau, 1987; Zagorodni, 2007). The literature also suggests that a wide range of specific functionalised resins have been studied extensively and demonstrated to be feasible in their application for selective recovery of PGE (Hubicki *et al.*, 2008; Kononova *et al.*, 1998; 2007; 2008; 2009; 2010a, b, c; 2011; 2013; Mel'nikov *et al.*, 2012a, b; Nikoloski and Ang, 2014; Wołowicz and Hubicki, 2011; Wołowicz *et al.*, 2011).

Throughout the course of the literature review, the present authors of this study found that Purolite S985 and Lewatit MP 600 WS excel among other anion exchangers. The recovery conditions of PGE from the chloride system on anion exchangers Lewatit MP 600 WS and Purolite S985 were extensively studied by Kononova *et al.* (2010a, c; 2011; 2013) and Mel'nikov *et al.* (2012a, b). These anion exchangers were recommended because of their comparatively better sorption and kinetic properties for PGE than other investigated resins. They also exhibited promising performance in the elution of PGE. Nonetheless, both anion exchangers have yet to be tested in any hydrometallurgical leaching solution, but were only demonstrated in synthetically made solution. The scope of the investigations by these authors was also limited to the recovery of either one PGE element or a combination of two PGE elements at most in the chloride media. Thus, it was deemed useful to investigate the sorption characteristics of these anion exchangers in chloride leach solution of spent automotive catalyst for the simultaneous recovery of Pt, Pd and Rh.

In addition to these two resins, a new ion exchanger XUS 43600.00 with thiouronium functional group was developed by Dow in the recent years and it is claimed to be very

selective for platinum group elements. Chelating resins containing thiouronium (thiourea) or its derivatives (*e.g.* isothiouronium) functional groups are widely used for the separation of platinum-group metal ions from other ions (Hubicki et al, 2008). Lewatit TP-214, Purolite S-920, Srafion NMRR and Monivex are among the few thiouronium-functionalised resins that have been reported to possess promising ability to separate and recover PGE (Blokhin *et al.*, 2007; Hubicki and Wołowicz, 2009; Hubicki *et al.*, 2007; Hubicki *et al.*, 1998; Warshawsky, 1987; Warshawsky et al, 1980). Nonetheless, there was no data readily available in regards to the use of thiouronium-functionalised resin in the simultaneous sorption of Pt, Pd and Rh from hydrometallurgical leaching solutions, *e.g.* chloride leach solution of spent automotive catalyst. Hence, it was also of great practical relevance to assess the performance of the new XUS 43600.00 thiouronium-functionalised chelating resin and to compare its performance with the other two resins.

The objective of the study therefore was to investigate the applicability and adsorption performance of the selected ion exchangers of different physical-chemical characteristics (*i.e.* Purolite S985, Lewatit M+ MP 600, and XUS 43600.00) in recovering Pt, Pd and Rh simultaneously present in the chloride leach solution collected from leaching spent automotive catalyst. The investigation also focussed on the achievable desorption from these resins using different eluent systems. Both the rates and extents of adsorption and desorption for Pt, Pd and Rh are reported and the mechanisms of the adsorption processes are discussed using relevant models. The main difference between the ion exchanger Lewatit MP 600 WS (a heterodisperse resin) studied previously and Lewatit M+ MP 600 (a monodisperse resin) used in this study is their bead size distribution.

2 Experimental materials and methods

2.1 Reagents and solutions

2.1.1 Loading solutions

Two different PGE-containing solutions were used in this study: (i) *process leach solution* which was a chlorine-saturated leach solution of spent automotive catalyst containing Pt, Pd and Rh and a range of impurity elements, and (ii) *synthetic solution* made up of analytical grade chemicals, thus containing only Pt, Pd and Rh with no other metal ions impurities.

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The *process leach solution* was a blend of PGE-containing leach liquors from a previous project involving leaching and recovery of PGE from used automotive catalytic converters conducted by Nicol and Nikoloski (2011). To generate the process leach solution, PGE-containing feed was subjected to a treatment which involved roasting under oxidative conditions and then under reducing conditions, followed by leaching in a hydrochloric acid leach solution in the presence of an oxidising agent. The produced leach liquors were then subjected to various recovery treatments resulting in the PGE-containing leach liquors. The *process leach solution* contained typically 2.35 mol/L hydrochloric acid (HCl), 0.129 mmol/L Pt and 0.125 mmol/L Pd, and 0.033 mmol/L Rh and a range of impurity elements, as listed in Table 1.

Table 1. Concentration of all elements present in *process leach solution*

Elements	Concentration (mM)	Elements	Concentration (mM)
Na	1,086	Fe	3.152
Mg	8.188	Co	0.085
Al	265.7	Ni	0.690
Si	1.442	Cu	0.110
K	0.640	Zn	0.956
Ca	2.046	Pb	0.333
Ti	0.105	Ce	2.174
V	0.020	Pt	0.129
Cr	0.115	Pd	0.125
Mn	0.965	Rh	0.033

The *synthetic solution* contained approximately 4 times the amount of Pt and Pd and 6 times the amount of Rh element present in the *process leach solution*. The *synthetic solution* was prepared by diluting concentrated HCl solution with deionised water, before addition of hydrated hydrogen hexachloroplatinate(IV), palladium(II) chloride, and hydrated rhodium(III) chloride salts. All chemicals used were of analytical grade. The *synthetic solution* was analysed and its working concentrations were reported as follow: 4.11 mol/L HCl, 0.513 mmol/L Pt, 0.470 mmol/L Pd, and 0.194 mmol/L Rh. In contrast to the *process leach solution*, the *synthetic solution* contains no other metal ions.

2.1.2 Eluent solutions

The PGE-loaded resins were chemically stripped using an elution reagent (eluant). Four different eluent solutions were tested: (i) 2 mol/L NaSCN; (ii) 2 mol/L HCl; (iii) 1 mol/L thiourea in 2 mol/L HCl; and (iv) 1 mol/L thiourea in 2 mol/L NaOH. These solutions were prepared by: (i) dissolving appropriate amount of solid NaSCN in deionised water; (ii) dilution of concentrated HCl with deionised water to the desired concentration; (iii) dissolving appropriate amount of thiourea salt in 2 mol/L HCl; and (iv) dissolving appropriate amount of thiourea salt in 2 mol/L NaOH. All chemicals were of analytical grade.

The PGE-loaded resins used in the elution tests were first equilibrated in the *process leach solution* for 24 hours. Subsequently, these resins were separated from the *process leach solution*, rinsed with ample amount of deionised water, and sealed in sample vials until the elution tests. Resins equilibrated in the *synthetic solution* were not used in the elution tests.

2.2 Resins used and method of pre-treatment

Three ion exchange resin types, each with a different functional group, were evaluated in this study. These were: (i) strong base resin (Lewatit M+ MP 600) produced by Lewatit (Germany); (ii) weak base resin (Purolite S985) produced by Purolite (UK); and (iii) chelating type resin (XUS 43600.00) produced by Dow (USA). Each resin was selected based on its selectivity for PGE ions as reported by the suppliers and in the published literature. The basic physicochemical properties of each resin are summarised in Table 2. Figure 1 shows the chemical structure of the functional groups of each resin (Zaganiaris, 2013; Wołowicz and Hubicki, 2011).

Table 2. Physicochemical properties of investigated resins

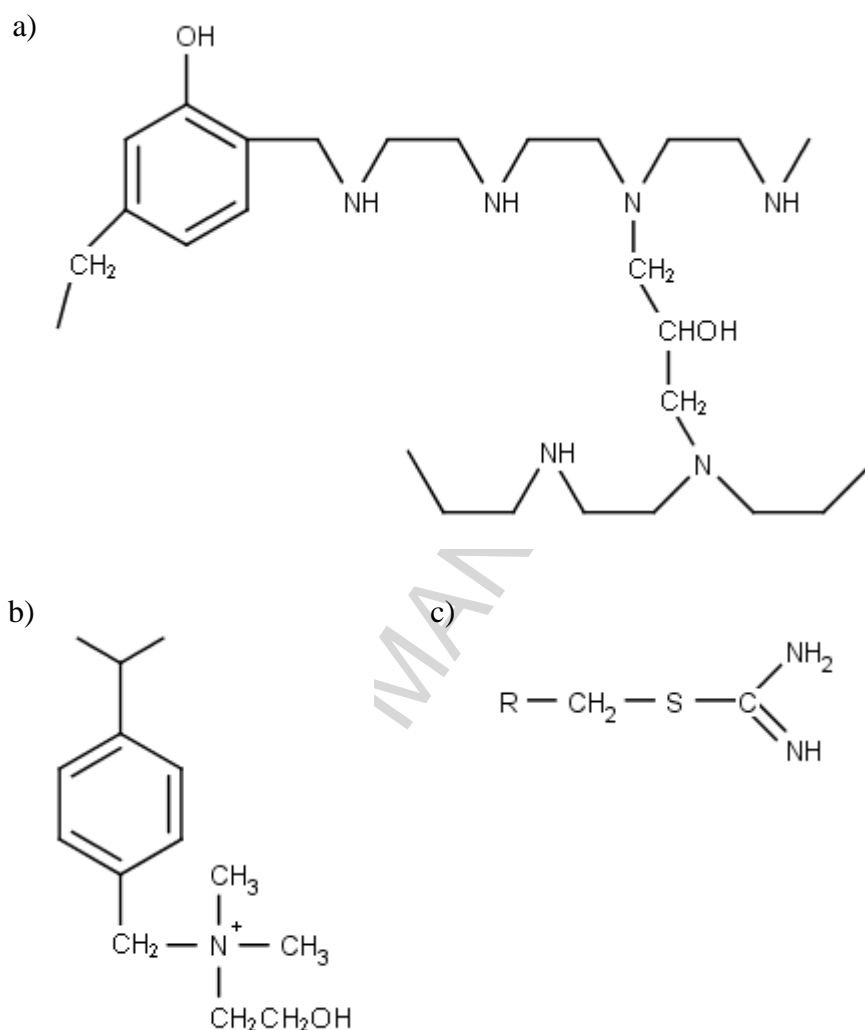| Trade name	Functional group	Matrix	Operating pH range	Capacity to Cl^- (mmol/g)
Lewatit *M+ MP* 600	Quaternary ammonium, type 2	Styrene-divinylbenzene	0-14	1.1
Purolite *S*985	Polyamine	Polyacrylic-divinylbenzene	0-10	2.3
XUS 43600.00	Thiouronium (Thiourea)	Styrene-divinylbenzene	0-7	1.1

Figure 1. Chemical structure of functional groups of a) Purolite S985, b) Lewatit M+ MP 600 and c) XUS 43600.00

All resins had a macroporous matrix and were supplied in free base form. They were converted to chloride form by passing 10 bed volumes (BV) of 1 mol/L sodium chloride, *i.e.* 10 times the volume of the wet settled resin. The pre-conditioning was carried out in a glass column containing the resin in a top-to-bottom flow setup at a rate of 2 bed volumes per hour (BV/h). This was followed by rinsing the resin with deionised (DI) water at a flow rate of 10 BV/h for 30 minutes to wash off any remaining chloride-containing solution. The prepared resins were stored in sealed flasks, with deionised water added to keep the resins hydrated, ready to be used for the isotherm and kinetic tests. The bead size ranges for each type of resin and the average grain radius of the resins, which were used to calculate the kinetic parameters, are obtained from the supplier or manufacturer data, as given in Table 3.

