

## RECOVERY OF PALLADIUM FROM A SPENT AUTOMOBILE CATALYST LEACHING SOLUTION BY A THIODIGLYCOLAMIDE DERIVATIVE

A.P. Paiva<sup>1</sup>, G.I. Carvalho<sup>1</sup>, M.C. Costa<sup>2</sup>, A.M.R. Costa<sup>3</sup> and C.A. Nogueira<sup>4</sup>

<sup>1</sup> Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

<sup>2</sup> Centro de Ciências do Mar, Departamento de Química e Farmácia, Faculdade de Ciências e de Tecnologia, Universidade do Algarve, Campus de Gambelas, Faro, Portugal

<sup>3</sup> Centro de Investigação em Química do Algarve, Departamento de Química e Farmácia, Faculdade de Ciências e de Tecnologia, Universidade do Algarve, Campus de Gambelas, Faro, Portugal

<sup>4</sup> Laboratório Nacional de Energia e Geologia, I.P., Campus do Lumiar, Lisboa, Portugal

### ABSTRACT

In the sequence of previous research on the development of novel liquid-liquid amide-type compounds to efficiently and selectively extract platinum-group metals (PGMs) from concentrated hydrochloric acid media, a specific thiodiglycolamide derivative – *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) – has been applied for the recovery of palladium(II) from a spent automobile catalyst leaching solution, containing palladium(II) and rhodium(III) as PGMs. The results obtained are rather promising, since the DMDCHTDGA behavior towards the two PGMs is similar to that observed for hydrochloric acid aqueous media studied before, simulating the real leaching phases. Within eleven metal elements co-existing in solution, the majority in high fold-excesses, only aluminum(III) and cerium(III) interfere in the palladium(II) liquid-liquid extraction process, requiring further optimization.

**Keywords:** Palladium(II) recovery; liquid-liquid extraction; thiodiglycolamide derivative; spent automobile catalyst leaching solution.

### INTRODUCTION

The request for palladium, platinum and related rare metals is growing worldwide due to their increasing application in top technological devices, *e.g.*, in fuel cells, electronics, and as catalysts (in oil refining, chemical industry, automobile catalytic converters, etc.) [1]. The PGMs primary resources are scarce and not enough to fulfill the current market needs; consequently, PGMs recycling has become a technical and financial necessity [2].

Nowadays the general PGMs contents affordable from recycling routes reach 50% of the overall production in Europe [3]. The main anthropogenic sources for PGMs recycling are the spent automobile catalysts, which are treated either by pyrometallurgical or hydrometallurgical methods [4]. Included in the latter alternative, liquid-liquid extraction is a common and reliable technique, used to separate, purify and concentrate different metal ions from leaching solutions [5]. Chloride hydrometallurgy is generally adopted for PGMs processing, in accordance with the particular chemical properties of this group of metals [5]. There is active research on the application of liquid-liquid extraction systems for PGMs recovery, either by optimizing already well-known performant extractants, *e.g.*, [6] or by proposing the use of new molecules. Within the novel compounds, amide derivatives deserve a special mention, for example, [7].

Previous research carried out by this group has demonstrated that a specific thiodiglycolamide derivative, *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) is a promising extractant to efficiently and selectively recover Pd(II) and Pt(IV) from complex chloride aqueous phases [8]. Accordingly, this article describes the application of DMDCHTDGA to recover Pd(II) from a real spent automobile catalyst leaching solution [9]. The treated spent automobile catalytic converter contained Pd and Rh as the only PGMs.

## EXPERIMENTAL

The synthesis and characterization of DMDCHTDGA is described elsewhere [8]. For the liquid-liquid extraction experiments, 0.02 M DMDCHTDGA in toluene was used as organic phase. As feed aqueous medium, a leaching solution coming from the hydrometallurgical treatment of a spent automobile catalyst, containing Pd and Rh as PGMs, was prepared as previously reported [9]. The loaded organic phase was scrubbed with water and subsequently stripped by a 0.2 M thiourea in 2 M HCl solution. Extraction, scrubbing and stripping experiments were carried out by stirring equal volumes of the aqueous and organic phase (A/O=1) for 30 minutes, at room temperature, and adopting a rotation speed between 900 and 1000 rpm [8]. The metal contents in the aqueous phases were determined by inductively coupled plasma – atomic emission spectrometry (ICP-AES, Horiba Jobin-Yvon, Ultima). Metal ion concentrations in the organic phase were calculated by mass balance. The uncertainties determined for the extraction, scrubbing and stripping results do not exceed  $\pm 5\%$ .

