



Recovery of palladium from a spent industrial catalyst through leaching and solvent extraction



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ABSTRACT

A hydrometallurgical approach to recover palladium from a spent industrial hydrogenating catalyst is described. The work aimed to enhance palladium and minimize aluminum recoveries. The efficiency of chloride leaching has been evaluated by varying the most determinant parameters affecting the leaching process. HCl solutions and mixtures of HCl and two chloride salts (MgCl₂ and NH₄Cl) were assessed. The use of H₂O₂ as oxidant was found essential to improve the Pd leaching to over 90%, together with low levels of chloride ion concentration (2.0 M) and temperature (25 °C). The use of the chloride salts enhanced the selectivity of Pd leaching over Al, but nevertheless Al is always present in the leachates. Aqueous phases composed by HCl + H₂O₂ and the respective salts, with optimized concentrations, were selected to be applied in liquid-liquid extraction using *N*-methyl-*N*-cyclohexyloctanthioamide (MCHTA) and *N,N*'-dimethyl-*N,N*'-dicyclohexylthiodiglycolamide (DMDCHTDGA). The results obtained from equilibrium Pd(II) extraction isotherms and reutilization experiments, using toluene as diluent and 0.1 M thiourea in 1.0 M HCl as stripping phase, show that MCHTA and DMDCHTDGA have similar loading capacities, with molar [extractant]:[Pd(II)] ratios of 3.5, but DMDCHTDGA exhibits a more reproducible extraction performance in the reutilization experiments. The liquid-liquid extraction efficiency of DMDCHTDGA for Pd(II) recovery from HCl + MgCl₂ + H₂O₂ and HCl + NH₄Cl + H₂O₂ media was also evaluated. Molar [extractant]:[Pd(II)] ratios of 3.8 for the former and 3.5 for the latter medium were achieved; accordingly, the overall results obtained for the three leaching phases are similarly encouraging. The reutilization experiments depict the recyclability robustness of the solvent to recover Pd(II). The whole data reported are promising regarding Pd recovery, but simultaneously evidence the deleterious effect Al has on the solvents, since it progressively accumulates in the organic phases.

1. Introduction

The recycling of anthropogenic end-of-life supplies is increasingly considered as a means to suppress the worldwide necessities of a given material, particularly in situations where its technological applications justify a demanding consumption. This is the case of the platinum-group metals (PGMs), whose criticality is both related with the scarcity and specific locations of their primary resources in the Earth's surface, and mainly to their multiple and growing technological functions (Hagelüken, 2012). The most important PGMs application is in catalysis, an ability that revolutionized the chemical processes in the 60's of last century, ranging from the oil refining and petrochemistry to the pharmaceutical industry (Steinlechner & Antrekowitsch, 2015). Furthermore, all vehicles come fitted with automobile catalysts already for decades, to reduce atmospheric pollution, and this specific function rely

on PGMs, formerly rhodium and platinum and, more recently, with a higher contribution of palladium (Steinlechner & Antrekowitsch, 2015).

The reprocessing of the spent automobile catalysts by dedicated industrial units provides about 50% of the worldwide PGMs consumption, although a ~10% decrease has been reported in 2015 (<http://www.platinum.matthey.com/services/market-research/pgm-market-reports>, n.d.).

It is well known that PGMs recycling involve both pyro and hydrometallurgical methods (Steinlechner & Antrekowitsch, 2015; Nogueira et al., 2014). When hydrometallurgy is involved, the leaching step is crucial, as it should promote the efficient dissolution of the desired metal(s) and minimize the presence of any contaminants. Chloride media are frequently used for PGMs leaching, with HCl as the chloride source, together with oxidants to promote the dissolution of metallic forms. Oxidants such as H₂O₂, HNO₃, NaOCl, Cu(II), among others,

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have been proposed (Nogueira et al., 2014; Jha et al., 2013; Barakat et al., 2006; Harjanto et al., 2006; Yoo, 1998; Potgieter et al., 2004; Aberasturi et al., 2011).

The subsequent concentration and/or purification of the leachates is frequently carried out by liquid-liquid extraction (or solvent extraction, SX). In this stage, efficient and selective extractant(s) is(are) the key component(s) of the organic solvent, promoting the successful separation of the desired PGMs from other contaminant metals, or even between each PGM itself (Anpilogova et al., 2016).

Intensive research is currently being conducted on the development of new molecules to suitably recover PGMs from leachates of spent materials, for example, thiacalixarene (Yamada et al., 2016; Gandhi et al., 2016; Yamada et al., 2015; Gandhi et al., 2015), dithioether (Traeger et al., 2012) and phosphonium ionic liquid (Gieszynska & Wisniewski, 2011) derivatives. Amide compounds have also been extensively investigated. Malonamide (Malik & Paiva, 2009; Malik & Paiva, 2010), sulfide-containing monoamide (Narita et al., 2014), thioamide (Ortet & Paiva, 2015a), thiodiglycolamide (Narita et al., 2008; Paiva et al., 2014; Ortet & Paiva, 2015b; Paiva et al., 2015), dithiodiglycolamide (Das et al., 2014) and succinamide (Costa et al., 2016) derivatives have been thoroughly tested as extractants to recover Pd(II) and Pt(IV). The promising efficiency and selectivity of Pd(II) liquid-liquid extraction by two thioamide compounds (Ortet & Paiva, 2015a) and one thiodiglycolamide (Ortet & Paiva, 2015b), from model hydrochloric acid solutions, have previously been appraised, a behavior justifying a systematic research of the involved metal ion extraction reactions (Ortet et al., 2016a; Ortet et al., 2016b).

