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### Highly Selective and Efficient Recovery of Pd, Pt, and Rh from Precious Metal-Containing Industrial Effluents with Silica-Based (Poly)Amine Ion Exchangers

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## Highly Selective and Efficient Recovery of Pd, Pt, and Rh from Precious Metal-Containing Industrial Effluents with Silica-Based (Poly)Amine Ion Exchangers

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### ABSTRACT

The recovery of Pd, Pt, and Rh from batches of authentic industrial precious metal refinery (PMR) effluents containing large amounts of Ni, Cu, and Fe ions and relatively small amounts of the expensive Pt, Pd, and Rh ions was investigated with silica-based anion exchangers containing monoamine, ethylenediamine, and diethylenetriamine functionalities.

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All platinum group metal (PGM) recoveries have proven to be highly selective over various base metal ions, such as  $\text{Cu}^{2+}$ . Quantitative recovery of Pd and Pt from some of the PMR effluents was effected by these ion exchangers, whereby HCl appears to be a powerful desorbent. Moreover, in most cases, Pd and Pt have been completely stripped from the ion exchangers with thiourea or with a combination of thiourea and HCl. Rh recovery from a base metal refinery (BMR) effluent was found to be less efficient, with maximum adsorption values of just over 20% and with a maximum desorption of about 50%. Rh stripping after extraction from one of the PMR effluents appeared to be much more successful. The well-known difficulties in Rh recovery can be largely attributed to the occurrence of several kinetically inert species in hydrometallurgical effluents.

*Key Words:* Ion exchange; Amine ligands; Silica; Selective extraction; PGMs.

## INTRODUCTION

The platinum group metals (PGMs), palladium, platinum, rhodium, iridium, ruthenium, and osmium are scarce elements. They occur in minerals in close association with one another, and with other transition-metal sulfides and selenides, especially nickel, cobalt, and copper sulfides.<sup>[1,2]</sup> The increased use of PGMs for numerous purposes, especially for automobile exhaust emission control catalysts, has led to a dramatic increase in their demand.<sup>[3–6]</sup>

Due to their importance and high price, it is essential to develop efficient recovery methods for these PGMs. However, the recovery of the small amounts of precious metals present in refinery plant effluents, which often also contain large quantities of other transition and nontransition metal ions, is a very difficult task. Furthermore, the complex speciation of the PGMs in these acidic hydrometallurgical leaching solutions, with high chloride content, makes their separation and recovery even more cumbersome, in view of the stable chlorocomplexes that these PGM metal ions generally form.

Several publications describe the application of solvent extraction and ion exchange for the recovery of PGMs with ligands bearing amine functionalities. Most of these focus on the recovery of precious metal ions from radioactive, high level liquid waste<sup>[4,7]</sup> or from spent automobile catalytic converters.<sup>[8–10]</sup> However, only few have reported on the separation of precious metals from the other transition metals in process leaching solutions,<sup>[11–13]</sup> while most of these studies are based on well-defined model solutions.<sup>[14]</sup>

Recently, the authors reported on the highly selective Pd, Pt, and Rh extractions from authentic industrial precious metal refinery (PMR) effluents, as well as from base metal refinery (BMR) effluents, with silica-based ion



exchangers containing monoamine, ethylenediamine, and diethylenetriamine functionalities.<sup>[15]</sup> This article presents an extension of these investigations to both stages (hence, adsorption and desorption) of the recovery process. The exploration on the PGM recovery has been restricted in the present study to the PGM present in the highest concentration (either Pd, Pt, or Rh) in each of the tested effluents.

## EXPERIMENTAL

### Reagents and Analytical Methods

All reagents and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. The silica-based ion exchangers containing monoamine, ethylenediamine, and diethylenetriamine functionalities were synthesized as reported elsewhere,<sup>[15]</sup> and some characteristics of the ion exchangers are listed in Table 1. The BMR and PMR effluents were obtained from a large precious metal refining company in South Africa.