Table 3. Resin bead size range and average bead radius of resins used

Resin	Bead size range (mm)	Bead radius (mm)	Bead density (kg/L)
Lewatit *M+ MP* 600	0.55-0.65	0.30 ± 0.03	1.05
Purolite *S*985	0.30-1.20	0.38 ± 0.23	1.07
XUS 43600.00	0.50-0.65	0.29 ± 0.04	1.06

2.3 Method used to generate adsorption isotherms

An adsorption isotherm was generated for each type of resin using a batch equilibration technique. The volume of wet settled resin added in each equilibration test was varied whereas the volume of the test solution was fixed. The resin additions were 5 mL, 2.5 mL, 1 mL, 0.5 mL, 0.25 mL, and 0.1 mL. These separate tests were carried out with *process leach solution* only and at a room temperature of approximately 25°C.

The batch equilibration test was carried out in roller bottles on a rolling machine in order to minimise the resin damage. This also enabled multiple tests to be run at the same time shortening the experimental period. The wet settled resin was added to a bottle along with 200 mL of test solution. The resin and solution were then allowed to equilibrate for 24 hours under constant rolling speed. The weight of the reactor containing both the resin and the solution was recorded at the start and at the end of each test and samples of the starting and final solution were analysed. These steps were repeated for each type of resin. The concentration of PGE in the collected solution samples were determined by inductively-coupled plasma atomic emission spectrophotometry (ICP-AES). The analyses were carried out by the Marine and Freshwater Research Laboratory, Murdoch University.

2.4 Method used to determine rate of adsorption

The rate of adsorption of PGE ions onto the resins was examined using a batch equilibration method. Solution samples collected during the approach to equilibrium were analysed for their PGE concentrations. This allowed the contact period necessary for the adsorption of PGE onto resin to be determined in order to obtain an efficient adsorption process. Tests were carried out with both the *process leach solution* and *synthetic solution*.

The batch equilibration method involved placing 5 mL of wet settled resin in contact with 200 mL test solution in a roller bottle and agitating at a rate sufficient to suspend the

resins for 24 hours. At specified time intervals (0, 5, 10, 15, 30, and 45 minutes; 1, 2, 3, 6, and 24 hours), the weight of the reactor containing both the resin and the solution was weighed and 2 mL of solution was extracted using an adjustable positive displacement pipette. The solution samples were sent to Marine and Freshwater Research Laboratory, Murdoch University for analysis to determine their PGE concentrations via ICP-AES. Care was taken not to remove any resin while collecting the solution sample. At the end of the 24 hours equilibration period, the resin was separated from the solution by filtering. These steps were followed for each type of resin.

2.5 Method used to determine relative desorption

The PGE-loaded resins were batch-eluted using the roller bottle technique. 2 bed-volumes (BV) of eluent solution, *i.e.* 2 times the volume of the wet settled resin, was allowed to equilibrate with the PGE-loaded resin for 2 hours. This was followed by screening and washing with 2 BV of deionised water for 30 minutes. These steps were then repeated, amounting to a total elution of 5 hours. Samples of solution were collected for analysis each time the eluent was changed. These steps were reiterated for each combination of three different resins and four different eluent solutions.

2.6 Method used to determine rate of desorption

Once the most effective eluent (in terms of percentage of PGE stripped from the resin) was identified, the rate of desorption of PGE from the PGE-loaded resin was examined. These tests were set-up at room temperature using a glass chromatographic column with an inner diameter of 10 mm. The column was filled with a slurry of the PGE-loaded resin (5.0 mL of wet-settled resin), which gives an approximate ratio of resin bed height to column diameter of 6:1. The PGE in the resin were then selectively eluted with eluent pumped bottom-to-top using a peristaltic pump at the rate of 2 BV/h (10 mL/h) for 5 hours. Samples of 1 BV (5 mL) of eluent that passes through the resin were collected every 30 minutes until a total of 10 BV (50 mL) of eluent had passed through the column. Following the 5 hours of elution, the resin was washed with deionised water at a rate of 10 BV/h. The volume of deionised water used was measured and recorded, and a solution sample was taken for analysis. These steps were repeated for each of the three different resins.

3   Results and Discussion

3.1   PGE sorption from *synthetic solution* and *process leach solution*

Table 4 below shows the IX sorption recovery of Pt, Pd and Rh from the *synthetic solution* and the *process leach solution* in a 24-hours sorption test. Among the three investigated ion exchangers, it can be seen from the tabulated data that the ion exchanger XUS 43600.00 has the best overall sorption recovery of PGE in both *synthetic solution* and *process leach solution*. The highest sorption recovery of Pt and Pd from the *synthetic solution* and the *process leach solution* was achieved by XUS 43600.00, whereas Purolite S985 recovers the greatest amount of Rh in both *synthetic solution* and *process leach solution*.

Table 4. 24-hours PGE sorption from *synthetic solution* and *process leach solution* (5 mL wet-settled resin in 200 mL solution)

Trade name	Metal	Recovery (%)	
		Synthetic solution	Process leach solution
XUS 43600.00	*Pt*	99.9	99.7
	Pd	99.9	99.6
	Rh	86.4	75.3
Lewatit *M+ MP* 600	*Pt*	97.3	97.2
	Pd	84.1	91.8
	Rh	37.0	8.2
Purolite *S*985	*Pt*	75.6	81.6
	Pd	52.3	58.8
	Rh	94.8	87.8

The strongly basic anion exchanger Lewatit M+ MP 600 exhibited a high sorption affinity to Pt, as seen in the sorption recovery of Pt from both *process leach solution* and *synthetic solution*. This is consistent with the observations by Kononova *et al.* (2010c) and Mel'nikov *et al.* (2012b) who tested a heterodisperse version of this ion exchanger. On the other hand, the sorption recovery of Rh from both *synthetic solution* and *process leach solution* was markedly unfavourable, which was also observed by Kononova *et al.* (2009). The degree of sorption recovery of Pd from the *synthetic solution* was comparatively lower than from the *process leach solution*. This is likely because of the competing effect from the higher chloride concentration in the *synthetic solution* than in the *process leach solution*. It

should be noted that this is unlikely to be due to the effect of the acidity of the contacting solution (Kononova *et al.*, 2009; 2010c; Mel'nikov *et al.*, 2012b) which is explained further in the latter section of this paper.

As shown in Table 4, it appears that the sorption ability of the weakly basic anion exchanger (Purolite S985) was reduced in the *synthetic solution*, which had higher acidity level than the *process leach solution*. This suggests that the acidity of the contacting solution may have some detrimental effects towards the sorption recovery of Pt and Pd. The effect of acidity of the contacting solution towards the sorption ability of Purolite S985 has also been reported by Kononova *et al.* (2013; 2011; 2009) and Mel'nikov *et al.* (2012b). The possible reason for such behaviour of the weak base resin is included in the latter section of this paper. In contrast, the sorption recovery of Rh by Purolite S985 was not affected by the acidity of the contacting solution but increased in the *synthetic solution*. This is most likely due to the competing effect of other metal ion impurities present in the *process leach solution* which were not present in the *synthetic solution*.

In both *synthetic solution* and *process leach solution*, the XUS 43600.00 chelating resin exhibited a remarkable degree of sorption recovery of Pt and Pd of above 99%. This high sorption ability of ion exchangers containing functional thiourea or isothiourea groups for the so-called 'primary' PGE (*i.e.* Pt and Pd) is also acknowledged by several authors (Hubicki and Wołowicz, 2009; Hubicki *et al.*, 2007; Warshawsky, 1987; Warshawsky *et al.*, 1980). The sorption recovery of Rh by XUS 43600.00, however, was only of average performance. Warshawsky (1987) explained that the recovery of 'secondary' PGE (*i.e.* Rh, Ru, Ir, Os) is subject to lower binding constants as compared to the 'primary' PGE. The sorption recovery of Rh is also likely to have been affected by the competing effect of other metal ion impurities present in the *process leach solution*, as can be seen in Table 4.

3.2 Adsorption equilibrium isotherms study

The adsorption isotherms of Pt, Pd and Rh from the *process leach solution* on the resins investigated are presented in Figure 2 to Figure 4. Two different types of relationship are evident in these figures: some of the isotherms are convex, while others exhibit linear or near-linear behaviour. A convex shaped isotherm indicates that the resin has high selectivity for a particular platinum-group element (Helfferich, 1962). Conversely, an isotherm with a linear

or near-linear profile suggests that the resin has poor adsorption selectivity for a particular platinum-group element.
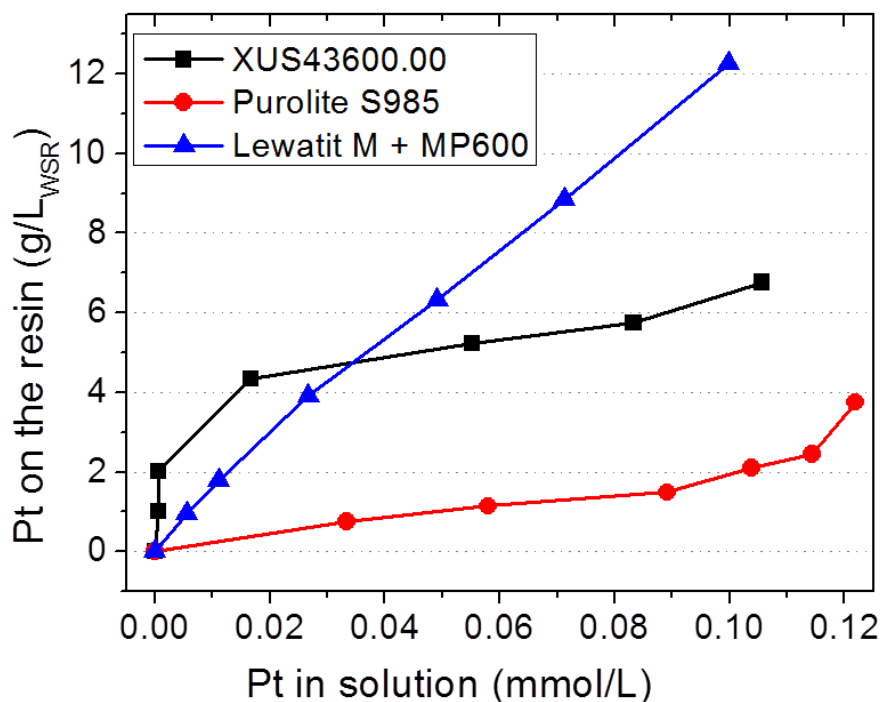