The aim of the present work is to test *N*-methyl-*N*-cyclohexylthiooctanthioamide (MCHTA) and *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA), Fig. 1, in the recovery of Pd from solutions resulting from the leaching of a spent industrial catalyst. Besides Pd, the main element contained in the source material is Al, and this latter metal was not co-extracted with Pd under the previously adopted experimental conditions of liquid-liquid extraction (Ortet & Paiva, 2015a; Ortet & Paiva, 2015b). Accordingly, the investigation started by the study of the main parameters influencing Pd leaching, namely the composition of the leach media (HCl and mixtures of HCl with the salts MgCl₂ and NH₄Cl, including oxidant addition), trying to improve efficiency and selectivity. Leaching temperature, liquid/solid ratio (L/S) and reaction time were factors also evaluated in the leaching experiments. The “best” Pd(II) pregnant solutions were then subject to liquid-liquid extraction to obtain the corresponding equilibrium extraction isotherms and reutilization profiles, since this information is the most relevant for the characterization of the SX systems from a practical point of view.

2. Experimental

The spent industrial catalyst tested in this work was provided by Repsol Polímeros SA, and was used in the petrochemical plant located at the industrial complex of Sines, in Portugal. The commercial designation of the catalyst is OleMax® 302, and it operated on the selective

hydrogenation of methylacetylene and propadiene to propylene and propane. The composition of the fresh catalyst consists of 0.03% Pd(II) oxide and 0.03% Cr(III) oxide, supported on an alumina matrix (Material Safety Data Sheet, 2006).

2.1. Grinding, particle size and leaching experiments

The as-received catalyst was composed by spheres of about 20 mm diameter, a dimension too large to be considered adequate to directly perform the leaching experiments. Moreover, the decrease of the particle size is normally accompanied by improvement of the reaction rate (Havlík, 2008); therefore, a grinding operation was firstly applied. The catalyst was ground with a lab cutting mill (IKA MF 10 Basic) using a two-step grinding procedure, to avoid the formation of fines due to the characteristic brittle of the material. In the first step, a discharge grid of 3 mm was used. After sieving the resulting material with a 0.59 mm sieve, the infra fraction was recovered and the supra fraction was ground again using a 1 mm discharge grid. The material produced in the second step was added to the previously recovered, constituting the feed solids for the leaching tests. The particle size analysis was assessed using standardized sieves. The samples for the leaching experiments were prepared using a rotating divider (Spinning Riffler Microscal), and their average dimension is 0.18 mm.

Several batches of the catalyst were used, and Pd contents were determined in each batch to serve as reference for determining the respective leaching yields. The solid samples were digested with acid mixtures (HNO₃/HCl/HF) and the resulting solutions were analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES, Horiba Jobin–Yvon, Ultima).

The preparation of the leaching solutions was made from dilution or dissolution of the appropriate reagents (of analytical purity) in demineralized water. The leaching tests were carried out in 250 mL closed cylindrical glass reactors, with controlled temperature (measured inside the reaction pulp) and provided with mechanically controlled stirring (with two-blade impellers) at 250 min⁻¹. The solids were added to the reactor containing the liquid at the set temperature and the reaction time was controlled. When necessary, small sample volumes of the pulp were withdrawn from the reactor, centrifuged and analyzed to assess the evolution of the Pd leaching yields with time. At the end of each test the pulp was filtered and the solid was washed with demineralized water, dried and weighed. The leaching yields were determined from the analysis of the leachates, referring to the initial Pd concentration in each batch. Typical errors affecting the leaching yields were in the range ± 3–5%, as verified by replicates carried out for some experiments in the present work. For the preparation of larger volumes of solutions to be used in the SX experiments, 3 L glass reactors were utilized, with similar features as those of the smaller one previously described.

2.2. Liquid-liquid extraction experiments

The syntheses and characterization of MCHTA (Ortet & Paiva,

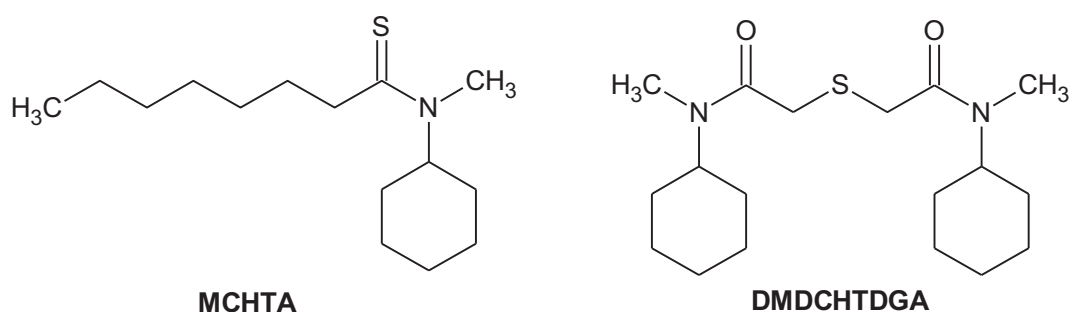


Fig. 1. Structures of the extractants tested in this work.

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