All metal analyses were performed on an inductively coupled plasma-atomic emission spectrometer (Varian Liberty II ICP-AES) using a linear calibration method.

### General Remarks

The PGM content of the effluents and the error ranges of the extractions were established by comparison of the undoped effluents with the same effluent, doped with a known amount of Rh. In the case of the doped effluents, a fixed amount of 3 mg of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  ( $46.9 \text{ mg L}^{-1}$ ) was added to the effluent prior to the extraction experiment. The Rh-doped effluents were measured after linear calibration using various different diluted acid matrices. In this way, the matrix effects have been corrected for, and the variation in the

**Table 1.** Ion exchanger characteristics.

Ion exchanger	Grafted group	Ligand concentration
		(mmol/g) <sup>a</sup>
1	$-(\text{CH}_2)_3\text{NH}_2$	1.15
2	$-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$	1.00
3	$-(\text{CH}_2)_3\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_2\text{H}$	0.90

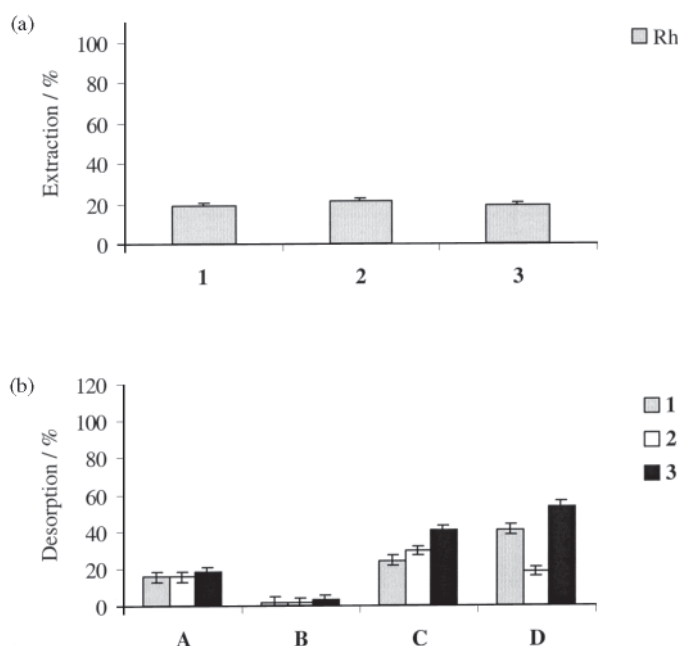
<sup>a</sup>Based on the N content.



corrected final average PGM values gave rise to the uncertainty bars, as indicated in Figs. 1 through 5.

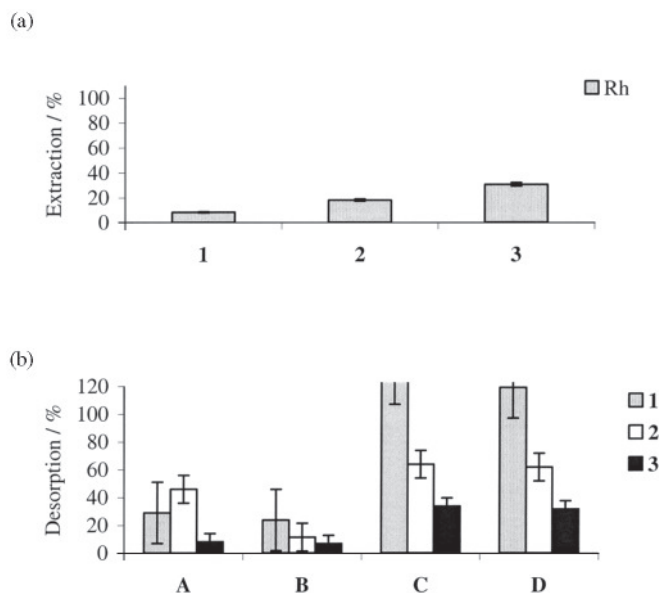
The extraction efficiency (as a percentage of total PGMs present) was established via measurement of the amount of PGM ions left in the effluent (filtrate) after contact with the extractant, since measurement of the PGM content of the extractants after treatment with the effluent proved less reliable for Pd and, to a much larger extent, for Pt.<sup>[15]</sup> The possible contribution of the surface silanol groups to the extraction of Pd, Pt, and Rh was tested under various acidic conditions (up to 5-M HCl). No significant uptake was detected.