Figure 2. Adsorption isotherms of Pt from *process leach solution* containing Pd, Rh and other impurities on the resins investigated

The adsorption isotherm of Pt on XUS 43600.00 anion chelating resin presented in Figure 2 appears convex, which indicates that this resin has high adsorption selectivity for Pt in the presence of other competing platinum-group metallic compounds. The experimental results reveal that near-complete recovery of Pt is achievable even when the volume ratio of solution to resin is 80:1. It should be noted that the *process leach solution* has been kept for a long period of time (*i.e.* more than 3 months) and contained considerably high acid concentration of > 2 mol/L HCl. On the other hand, the isotherms of Pt on Purolite S985 and Lewatit M+ MP 600 show relatively straight lines up until a higher concentration of Pt in the solution at equilibrium, indicating poor adsorption selectivity of these two resin types for Pt in the given system.

The adsorption isotherms of Pd on the three resins are presented in Figure 3. It is apparent that the adsorption isotherm of Pd on XUS 43600.00 follows a convex profile, similar to the isotherm profile for the adsorption isotherm of Pt on XUS 43600.00. This indicates that XUS 43600.00 also has high adsorption selectivity for Pd in the given system.

In contrast, Purolite S985 has a near-linear-shaped isotherm (up until a higher concentration of Pd in the solution at equilibrium) revealing that this resin has poor adsorption selectivity for Pd in the given system.
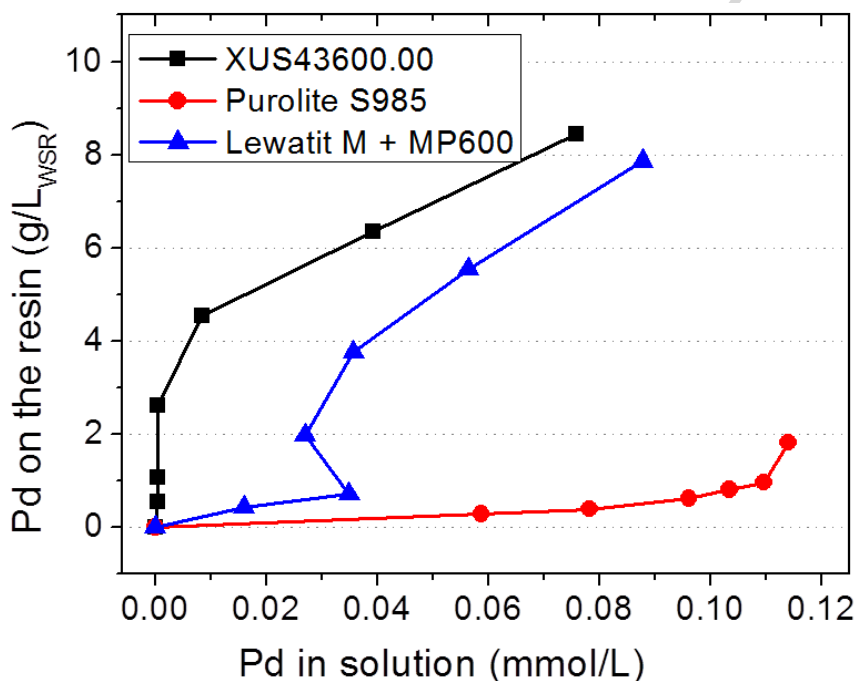

Figure 3. Adsorption isotherms of Pd from *process leach solution* containing Pt, Rh and other impurities on the resins investigated

Lewatit M+ MP 600, on the other hand, exhibits a different curve pattern; an initially linear-shaped isotherm which later changes into a convex curve, which suggests that the adsorption selectivity of Lewatit M+ MP 600 for Pd increases during ion exchange process (Zagorodni, 2007). In other words, this resin will only be selective for Pd given a sufficiently high concentration of Pd in the solution. Such phenomenon of enhanced affinity of the anion exchanger for traces of exchanged PGE ions was also observed by Kononova *et al.* (2011), whereby convex segments of the isotherms were reported.

The adsorption isotherms of Rh on the three resins are presented in Figure 4. Assessment of these isotherms indicates that both XUS 43600.00 and Purolite S985 exhibit poor adsorption selectivity for Rh in the given system. On the other hand, random patterns of data were observed in the case of Lewatit M+ MP 600 which suggests that the resin has little or no adsorption selectivity for Rh in the given system. This could be related to the nature of the resin and attributed to poor adsorption affinity between the resin and the particular ionic state

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in which Rh is present in the system (Nikoloski and Ang, 2014), but it may also be attributed to the very low concentration of Rh in the process leach solution.
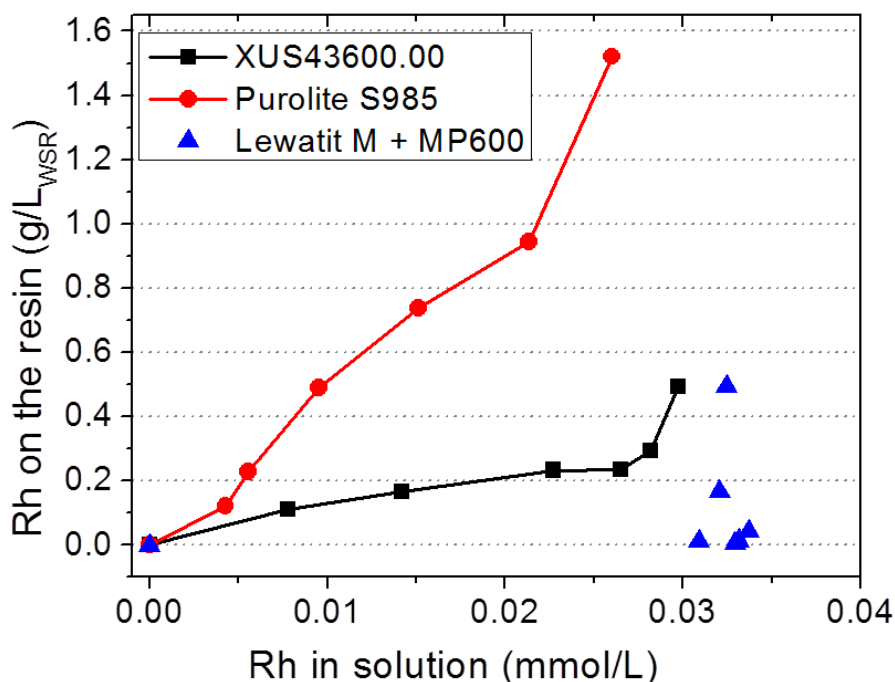

Figure 4. Adsorption isotherms of Rh from *process leach solution* containing Pt, Pd and other impurities on resins investigated

3.2.1 Modelling the adsorption equilibria

The *Langmuir* and *Freundlich* models are among the isotherms generally used to describe the adsorption equilibrium ion exchange relation between the solid and solution phases (Grimshaw and Harland, 1975; Slater, 1991). The equations for these two isotherms are commonly expressed as:

$$R_e = \frac{\bar{K} R_{max} C_e}{1 + K C_e}$$

Langmuir (1)

Freundlich $\qquad\qquad R_e = a(C_e)^b$ (2)

where R_e refers to the resin loading at equilibrium (mmol/g), R_{max} is the maximal equilibrium resin loading (mmol/g), C_e is the solution concentration at equilibrium (mmol/L), and K, a and b are the ion exchange equilibrium constants of the adsorption equilibrium.

The ion exchange equilibrium constants are related to Gibbs free energy and consequently determine the ion exchange affinity between the sorbent and the metal ion (Helfferich, 1962). In the *Freundlich* isotherm, this is measured by the value of the constant *b*. The closer the value of the constant *b* is to zero, the greater the affinity is between the resin and the metal ion species. However, the value of the constant *b* when it is equivalent to zero indicates irreversible adsorption, and a value above 1 indicates unfavourable adsorption. In the *Langmuir* isotherm, a large value of the constant *K* indicates high adsorption selectivity of the resin for a particular metal ion species. A dimensionless separation constant or equilibrium parameter K_R can be used to express whether an adsorption system is favourable or unfavourable (Hall *et al.*, 1966), with the following equation:

$$K_R = \frac{1}{1 + \bar{K} C_0}$$

(3)

where C_0 is the initial solution concentration (mmol/L), and *K* is the *Langmuir* constant (L/mmol). The value of K_R can then be used to describe the isotherm as follow: $K_R = 0$ for irreversible case, $0 < K_R < 1$ for favourable adsorption, $K_R = 1$ for linear case, and $K_R > 1$ for unfavourable adsorption.

In order to determine the values of the constants R_{max}, *K*, *a* and *b*, Eq. 1 and Eq. 2 have to be re-written into linear form (Nikoloski and Ang, 2014; Wołowicz *et al.*, 2011). By plotting C_e/R_e versus C_e, the slope and intercept of the linearised *Langmuir* equation are equivalent to $1/R_{max}$ and $1/(KR_{max})$ respectively. Eq. 1 is thus rearranged to the following linear form:

$$\frac{C_e}{R_e} = \frac{1}{\bar{K} R_{max}} + \frac{1}{R_{max}} C_e$$

(4)

Likewise, the slope and intercept for the linearised *Freundlich* equation are equivalent to *b* and log *a* respectively when log R_e is plotted against log C_e. Eq. 2 is also rearranged to the following linear form:

$$\log R_e = \log a + b \log C_e$$

(5)

Using Eq. 4 and Eq. 5, the *Langmuir* and *Freundlich* isotherms were plotted, and their respective parameters were calculated. Table 5 and Table 6 below show the values of the

Langmuir apparent constant K (L/mmol) and the *Freundlich* apparent constant b respectively, along with the coefficient of determination R^2 for each case. The values of the dimensionless equilibrium parameter K_R for the *Langmuir* isotherm were also calculated and tabulated in Table 5.