## RESULTS AND DISCUSSION

Automobile catalysts are composed by one or more monoliths, commonly of ceramic type, having a cordierite support matrix with a honeycomb structure, and a washcoat layer with  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ , other oxides, and the PGMs. The main PGM in the current automobile catalysts is Pd [9]. A suitable leaching process for the hydrometallurgical treatment of a Pd-Rh automobile catalyst was developed and optimized by this group [9], for which copper(II) chloride in about 5 M HCl was used as the leaching agent. Accordingly, the Cu content of the feed leaching solution is part of the optimized leaching step, not belonging to the catalyst itself.

In Table 1, the general metallic composition of the pregnant automobile catalyst leaching solution can be observed, together with the data related with the metal contents in the organic solution after extraction by DMDCHTDGA, the concentrations of metals scrubbed from the loaded organic solution by water, and finally the metal contents found in the thiourea stripping solution. The indicated oxidation states for the metallic elements should be the most abundant and were not confirmed experimentally. The overall collected information is in general agreement with that obtained by liquid-liquid extraction of a simulated leaching solution, with a similar metal ion composition, and also involving DMDCHTDGA.

**Table 1:** Concentrations of the metal ions in the feed automobile catalyst leaching solution in about 5 M HCl, in the DMDCHTDGA toluene phase after extraction, in the scrubbing water resulting from the washing of the loaded organic phase, and in the stripping aqueous solution.

| Metal ions in 5 M HCl | Concentrations in the initial feed solution [mg/L] | Concentrations in the DMDCHTDGA solution [mg/L] | Concentrations in the scrubbing water [mg/L] | Concentrations in the stripping thiourea solution [mg/L] |
|-----------------------|--|---|--|--|
| Al(III)               | 12089  | 420   | 1  | 0  |
| Ca(II)                | 136  | 4   | 1  | 72   |
| Ce(III)               | 1471   | 11  | 0  | 0  |
| Cr(III)               | 23   | 0   | 0  | 0  |
| Cu(II)                | 6173   | 259   | 36   | 0  |
| Fe(III)               | 242  | 240   | 226  | 0  |
| La(III)               | 212  | 2   | 0  | 0  |
| Ni(II)                | 8  | 0   | 0  | 0  |
| <b>Pd(II)</b>         | <b>61</b>  | <b>60</b>                                       | <b>2</b>                                     | <b>60</b>  |
| Rh(III)               | 9  | 0   | 2  | 1  |
| Zn(II)                | 3  | 0   | 0  | 0  |

Despite the complex composition of the automobile catalyst leaching solution, the DMDCHTDGA performance towards Pd(II) is remarkable, since this PGM is completely recovered in the final aqueous medium. However, DMDCHTDGA also extracts Ce(III), and significant concentrations of Al(III), Cu(II) and Fe(III). Some pertinent comments about this situation are listed in sequence.

i) Al(III) and Ce(III) are a concern; although an Al(III) extraction of 420 mg/L over 12089 mg/L can be considered residual, this metal ion is not scrubbed by water or by any other acid, base or salt aqueous solution that was tested, and the same happened with Ce(III). Without a proper agent to remove Al(III) and Ce(III) from the organic phase, a real process with DMDCHTDGA may be vulnerable, since the organic media becomes poisoned by these metal ions in a short term. The Al(III) and Ce(III) contents can be further reduced, but their complete absence in the leaching solution seems impossible.

ii) Fe(III) is not a problem; although extensively extracted, it is totally scrubbed from the organic solvent with water. Cu(II) is partially extracted but only partially scrubbed; hence, its presence in the leaching medium is undesirable.

iii) At a first sight, it seems there are analytical errors associated with the results involving Rh(III) and Ca(II). Taking into account the group's experience in the analysis of this PGM, it can be considered that Rh(III) is not extracted. The Ca(II) concentration surprisingly found in the thiourea stripping solution is likely to come from the thiourea itself, since the industrial process to produce this organic compound involves this element.

## CONCLUSIONS

The novel amide-type compound DMDCHTDGA is able to efficiently and selectively recover palladium from a spent automobile catalyst leaching solution, despite its rather low concentration when compared with the aluminum and cerium contents, and separates it from rhodium. Further research is in progress aiming at the removal or minimization of critical contaminants in the organic phase, particularly aluminum and cerium, and to concentrate palladium in the final stripping aqueous medium.

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AUTHORS

Cândida Vilarinho, Fernando Castro, Joana Carvalho, Mário Russo,  
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