In the case of relatively low PGM concentrations of the effluent, or in the case of low extractions, the maximum possible desorption becomes low, too. This results in low ICP desorption values, consequently giving rise to large error percentages. Hence, the effluents that contain high concentrations of (some of) the desired metal ions have been found most reliable.



**Figure 1.** (a) Rh extraction at room temperature with ion exchangers 1 to 3 from BMR effluent TLL (pH  $\sim 1.1$ ). Initial concentrations of the effluent ( $\text{mg L}^{-1}$ ): Rh  $755 \pm 50$ . The following concentrations ( $\text{in g L}^{-1}$ ) for the other transition metals were obtained: Cu  $> 10$ , Ni  $> 20$ , Fe  $> 5$ . (b) Rh desorption from ion exchangers 1 to 3 with 2-M  $\text{HNO}_3$  (A), 2-M HCl (B), 2-M HCl/1-M tu (C), or 1-M tu (D).





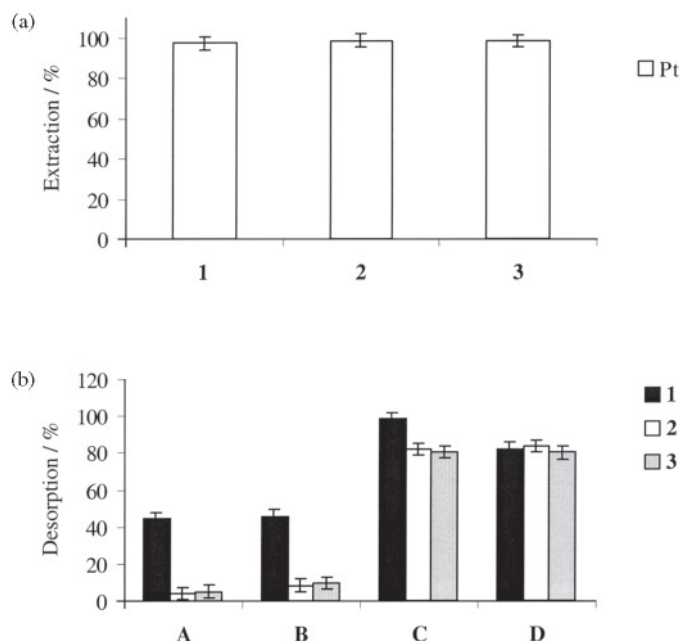
**Figure 2.** (a) Rh extraction at room temperature with ion exchangers 1 to 3 from PMR effluent A (pH  $\sim 1.6$ ). Initial concentrations of the effluent ( $\text{mg L}^{-1}$ ): Pd  $< 1$ , Pt  $59.5 \pm 2.0$ , Rh  $179.3 \pm 8.4$ . The following concentrations (in  $\text{mg L}^{-1}$ ) for the other transition metals were obtained: Cu  $> 1,500$ , Ni  $> 10,000$ , Fe  $\sim 30$ . (b) Rh desorption from ion exchangers 1 to 3 with 2-M HNO<sub>3</sub> (A), 2-M HCl (B), 2-M HCl/1-M tu (C), or 1-M tu (D).

Concentrations of Cu, Fe, and Ni in the filtrates after desorption were investigated for the determination of the recovery selectivity.