Table 5. Parameters for the *Langmuir* adsorption isotherm

Resin	Adsorption of *Pt*			Adsorption of *Pd*			Adsorption of *Rh*		
	K	K_R	R^2	K	K_R	R^2	K	K_R	R^2
XUS 43600.00	176.44	0.04	0.979	175.86	0.04	0.976	38.91	0.46	0.965
Purolite *S*985	1.07	0.88	0.076	-5.59	3.66	0.874	-16.06	1.93	0.975
Lewatit *M+ MP* 600	4.27	0.64	0.870	3.86	0.67	0.999	-	-	-

Table 6. Parameters for the *Freundlich* adsorption isotherm

Resin	Adsorption of *Pt*		Adsorption of *Pd*		Adsorption of *Rh*	
	b	R^2	b	R^2	b	R^2
XUS 43600.00	0.28	0.908	0.40	0.774	0.64	0.988
Purolite *S*985	0.91	0.950	1.88	0.946	1.24	0.961
Lewatit *M+ MP* 600	0.87	0.999	0.82	0.999	-	-

From the results tabulated above, it can be seen that not all the adsorption isotherms are compatible to both *Langmuir* and *Freundlich* isotherms. The resulting R^2 values imply that the adsorption of PGE by Purolite S985 and Lewatit M+ MP 600 follows the *Freundlich* isotherm more closely, whereas the adsorption of PGE by XUS 43600.00 is more apt to observe the *Langmuir* isotherm. It is also interesting to note that the *Freundlich* isotherm is shown to be satisfactory in all cases, probably because of the low metal ion concentrations in the solution (Zainol and Nicol, 2009). On the other hand, the *Langmuir* isotherm is shown to give a better fit than the *Freundlich* isotherm at higher loading values, which was seen in the adsorption of Pt and Pd by XUS 43600.00.

The result above is also suggestive of the adsorption mechanism in which PGE is loaded on the resin. The high R^2 value for *Langmuir* isotherm indicates a monolayer adsorption mechanism, while the high R^2 value for *Freundlich* isotherm indicates a multilayer adsorption mechanism (Nikoloski and Ang, 2013; Zainol and Nicol, 2009). In the case of XUS 43600.00, the adsorption of Pt and Pd is seen to follow that of a monolayer adsorption

mechanism because of their higher R^2 value for the *Langmuir* isotherm. The adsorption of Rh by XUS 43600.00, on the other hand, is a combination of monolayer and multilayer adsorption mechanisms since the resulting values of R^2 are high for both isotherms. In the case of Purolite S985, the adsorption of Pt and Pd follows a multilayer adsorption mechanism, while the adsorption of Rh has a combination of monolayer and multilayer adsorption mechanisms. In the case of Lewatit M+ MP 600, the adsorption of Pt follows a multilayer adsorption mechanism, whereas the adsorption of Pd follows both the monolayer and multilayer adsorption mechanisms.

Majority of the ion exchangers, according to the quantitative assessments above, reveal good affinity to chloride complexes of Pt, Pd and Rh. In the case of Purolite S985, the calculated *b* value in the *Freundlich* isotherm in Table 6 for the adsorption of Pt on the resin falls between values of 0 to 1, thus indicating favourable adsorption of Pt on Purolite S985. Likewise, the reported K_R value of 0.88, which falls between 0 and 1, also indicates a favourable adsorption. It should also be noted that the calculated K value in the *Langmuir* isotherm in Table 5 for the adsorption of Pt on Purolite S985 compares reasonably well with previously published data (Kononova *et al.*, 2011; 2013) albeit its poor R^2 value. On the other hand, the adsorption of Pd and Rh on Purolite S985 is deemed unfavourable, as implied by the *Freundlich* constant *b* and the *Langmuir* K_R values of greater than 1.

In the case of Lewatit M+ MP 600, the calculated *b* values in the *Freundlich* isotherm in Table 6 for the adsorption of Pt and Pd on the resin fall between values of 0 to 1, indicating favourable adsorption of Pt and Pd on Lewatit M+ MP 600. This is also implied by the K_R values in Table 5. The calculated K value in the *Langmuir* isotherm in Table 5 for the adsorption of Pt on Lewatit M+ MP 600 was also compared with previously published data (Kononova *et al.*, 2010c). Despite its difference with Lewatit MP 600 WS in terms of bead size distribution, both values compare reasonably well and are of the same magnitude. No quantitative data was obtained for the adsorption of Rh on Lewatit M+ MP 600 due to the random patterns of data obtained experimentally, as seen in Figure 4.

The most notable result from this quantitative assessment, as was also observed from the qualitative assessment, is the ion exchange affinity of XUS 43600.00 for Pt and Pd. The calculated constants K in the *Langmuir* isotherm for the adsorption of Pt and Pd on the resin XUS 43600.00 in Table 5 are significantly higher than the other calculated K values. Likewise, the K_R reported reflects the most favourable equilibrium in this instance since the

K_R values are closest to zero (Zainol and Nicol, 2009). The constants b in the *Freundlich* isotherm for the sorption of Pt and Pd on the resin XUS 43600.00 in Table 6 are also notably closer to zero than the other b values. This clearly demonstrates the superiority of XUS 43600.00 in terms of its sorption selectivity for Pt and Pd compared to Purolite S985 and Lewatit M+ MP 600. Moreover, the quantitative assessment from both *Langmuir* and *Freundlich* parameters implies that XUS 43600.00 has favourable sorption for Rh.

3.2.2 Adsorption selectivity

The adsorption selectivity of ion exchangers for chloride complexes of Pt(IV), Pd(II), and Rh(III) is largely dependent on the chemistry or functional groups of the ion exchangers and the equilibrium ionic state of PGE in solution (Hubicki *et al.*, 2008; Koster and Schmuckler, 1967; Nikoloski and Ang, 2014). It is known that the predominant ionic state of PGE in solution vary according to the conditions of the contacting medium, such as, acidity, concentration of chloride and other competing ions present in the solution, and "ageing" process in the media (Al-Bazi and Chow, 1984; Beamish, 1966; Cotton and Wilkinson, 1969; Livingstone, 1967; Nikoloski and Ang, 2014; Zolotov *et al.*, 2003). These factors will affect and ultimately determine the sorption selectivity of the resin for a particular PGE.

For instance, the experimental results show that Purolite S985, despite its high loading capacity, has relatively low selectivity for the anionic form of Pt(IV) in strong acid media when compared to XUS 43600.00. It has been suggested that this may be related to the effect of high acidity in the contacting medium which reduces the deprotonation of the nitrogen atom in the functional amine group of the sorbent (Kononova *et al.*, 2013; 2011; 2009). In other words, the strong acidic media reduces or deactivates the complexation ability of the weak base sorbent Purolite S985 which results in the sorption of chloride complexes of Pt(IV) exclusively through anion exchange mechanism. Hence, the chemical structure of Purolite S985, being a weak base anion exchange resin with functional amine group, reveals itself as a poor option for the adsorption recovery of Pt and Pd in highly acidic media.

On the other hand, Lewatit M+ MP 600 which is a strong basic exchanger, has no complexation ability since its quaternary ammonia base functional group maintains equal adsorption ability in a broad range of pH values, in contrast to weak and intermediate basic anion exchangers (Kononova *et al.*, 2010c, 2011; Mel'nikov *et al.*, 2012b). The adsorption ability of this resin for Pt and Pd is therefore not greatly affected by the low pH of the

contacting medium, but more likely to be affected by the competing effect of the high chloride concentration in the strong acidic media, as illustrated by the following reaction scheme:

$$2R\overline{Cl} + [MeCl_n]^{2-} \rightleftharpoons \overline{R_2^-}[\overline{Me}\overline{Cl_n}] + 2Cl^- \tag{6}$$
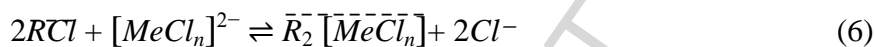
where,

$R\overline{Cl}$ refers to the resin in chloride form

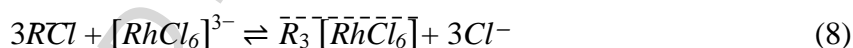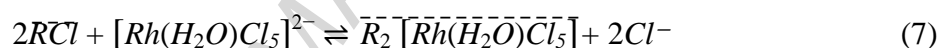Me can be either Pt or Pd where $n = 6$ for Pt and 4 for Pd.

Hence, both conventional Purolite S985 and Lewatit M+ MP 600 ion exchangers (*i.e.*, weak-basic and strong-basic exchanger types) that were investigated in this present work demonstrate relatively poor adsorption selectivity for Pt and Pd in the simultaneous recovery of PGE from strongly-acidic chloride media as compared to XUS 43600.00.

The chelating weak-base resin XUS 43600.00 with a thiouronium functional group was introduced in this work based on the consideration of the hard and soft acids and base theory (HSAB). According to this theory, ion exchangers which have a functional group that contains S donor atoms will interact strongly with soft acids such as precious metal ions (Hubicki *et al.*, 2007; Hubicki *et al.*, 2008). This is in line with the experimental results obtained in this present study wherein XUS 43600.00 exhibited high selectivity for Pt and Pd regardless of the high acidity in the media and the competing effect from the high chloride concentration. Nonetheless, the sorption recovery of Rh by XUS 43600.00 was of a lesser extent compared to its sorption recovery of Pt and Pd. This was more notably observed in the case of Lewatit M+ MP 600, *i.e.*, Rh was recovered to a much lesser extent than Pt and Pd.

The widely acceptable explanation behind the relatively small extraction of Rh is the higher kinetic inertness of Rh chloride complexes as compared to Pt and Pd chloride complexes (Benguerel *et al.*, 1996; Nikoloski and Ang, 2014; Zolotov *et al.*, 2003). This follows the order in which metal-chloro complexes are more likely to form ion pairs with anion-exchangers: $[MCl_6]^{2-} > [MCl_4]^{2-} \gg [MCl_6]^{3-}$ > aqua species (Bernardis *et al.*, 2005). According to Kononova *et al.* (2010b), the predominant Rh(III) species within the range of 2 mol/L to 6 mol/L HCl are $[RhCl_6]^{3-}$ and $[Rh(H_2O)Cl_5]^{2-}$ complexes. Therefore, the existing Rh chloride complexes in the solution are kinetically inert and hardly adsorbed on the resins, especially more so in the "aged" *process leach solution*. Other plausible factors contributing to the poor adsorption performance observed in the ion exchangers are the high concentration

of chloride ions which compete with PGE for adsorption sites on the resins, and the higher concentrations of Pt and Pd competing with the considerably lower concentration of Rh.