### Recovery Experiments

All extractions were performed as follows: 300 mg of ion exchanger 1 to 3 was added to a solution of 5.0 mL of effluent and 20.0 mL of deionized water. In this way, theoretically all PGMs could be extracted by a single batch of extractant. The suspension was agitated in polyethylene bottles mounted on a shaker for 24 hr at room temperature to attain equilibrium. The samples were filtered, and the PGM content of the filtrate was measured. The residual loaded extractants were washed (three times) with deionized water, acetone, and Et<sub>2</sub>O and thoroughly dried on the filter. Several desorption studies of extracted Pt were performed, both after drying of the loaded ion exchanger on the air and after drying in vacuo (200 mbar) at 50°C for 24 hr. These studies indicated substantial reduction of Pt ions to nonrecoverable Pt<sup>0</sup>, as a significant drop in



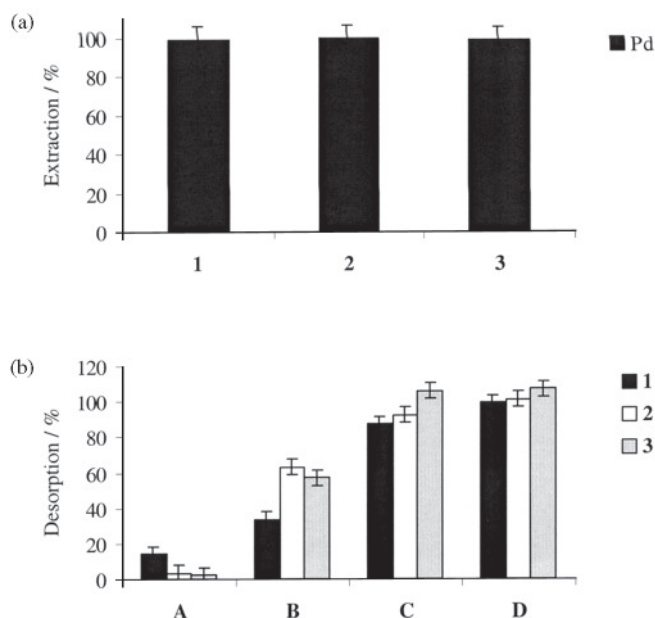


**Figure 3.** (a) Pt extraction at room temperature with ion exchangers 1 to 3 from PMR effluent B (pH  $\sim 1.2$ ). Initial concentrations of the effluent ( $\text{mg L}^{-1}$ ): Pd  $28.0 \pm 1.5$ , Pt  $185.2 \pm 6.1$ , Rh  $36.6 \pm 0.4$ . The following concentrations (in  $\text{mg L}^{-1}$ ) for the other transition metals were obtained: Cu  $\sim 60$ , Ni  $\sim 100$ , Fe  $\sim 70$ . (b) Pt desorption from ion exchangers 1 to 3 with 2-M  $\text{HNO}_3$  (A), 2-M  $\text{HCl}$  (B), 2-M  $\text{HCl}$ /1-M tu (C), or 1-M tu (D).

the desorption was observed. The replacement of EtOH (absolute) with acetone, as well as the avoidance of high temperatures during the drying process, were precautions taken to avoid metal ion reduction.

Desorptions were performed as follows: samples of about 40 mg of weighed loaded ion exchanger were added to exactly 25.0 mL of the desired desorbent, i.e., 2-M  $\text{HNO}_3$ , 2-M  $\text{HCl}$ , 2-M  $\text{HCl}$ /1-M thiourea (tu), or 1-M tu. The suspension was agitated in polyethylene bottles mounted on a shaker for 24 hr at room temperature to attain equilibrium. The samples were filtered, and the PGM content of the filtrate was measured. As the desorption samples in 2-M  $\text{HCl}$ /1-M tu and tu showed significant matrix effects, all desorption values using 2-M  $\text{HCl}$ /1-M tu as a desorbent were measured applying 2-M  $\text{HCl}$ /1-M tu linear calibration standards, whereas desorption values using 1-M tu as a desorbent were measured applying 1-M tu linear calibration standards. Desorptions using 2-M  $\text{HNO}_3$  and 2-M  $\text{HCl}$  were measured applying 0.05-M  $\text{HCl}$  standards, as no matrix effects had been observed for these desorbents.