It is interesting to note that the degree of sorption recovery of Rh by Purolite S985 and XUS 43600.00 is significantly higher than by Lewatit M+ MP 600. This may be indicative of the advantage of a weak base resin over a strong base resin in the sorption recovery of Rh from strong chloride acidic solution. Due to the "ageing" process in the solution, ionic forms of Rh(III) other than the hexachloro equivalent, $[RhCl_6]^{3-}$, can exist in the solution, *e.g.*, $[Rh(H_2O)_3Cl_3]$, $[Rh(H_2O)_4Cl_2]^+$, $[Rh(H_2O)_5Cl]^+$ (Alam *et al.*, 1998a; Benguerel *et al.*, 1996; Nikoloski and Ang, 2014; Zolotov *et al.*, 2003). In the case of a strong-basic anion exchanger, such as Lewatit M+ MP 600, these species of Rh chloride complexes are adsorbed on the resin via anion exchange mechanism. The reaction scheme for the anion exchange recovery of Rh chloride complexes (Kononova *et al.*, 2010b; 2011) are as shown below:

$$2\overline{RCl} + [Rh(H_2O)Cl_5]^{2-} \rightleftharpoons \overline{R_2}\left[\overline{Rh(H_2O)Cl_5}\right] + 2Cl^- \tag{7}$$

$$3\overline{RCl} + [RhCl_6]^{3-} \rightleftharpoons \overline{R_3}\left[\overline{RhCl_6}\right] + 3Cl^- \tag{8}$$

Although aqua chloro- and hydroxo- complexes can be recovered by the sorbent via anion exchange mechanism, such recovery is not as favourable as it would be for typical metal ion complexes such as $[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$, and $[RhCl_6]^{3-}$ (Bernardis *et al.*, 2005; Dubiella-Jackowska *et al.*, 2007). Therefore, the additional complexation ability of a weak base resin, which can take effect besides its anion exchange mechanism, will enable a better sorption recovery of the range of Rh species in the chloride solution environment. The reaction scheme for the complexation between Rh complexes and the resin was formulated by Kononova *et al.* (2010b; 2011) as below:

$$m\overline{RN} + [RhL_6] \rightleftharpoons \left[\overline{Rh\,(RN)_m\,L_{6\text{-}m}}\right] + mL^- \tag{9}$$
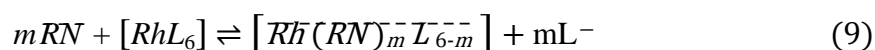
where, RN = resin with weak and intermediate base functional groups; $L = Cl^-$, H_2O; and m = 1, 2, 3, ..., 6. This may well explain the unexpectedly good sorption recovery of Rh by the weak base anion exchanger Purolite S985 in Table 4 even though the adsorption isotherm of Rh indicates that all three resins exhibit poor adsorption selectivity for Rh.

3.3 Rate of adsorption (kinetic) study

The kinetic curves describing the saturation of the ion exchangers under investigation with PGE from *process leach solution* and *synthetic solution* are shown in Figure 5 to Figure 7. It can be seen from these curves which show only the first hour, that the sorption rate (*v*) increases sharply at the initial period of contact between the resin and the PGE-containing solution, and gradually decreases to an equilibrium value as the sorbents reach a saturation point over 24 hours. The *synthetic solution* was used in this part of the study in order to compare and assess any unexpected variations of results, relative to using the *process leach solution*. It has been observed that the recovery of PGE from the *synthetic solution* by the ion exchangers generally follows similar patterns but has a higher sorption rate than that observed with the *process leach solution*.

Evaluation on the kinetics of the sorption process of the ion exchangers revealed that over 50% Pt and Pd were recovered from the *process leach solution* within 30 minutes contact time. Among the three resins, Lewatit M+ MP 600 demonstrated the greatest exchange kinetics towards Pt, whereas Purolite S985 and XUS 43600.00 demonstrated the greatest exchange kinetics towards Pd with an astonishing degree of saturation of up to 97% of their total exchange capacity within 30 minutes contact time. Nevertheless, it should be noted that the actual recovery of Pd from the *process leach solution* by XUS 43600.00 was 97% as compared to 58% by Purolite S985. On the other hand, Purolite S985 is the only resin that recovered over 50% Rh from the *process leach solution* within 30 minutes contact time. From Figure 7, the Rh sorption rates of XUS 43600.00 and Lewatit M+ MP 600 appear to be similar. However, it is worth mentioning that the recovery of Rh by XUS 43600.00 proceeds slowly but towards completion as evident by its final 24-hours recovery listed in Table 4, unlike Lewatit M+ MP 600 which exhibits a final Rh recovery of less than 10%.
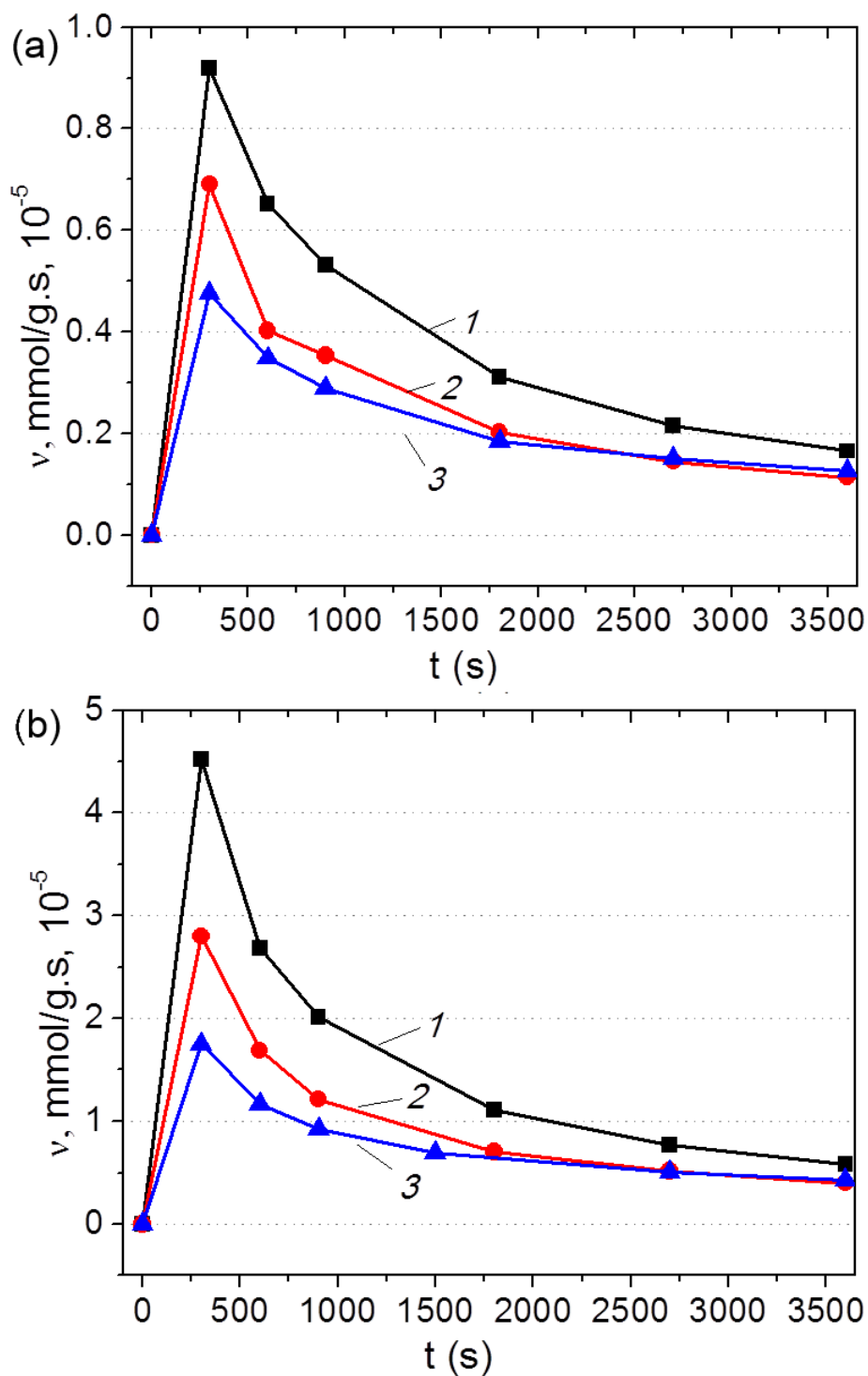
Figure 5. Kinetic curves describing the saturation of (*1*) Lewatit M+ MP 600, (*2*) Purolite S985, and (*3*) XUS 43600.00 ion exchangers in platinum (IV) recovery from (a) *process leach solution* **and (b)** *synthetic solution*. **(*v*) Rate of sorption concentration of platinum (IV) and (*t*) process duration.**
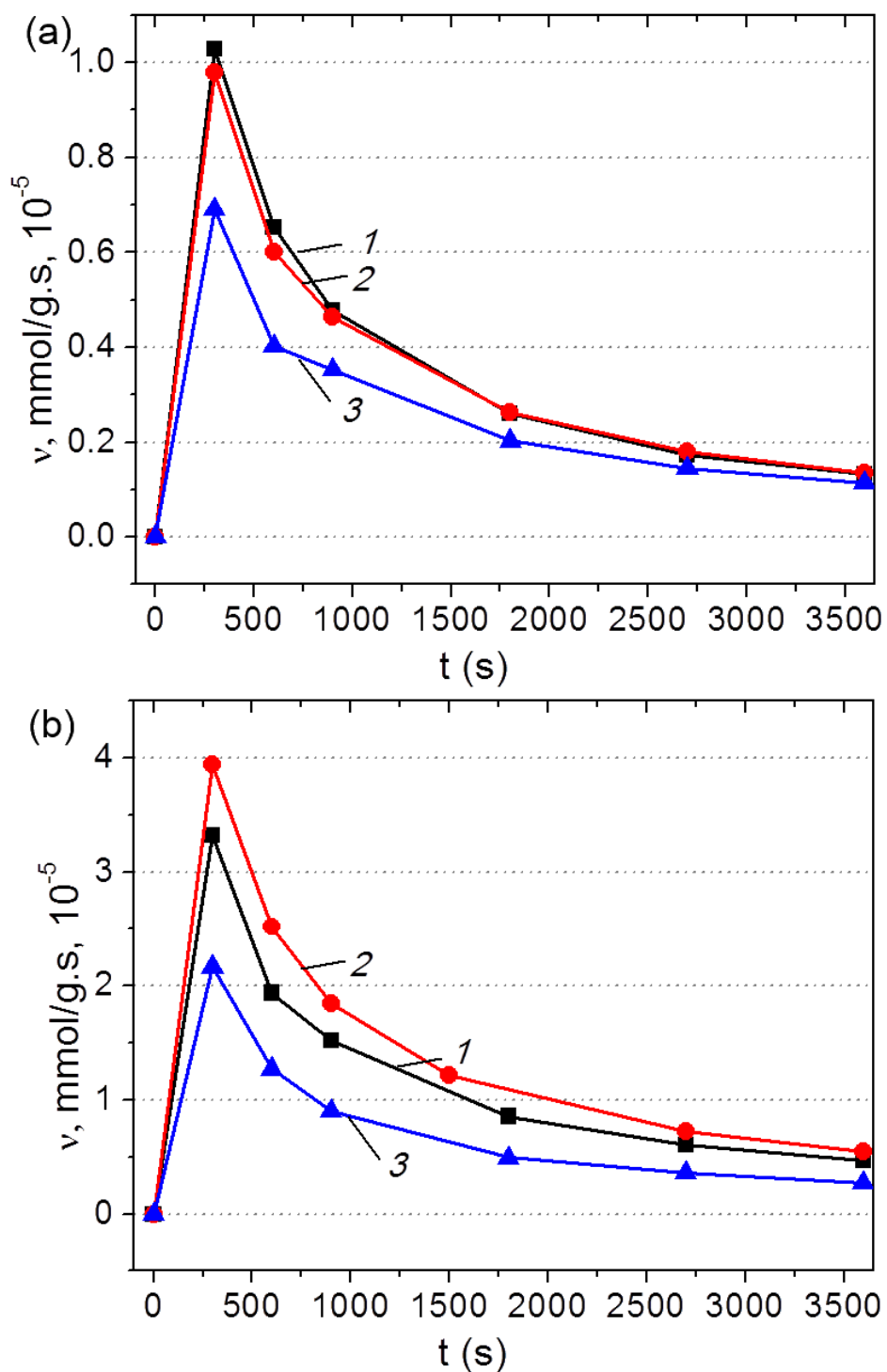
Figure 6. Kinetic curves describing the saturation of (*1*) Lewatit M+ MP 600, (*2*) XUS 43600.00, and (*3*) Purolite S985 ion exchangers in palladium (II) recovery from (a) *process leach solution* **and (b)** *synthetic solution*. **(*v*) Rate of sorption concentration of palladium (II) and (*t*) process duration.**
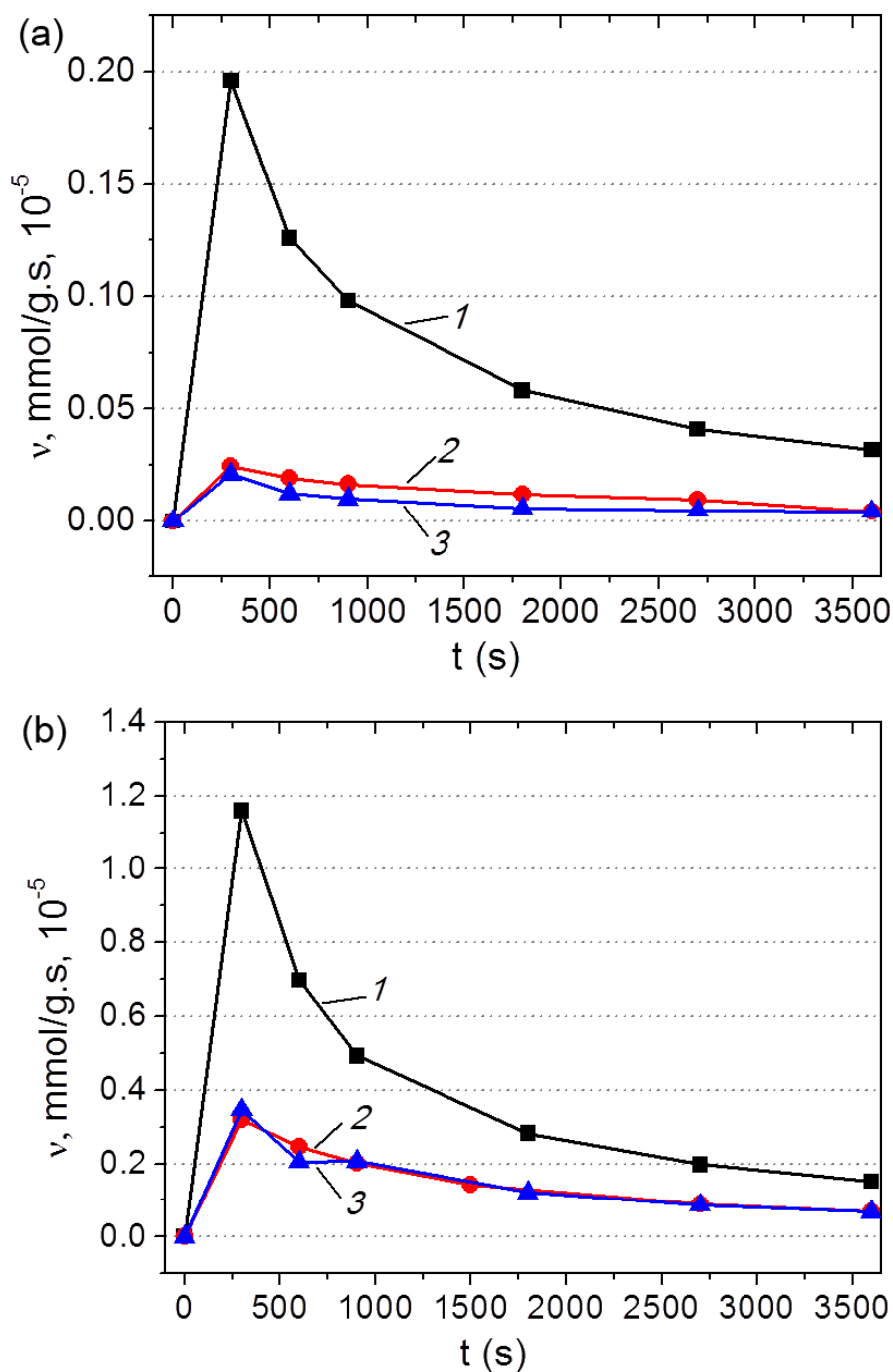
Figure 7. Kinetic curves describing the saturation of (*1*) Purolite S985, (*2*) XUS 43600.00, and (*3*) Lewatit M+ MP 600 ion exchangers in rhodium (III) recovery from (a) *process leach solution* **and (b)** *synthetic solution*. **(*v*) Rate of sorption concentration of rhodium (III) and (*t*) process duration.**

The mechanism by which the sorption of PGE occurs for each resin was investigated by correlating the experimental data to the Lagergren pseudo-first order and the Ho pseudo-second order rate expressions (Azizian, 2004; Ho, 2006). The mathematical expressions

corresponding to the Lagergren pseudo-first order model (Eq. 10) and the Ho pseudo-second order model (Eq. 11) are shown below in their linear forms:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{10}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e}t \tag{11}$$

where q_e is the resin sorption capacity of PGE complexes at equilibrium (mg/g), q_t is the amount of PGE complexes adsorbed on the surface of the resin at any time t (mg/g), k_1 is the rate constant of the pseudo-first order adsorption (min^{-1}), and k_2 is the rate constant of the pseudo-second order adsorption (g/mg·min).

Accordingly, the kinetic parameters for each resin under investigation were obtained from the slopes and intercepts of the plot log ($q_e - q_t$) versus t (based on the Lagergren pseudo-first order equation) and of the plot t/q_t versus t (based on the pseudo-second order equation proposed by Ho), as shown below:

Lagergren pseudo-first order adsorption:

$$k_1 = -2.303 \times \text{slope} \tag{12}$$

$$q_e = 10^{\text{intercept}} \tag{13}$$

Ho pseudo-second order adsorption:

$$k_2 = \frac{\text{slope}^{2}}{\text{intercept}} \tag{14}$$

$$q_e = \frac{1}{\text{slope}} \tag{15}$$

$$h = k_2 \cdot q_e^{2} \tag{16}$$

where h is the initial sorption rate (mg/g·min). The calculated values of the kinetic parameters for the Lagergren and Ho equations for the sorption of PGE in the *process leach solution* and the *synthetic solution* are tabulated respectively in Table 7 and Table 8 below. Figure 8 shows the plots from kinetic modelling using both Lagergren and Ho models for

XUS 43600.00 resin in *process leach solution*, which reveals that the Ho pseudo-second order kinetic model provides a better fit to the experimental data.

Table 7. Kinetic parameters for the Lagergren and Ho equation models for the sorption of PGE in *process leach solution*

Trade name	Metal	Pseudo-first order kinetic equation			Pseudo-second order kinetic equation			
		q_e	k_1	R^2	q_e	k_2	h	R^2
XUS 43600.00	*Pt*	1.16	0.03	0.989	1.14	0.06	0.08	1.000
	Pd	0.02	0.03	0.510	0.52	1.53	0.41	1.000
	Rh	0.08	0.00	0.902	0.10	0.08	0.00	0.988
Lewatit *M+ MP* 600	*Pt*	0.33	0.01	0.660	1.25	0.15	0.24	1.000
	Pd	0.09	0.01	0.727	0.53	0.76	0.21	1.000
	Rh	0.01	0.01	0.829	0.02	2.29	0.00	0.999
Purolite *S*985	*Pt*	0.49	0.01	0.775	1.05	0.07	0.07	1.000
	Pd	0.03	0.01	0.519	0.32	2.00	0.21	1.000
	Rh	0.05	0.02	0.898	0.13	1.51	0.03	1.000