**Figure 4.** (a) Pd extraction at room temperature with ion exchangers 1 to 3 from PMR effluent C (pH  $\sim 0.4$ ). Initial concentrations of the undoped effluent ( $\text{mg L}^{-1}$ ): Pd  $187.2 \pm 12.6$ , Pt  $19.2 \pm 2.0$ . The following concentrations (in  $\text{mg L}^{-1}$ ) for the other transition metals were obtained: Cu  $\sim 20$ , Ni  $\sim 30$ , Fe  $\sim 0$ . (b) Pd desorption from ion exchangers 1 to 3 with 2-M HNO<sub>3</sub> (A), 2-M HCl (B), 2-M HCl/1-M tu (C), or 1-M tu (D).

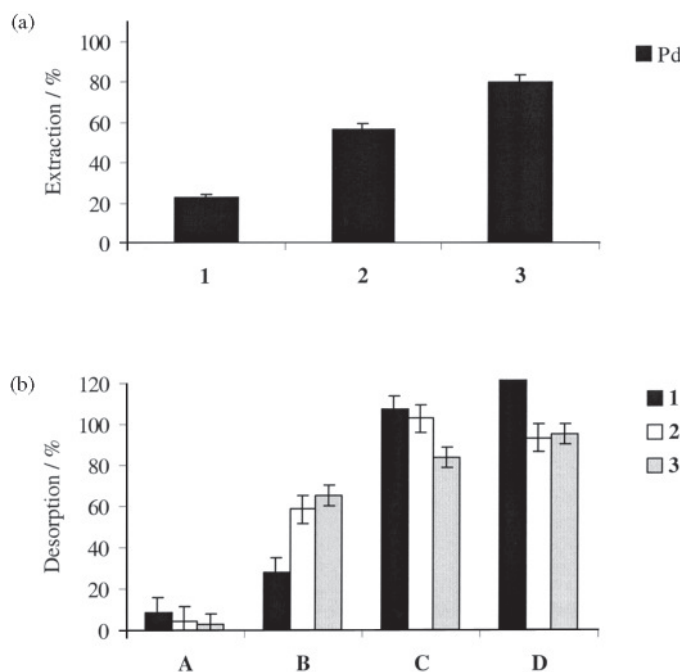
## RESULTS AND DISCUSSION

### Selectivity

To determine the PGM recovery efficiency of the ion exchangers for the various effluents, the filtrates after desorption were checked on their Cu, Ni, and Fe content. The Cu and Ni concentrations of the desorption filtrates were always found to lie below  $0.5 \text{ mg L}^{-1}$ , and  $< 1 \text{ mg L}^{-1}$  amounts of Fe were observed with some of the effluents that were high in Fe concentrations. Hence, all recoveries can be considered to be very selective. The observed PGM selectivity is consistent with earlier extraction selectivity studies,<sup>[15]</sup> and is explained as follows. Since the amine groups in the ion exchangers are protonated in the effluents (pH  $< 2$ ), these materials can be considered to be anionic exchangers and the extraction is believed to be based on the substitution of  $\text{Cl}^-$  by  $[\text{MCl}_x]^{n-x}$ .<sup>[10,16,17]</sup> Anionic PGM complexes with the







**Figure 5.** (a) Pd extraction at room temperature with ion exchangers 1 to 3 from PMR effluent D (pH  $\sim 1.6$ ). Initial concentrations of the effluent ( $\text{mg L}^{-1}$ ): Pd  $357.2 \pm 16.4$ , Pt  $33.0 \pm 1.6$ . The following concentrations (in  $\text{g L}^{-1}$ ) for the other transition metals were obtained: Cu  $> 1$ , Ni  $> 5$ , Fe  $> 10$ . (b) Pd desorption from ion exchangers 1 to 3 with 2-M  $\text{HNO}_3$  (A), 2-M  $\text{HCl}$  (B), 2-M  $\text{HCl}/1\text{-M tu}$  (C), or 1-M  $\text{tu}$  (D).