Table 8. Kinetic parameters for the Lagergren and Ho equation models for the sorption of PGE in *synthetic solution*

| Trade name	Metal	Pseudo-first order kinetic equation			Pseudo-second order kinetic equation			
		q_e	k_1	R^2	q_e	k_2	h	R^2
XUS 43600.00	*Pt*	3.01	0.01	0.975	4.27	0.01	0.20	1.000
	Pd	0.41	0.02	0.760	2.17	0.19	0.89	1.000
	Rh	0.38	0.00	0.856	0.54	0.03	0.01	0.994
Lewatit *M+ MP* 600	*Pt*	0.82	0.01	0.623	4.30	0.07	1.34	1.000
	Pd	0.63	0.03	0.884	1.93	0.14	0.52	1.000
	Rh	0.08	0.01	0.674	0.27	0.62	0.04	1.000
Purolite *S*985	*Pt*	1.10	0.01	0.561	3.26	0.03	0.29	1.000
	Pd	0.37	0.01	0.555	1.21	0.08	0.12	1.000
	Rh	0.12	0.01	0.678	0.59	0.58	0.20	1.000
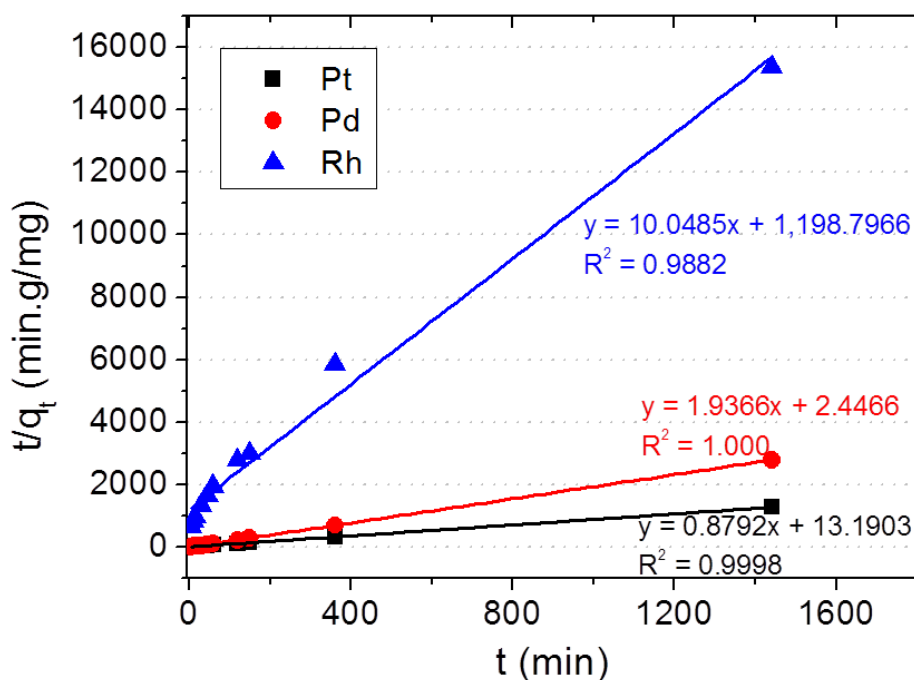
Figure 8. Plots from kinetic modelling using Ho pseudo-second order kinetic model fitted with the experimental results for XUS 43600.00 resin in *process leach solution*.

The R^2 values in Table 7 and Table 8 show that the pseudo-first order kinetic model is less suitable in describing the kinetics for the entire 24-hours sorption process for both *process leach solution* and *synthetic solution* systems. The coefficients of determination are low indicating that the plots log (q_e – q_t) versus *t* for all resins under investigation are not linear. Instead, the kinetic behaviour of the sorption of PGE complexes was better predicted using the Ho pseudo-second order kinetic model for both *process leach solution* and *synthetic solution* systems. The plots t/q_t versus *t* give linear relationships (the R^2 is in the range from 0.99 to 1.00) indicating that the adsorption process follows the Ho pseudo-second order kinetic model. This indicates that the rate-limiting step controlling the adsorption process might be chemisorption, *i.e.*, chemical reaction between the PGE complexes and the functional groups present in the matrix of the resin (Ho and McKay, 2000; Plazinski *et al.*, 2009; Wołowicz and Hubicki, 2010).

3.4   Evaluation of different reagents for elution

The difficulty associated with the elution of noble metals from highly selective sorbents has been investigated by a number of researchers (Alam *et al.*, 1998a; 1998b; Blokhin *et al.*, 2007; Zolotov *et al.*, 2003; Jeffrey *et al.*, 2010). It is known that the elution of noble metals

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from highly selective ion exchangers is difficult to achieve because of strong retention of adsorbed metal ions by functional groups on the resins (Alam *et al.*, 1998b; Kononova *et al.*, 2009). Thus, to achieve successful regeneration of PGE-loaded resins, it is necessary to use eluent reagents that form more stable complexes with the PGE ions than the complexes of these metal ions existing in the resin phase. The two main eluents considered to date and found to be effective are acidic thiourea solution and basic thiourea solution (Anon., 1992; Kononova *et al.*, 1998; 2007; 2008; 2009; Zolotov *et al.*, 2003; Venkatesan *et al.*, 2007).

Several eluents were tested in this study in order to assess their relative effectiveness and to select a preferred one for further study of the elution process. The tested eluents are described in Section 2.3. The elution of PGE from PGE-loaded resins was tested using a batch equilibration method described in Section 2.6. The elution results are given in Table 10.

Table 10. Comparison of the elution of PGE from the loaded resin by using different reagents

Trade name	Elution agent	PGE concentration on resin (g/L)			Final Elution (%)		
		Pt	*Pd*	*Rh*	*Pt*	*Pd*	*Rh*
XUS 43600.00	HCl 2 M	4.3	2.6	0.2	0.0	0.0	0.4
	NaSCN 2 M	5.2	4.5	0.2	0.2	0.7	1.6
	Thiourea 1 M in HCl 2 M	1.0	0.5	0.1	97.9	93.3	12.3
	Thiourea 1 M in NaOH 2 M	2.0	1.1	0.2	0.3	0.1	2.8
Lewatit *M+ MP* 600	HCl 2 M	3.9	2.0	0.0	0.6	1.2	/
	NaSCN 2 M	6.3	3.8	0.0	1.4	0.9	/
	Thiourea 1 M in HCl 2 M	1.0	0.4	0.0	>99.5	98.1	/
	Thiourea 1 M in NaOH 2 M	1.8	0.7	0.0	0.9	0.1	/
Purolite *S*985	HCl 2 M	1.5	0.6	0.5	2.3	8.1	1.7
	NaSCN 2 M	2.1	0.8	0.7	3.6	6.3	5.6
	Thiourea 1 M in HCl 2 M	0.8	0.3	0.1	>99.5	91.1	23.6
	Thiourea 1 M in NaOH 2 M	1.1	0.4	0.2	7.9	4.1	2.8

The results show that the eluants 2 mol/L HCl, 2 mol/L NaSCN and 1 mol/L Thiourea in 2 mol/L NaOH were relatively ineffective in eluting the PGM from the tested loaded resins. It was found that 1 mol/L thiourea in 2 mol/L HCl was the only eluent capable of providing significant desorption. The acidic thiourea reagent desorbed > 97% Pt and > 91% Pd from

each type of resin whereas the elution percentage of these two elements with the former three eluent solutions was less than 10%, even though the PGE concentrations on the loaded resins used with these eluent solutions were considerably higher than that of the acidic thiourea.

The results using 1 mol/L thiourea in 2 mol/L HCl as the eluent, however, showed very low elution recovery of Rh (the maximum elution was 23.6%, which was observed from Purolite S985). The recovery of Rh from XUS 43600.00 was 12.3% and virtually no elution recovery of Rh was observed from Lewatit M+ MP 600 using this eluent.

Such differences in the elution results between Rh and the other two PGE elements can be attributed to the kinetic inertness of the Rh complexes as well as to the stereochemistry of these complexes (Livingstone, 1967; Cotton and Wilkinson, 1969). In other words, Rh ions are more strongly retained to the ion exchangers than to the eluents considered in this paper.

3.5 Rate of desorption with the preferred eluent

The elution process using the best-performing eluent in the preliminary experiments was investigated further to develop a better understanding of the desorption kinetics. The elution results are tabulated in Table 11. The rates of desorption for all three resins are illustrated in Figure 9 to Figure 11.

Table 11. Elution of PGE from the loaded resin by acidic thiourea

Trade name	PGE concentration on resin (g/L)			Final Elution (%)		
	Pt	*Pd*	*Rh*	*Pt*	*Pd*	*Rh*
XUS 43600.00	1.1	0.5	0.1	98.7	>99.5	12.7
Lewatit *M+ MP* 600	1.2	0.5	0.0	88.5	91.4	/
Purolite *S*985	1.0	0.3	0.1	70.0	93.0	7.0

It should be noted that deionised water was used in calibration of the flowrate through the bed of resins in the column. Thus the initial few bed volumes (BV), i.e. BV 1 to 3 show little or no elution of PGE, as shown in the elution profiles in Figure 9 to Figure 11.

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Therefore, the initial peak in Rh elution from Lewatit M+ MP 600 resins was most likely due to sample contamination.

As shown in the figures, after the initial 3 BV, the bulk of Pt and Pd were recovered in the subsequent bed volumes, with gradual decrease in the later bed volumes for all three resins investigated. This behaviour demonstrates a fast rate of desorption for these two PGE. Rh, on the other hand, exhibited a slower rate of desorption, and returned a much lower elution recovery than the other two PGE. The difference in the percent elution recovery between Rh and the other two PGE is consistent with that observed during the evaluation of different reagents for elution. This indicates that acidic thiourea has stronger affinity for Pt and Pd than for Rh, leading to slower rate and lower overall elution recovery of Rh from all three resins. As expected, the elution of Rh is difficult, which is consistent with the observations reported in the study of rhodium stripping (Alam and Inoue, 1997; Alam *et al.*, 1998a; 1998b).
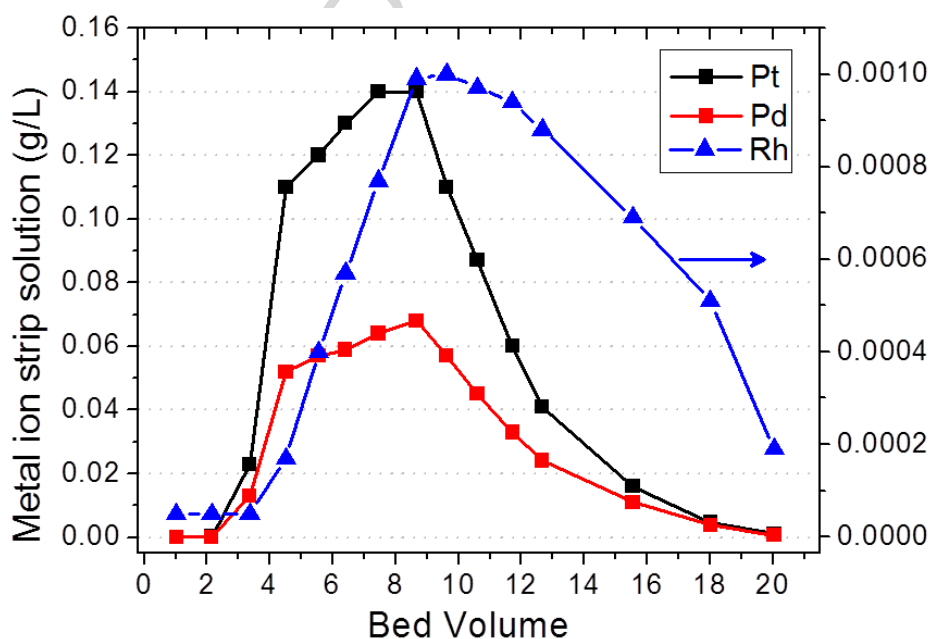

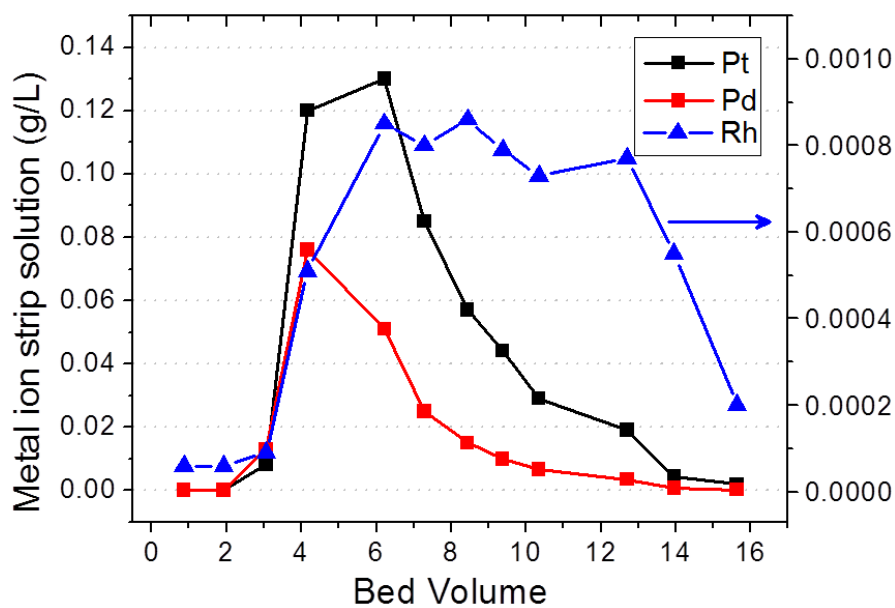**Figure 9. Elution profile for XUS 43600.00, 1 mol/L thiourea in 2 mol/L HCl, 2 BV/h**

Figure 10. Elution profile for Purolite S985, 1 mol/L thiourea in 2 mol/L HCl, 2 BV/h
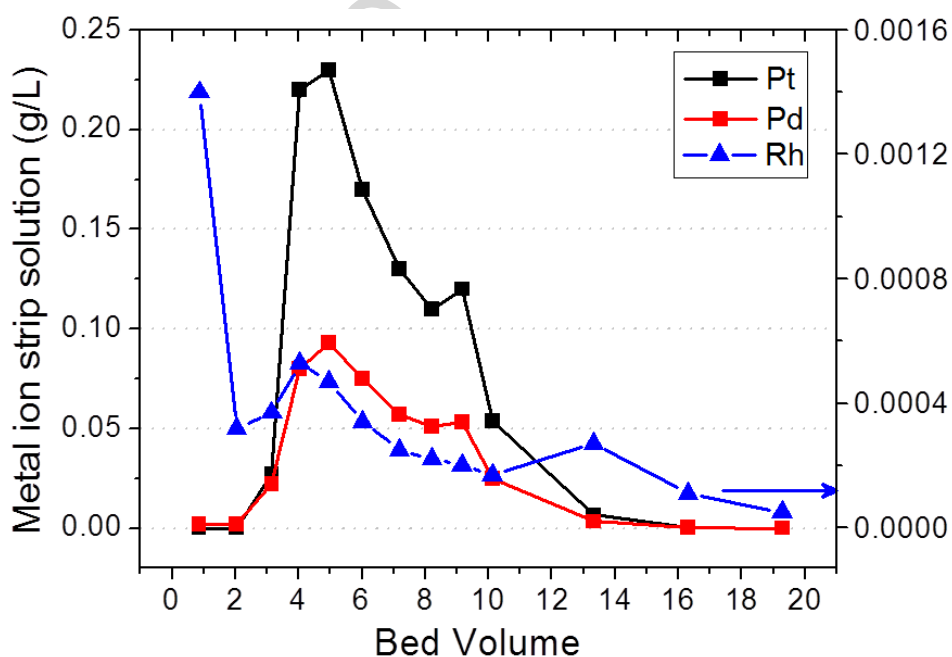

Figure 11. Elution profile for Lewatit M+ MP 600, 1 mol/L thiourea in 2 mol/L HCl, 2 BV/h

The issue of poor Rh elution from resins is well known in the PGE industry. It has been reported that the desorption of Rh from a resin can be improved by the addition of oxidising agents such as NaClO and NaClO$_3$ to the eluent solution (Alam and Inoue, 1997; Alam *et al.*,

1998a; 1998b). This approach has been examined using various eluent solutions and the studies have shown that the desorption of Rh can be increased to over 90% in a single contact with the media (Alam *et al.*, 1998a). However, the use of strongly oxidising reagents can cause severe damage to the resin. Considering that ion exchange resins used in industry present a significant operating cost and resins need to withstand multiple cycles of loading and elution, the repetitive use of aggressive elution media which degrades the resin may not be justifiable.

A second approach suggested to improve desorption of Rh from ion exchange resin involves the use of higher temperature during the adsorption process (Kononova *et al.*, 2010b). The observed improvement was attributed to reduced formation of cationic and neutral Rh chloride complexes at higher temperature, which in turn reduces the so-called "ageing" of the feed PGE solution (Nikoloski and Ang, 2014). As a result, more Rh would be adsorbed on the resin in $[RhCl_6]^{3-}$ form, by means of anion exchange reaction mechanism, rather than in the form of oxidised Rh complexes by chelating or coordination mechanisms. Consequently, the anionic complex of the type $[RhCl_6]^{3-}$ can be more effectively released by the resin (R) when the negatively charged chloride ions are replaced by the neutral thiourea ligand, forming a positively charged Rh(III) thiourea complex (Warshawsky, 1987), as shown below in a simplified reaction. This approach may offer a suitable solution to the difficulties associated with the elution of Rh.
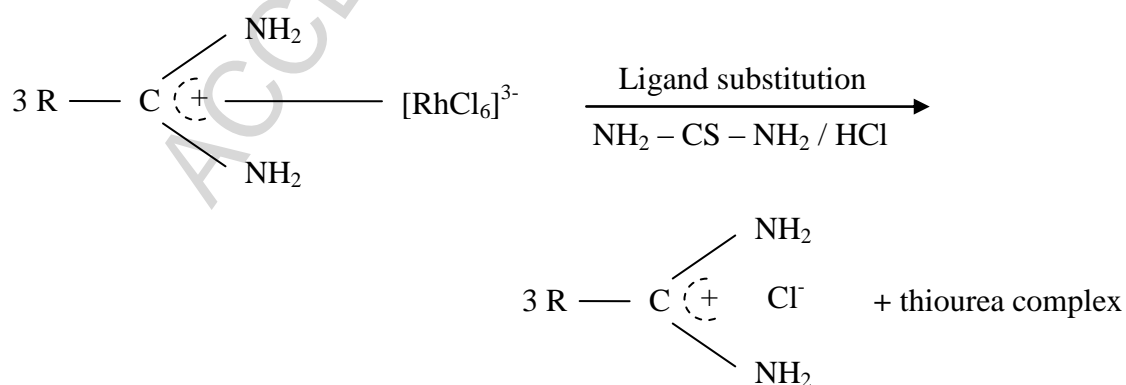
Potential reasons, however, for reluctance of the PGE industry to apply such elution are the considerable toxicological problems with using thiourea, as well as considerations inherently related to the use of elution techniques in a commercial or semi-commercial environment. The main considerations referred here are the higher capital cost, which is associated with the installation of additional tanks that would be needed to contain the additional volume of eluent, and the additional permissions that would be necessary for

extensive organics handling. In addition, elution is not a quantitative process and there is typically some degree of irreversible binding of PGE to the resin (Anon., 1992). For these reasons, a scheme to recover Rh strongly retained by the resin via fuming, whereby resin is incinerated and Rh is recovered from the resulting ashes remains plausible (Hubicki *et al.*, 2007). Such an approach may be economical and feasible for industrial application as the revenue from the metal recovered usually exceeds the losses due to the cost of the resins replacement even after a single adsorption (Brykina *et al.*, 1995; Kononova *et al.*, 2008; 2009; 2010c).

Another option might be to subject the loaded resin to elution for the recovery of Pt and Pd with acidic thiourea solutions, before the Rh remaining on the resins is treated by the fuming method in a second stage. This recovery scheme may allow adequate separation of Rh from Pt and Pd, since the bulk of Rh is not recovered by the acidic thiourea elution. Besides, according to common industrial practices, the resins usually undergo multiple cycles of PGE adsorption and elution until they are deemed no longer effective due to the irreversible binding of impurities. Therefore, the resins could be better utilised before they are incinerated to recover the Rh remaining on the resins, making a more favourable strategy from an economic perspective.

4 Conclusions

Three ion exchangers of different functional groups have been studied for the simultaneous sorption recovery of Pt(IV), Pd(II) and Rh(III) present in chloride solution collected from leaching platinum group metal-containing spent automotive catalyst. The weak-base thiouronium-functionalised XUS 43600.00 chelating resin exhibits significantly greater adsorption selectivity for chloride complexes of Pt(IV) and Pd(II) in acidic chloride solutions. The adsorption process of PGE for ion exchanger XUS 43600.00 was described by the Langmuir model, whereas for ion exchangers Lewatit M+ MP 600 and Purolite S985, the sorption of PGE was described using the Freundlich model. The sorption recovery of Rh, however, exhibits poor selectivity for all three resins investigated. Kinetic modelling shows that the adsorption of PGE followed the Ho pseudo-second order kinetic expression. Desorption from the PGE-pregnant ion exchangers was investigated by elution with various elution agents. It was demonstrated that the complete elution of Pt and Pd using acidic thiourea solution can be achieved for all ion exchangers investigated. However, the elution of

Rh from all three ion exchangers proved difficult and other desorption strategies are recommended, particularly the fuming method.

Acknowledgements

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Highlights

- Simultaneous adsorption of Pt, Pd and Rh from acidic chloride leach solution
- High adsorption affinity to chloride complexes of Pt and Pd but weaker for Rh
- Pt and Pd effectively eluted with acidic thiourea but desorption of Rh difficult