general formula  $[\text{MCl}_x]^{n-x}$ , predominantly present under these acidic conditions, are much more stable compared to anionic first row transition metal complexes.<sup>[13,14,16,18]</sup>

### Rh Recovery

The results of Rh extraction and stripping with ion exchangers 1 to 3, as obtained with BMR effluent TLL are depicted in Fig. 1. The BMR effluent that was tested is a tertiary leach liquor (TLL) containing very large amounts of base metals with a Ni (sulfate) concentration of over  $10 \text{ g L}^{-1}$  ( $10 \text{ kg ton}^{-1}$ ).

A maximum extraction of about 20% was observed for all ion exchangers. Concerning the desorption, both thiourea and a combination of thiourea and  $\text{HCl}$  showed reasonable elution. Maximum desorption values of about 50% were



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found when 1-M tu was used as a desorbent, apparently due to the very stable complexes that most precious metals form with these ligands.<sup>[14,19–21]</sup> Surprisingly, the desorption appears to increase to some extent with an increasing number of amine groups, even though the presence of secondary amine groups in 2 and 3 increases the basicity and therefore the ion-pair formation.<sup>[22]</sup> The Rh recovery from PMR effluent A was subsequently tested. In effluent A the transition metal ions are present in very large excess with respect to the PGMs (see Fig. 2). The recovery appears somewhat more promising, as quantitative desorptions with tu and tu/HCl could be achieved, after adsorption with monoamine ion exchanger 1. Unfortunately, while Rh adsorptions significantly increase from monoamine (8%) to diamine (18%) to triamine (30%), the desorptions follow the opposite trend. This is consistent with the expected binding strength of the ion exchangers, as mentioned previously.

The relatively small extraction has been discussed previously<sup>[15]</sup> and is first of all connected with the presence of large amounts of base metal ions, giving rise to a high concentration of anions. These anions, mainly sulfates for TLL and chlorides in the case of effluent A, compete with the anionic Rh complexes for the binding sites of the ion exchangers, presumably hampering the extraction.

Another plausible explanation for the extraction problems is the occurrence of several aquated species, i.e.,  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ ,  $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ , and  $[\text{RhCl}_3(\text{H}_2\text{O})_3]$  in acidic aqueous solutions.<sup>[23]</sup> These hydrated species have been found to be kinetically rather inert and are consequently less readily extracted than the hexachloro equivalent,  $[\text{RhCl}_6]^{3-}$ .<sup>[3,9,17,24]</sup> The validity of this explanation is demonstrated by the desorption results obtained with HCl. HCl does not appear to be a useful desorbent, presumably since it increases the  $[\text{RhCl}_6]^{3-}$  concentration, and this species is most readily adsorbed by the ion exchangers.

The problems associated with the desorption of Rh are more difficult to understand. In one of the few publications on the recovery of  $\text{Rh}^{3+}$  from chloride media, Alam et al.<sup>[3,9]</sup> propose that these problems might be associated with partial reduction of  $\text{Rh}^{3+}$  to  $\text{Rh}^+$ . However, stripping under strongly oxidizing conditions did not lead to complete desorption.

## Pt Recovery

The Pt-recovery behavior of the ion exchangers was tested with PMR effluent B, a relatively PGM-rich effluent that contains only small amounts of the other transition metal ions (see Fig. 3). Clearly, Pt was found to be quantitatively extracted by all ion exchangers. At relatively high chloride concentrations,  $\text{Pt}^{2+}/\text{Pt}^{4+}$ , as well as  $\text{Pd}^{2+}$ , form similar complexes, essentially  $[\text{PtCl}_4]^{2-}/[\text{PtCl}_6]^{2-}$



and  $[\text{PdCl}_4]^{2-}$ .<sup>[23]</sup> These  $[\text{MCl}_4]^{2-}$  and  $[\text{MCl}_6]^{2-}$  complexes are more readily extracted than the anionic Rh species.<sup>[16,22,25]</sup>

Over 80% of the bound Pt ions were found to be eluted with the strong desorbents tu and tu/HCl. Furthermore, monoamine ion exchanger 1 appears to be the most efficient ion exchanger, as over 40% of the Pt ions could be removed by the acidic desorbents, whereas no significant desorption has been obtained in the case of the diamine and triamine ion exchangers. Quantitative desorption with tu/HCl was achieved and binding was sufficiently strong to ensure a quantitative adsorption.

### Pd Recovery

Quantitative Pd extraction was obtained from one of the PMR effluents that contained relatively small amounts of other transition metals (effluent C, see Fig. 4) with all three ion exchangers.

Concerning the desorption, about 60% of the bound Pd ions could be removed with 2-M HCl [see Fig. 4(b)]. This is highly advantageous, as HCl is abundantly used in other stages of the refining process<sup>[17,26,27]</sup> and is therefore a readily available and relatively cheap stripping agent. Moreover, the Pd-stripping capacity of the acid is most likely strongly improved when applied in a continuous flow. This can be explained by the fact that in this closed system, an equilibrium is formed, with part of the metal ions in solution and part on the ion exchanger, as the addition of HCl also converts the Pd into the  $\text{PdCl}_4^{2-}$  species,<sup>[23]</sup> which is likely to be readily extracted. This equilibrium can most probably be shifted toward the solution side when the desorptions are performed by means of a column.

The strong binding capacity of thiourea to PGMs was demonstrated by its desorption efficiency. The initially bound Pd ions could be stripped completely by tu or a combination of tu and HCl from all three amine-containing ion exchangers [see Fig. 4(b)].

The Pd extractions of plant effluent D, depicted in Fig. 5(a), were found to be lower than from effluent C, most likely due to the presence of much higher concentrations of the other transition metals. Still, about 80% of the Pd ions could be extracted from the effluent by diethylenetriamine ion exchanger 3. The desorption pattern is very similar to that displayed in Fig. 4(b), with good desorptions obtained with HCl (>60%) and where quantitative stripping is possible when thiourea is applied.

The complete recovery, hence adsorption followed by desorption, with diethylenetriamine ion exchanger 3 was pointed out to be most efficient. In particular, the following recovery values of the ca.  $350 \text{ mg L}^{-1}$  Pd, initially present, were obtained when tu or tu/HCl were applied:  $80 \text{ mg L}^{-1}$  for 1 (23%



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recovered), 200 mg L<sup>-1</sup> for 2 (56% recovered), and about 270 mg L<sup>-1</sup> (75% recovered) for 3.

## CONCLUSION

Successful PGM recovery results were obtained with three silica-based ion exchangers, containing monoamine, ethylenediamine, and diethylenetriamine functionalities. Quantitative Pt and Pd recovery (hence, adsorption and desorption) was obtained from some of the tested PMR effluents. Of the stripping agents tested, both thiourea and a combination of thiourea and HCl proved to be most effective. The recovery of Rh remains somewhat troublesome, with adsorption maximums not exceeding 30% and with maximum desorptions of about 50%.

For Pt and, to a lesser extent Rh, the desorption increases in the order: triamine (3) < diamine (2) < monoamine (1). No pattern can be distinguished among the three ion exchangers toward Pd desorption.

The high selectivity of PGM extraction over various base metals was underlined in these investigations, as the desorption filtrates did not contain detectable amounts of Cu or Ni and only very small amounts (<1 mg L<sup>-1</sup>) of Fe in some cases. In summary, it is shown that highly selective and efficient recovery of PGMs with the presented ion exchangers 1 to 3 is possible. The fact that they originate from relatively inexpensive starting materials and maximum extraction is obtained at room temperature would make the application in a continuous system commercially feasible.

## ACKNOWLEDGMENTS

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