



## A bridge between liquid–liquid extraction and the use of bacterial communities for palladium and platinum recovery as nanosized metal sulphides



Ana Assunção<sup>a</sup>, Ana Matos<sup>a</sup>, Ana M. Rosa da Costa<sup>b</sup>, António Candeias<sup>c</sup>, Maria Clara Costa<sup>a,\*</sup>

<sup>a</sup> Centro de Ciências do Mar (CCMAR), Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

<sup>b</sup> Centro de Investigação em Química do Algarve (CIQA), Departamento de Química e Farmácia, Faculdade de Ciências e de Tecnologia, Campus de Gambelas, Portugal

<sup>c</sup> Laboratório HÉRCULES, Universidade de Évora, Largo Marques de Marialva 8, 7000-809 Évora, Portugal

### ARTICLE INFO

#### Article history:

Received 16 October 2015

Received in revised form 19 February 2016

Accepted 14 March 2016

Available online 22 March 2016

#### Keywords:

Liquid–liquid extraction

Bacterial community

Metabolic products

Palladium

Platinum

Nanosized palladium and platinum sulphides

### ABSTRACT

The Platinum Group Metals (PGM) are rare in the Earth's crust and in the past years their use had a considerable expansion limiting their availability, which justifies PGM's high commercial value and demand. Therefore, PGM recovery from secondary sources is very important from both economic and environmental points of view.

In recent years, several methods for PGM removal have been investigated. Our research group has been studying the removal/recovery of PGM using both chemical (liquid–liquid extraction) and biological methods (using anaerobic bacterial communities).

The aim of this study was to combine these two chemical and biological approach technologies, for PGM recovery. For that purpose, Pd(II) and Pt(IV) present in aqueous phases, were extracted to organic phases composed by *N,N'*-dimethyl-*N,N'*-dicyclohexylsuccinamide (DMDCHSA) and *N,N'*-dimethyl-*N,N'*-dicyclohexyltetradecylmalonamide (DMDCHTDMA) in 1,2-dichloroethane, respectively, with an extraction efficiency of 79% for Pd(II) and 99% for Pt(IV). The metals in the loaded organic phases were then stripped with seawater, a low-cost solution largely available in nature, with efficiencies of 100% for Pd and 86% for Pt. Finally, the metals were precipitated and recovered using metabolic products produced by a community enriched for sulphate-reducing bacteria. The palladium precipitated completely, while 86% of platinum was precipitated. During the precipitation process sulphide concentration in the solution decreased and the analysis of the precipitates was consistent with the formation of nanosized PdS and PtS<sub>2</sub>.

To our knowledge, this research shows, for the first time, the potential of combining liquid–liquid extraction with the use of bacteria aiming platinum and palladium recovery, as metal sulphides, from aqueous media.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Platinum Group Metals (PGM), including platinum (Pt) and palladium (Pd), are a limited global resource, not only because they are rare in the Earth's crust, but also due to the increasing of their use as a primary raw material, resulting in the high PGM economic value and demand (Martins et al., 2013; Deplanche et al., 2014).

The exceptional properties of PGMs, such as high conductivity, thermal stability and catalytic properties (Loferski, 2011), turn the PGM attractive to many industries, particularly in electronic device industries, in chemical process industries, as catalysts, and in automotive industry, as catalytic converters. In this context, PGM recycling from manufactured materials is essential and can provide a secondary source of these metals (Butler, 2012).

Over the last years, the recovery and reutilization of PGM from industrial wastes have raised some interest and several methods have been pointed out and explored, such as chemical reduction (Konishi et al., 2007), electrochemical methods (Dean, 1979) and biological methods (Martins et al., 2013). However, not all methods achieve an efficient separation and recovery of PGM. For instance, the fraction of PGM recovered from spent catalysts by liquid–liquid extraction, achieves only around 40% of the total amount (Marinho et al., 2010).

Among the chemical methods, liquid–liquid extraction, also called solvent extraction (SX), has been used in nuclear chemistry technology for the separation of various radioisotopes and for the reprocessing of nuclear fuels (Lee et al., 2009a), or for integrating hydrometallurgical schemes for the recovery of metals from mineral ores or from secondary sources (Marinho et al., 2010). Moreover, SX has been studied for PGM recovery due to its advantages, as high selectivity and metal purity. The SX processes, allowing the separation of two or more components in two immiscible liquid phases, are usually used by hydrometallurgical industries for PGM recovery, because their metal ions can easily form

\* Corresponding author.

E-mail addresses: [afassuncao@ualg.pt](mailto:afassuncao@ualg.pt) (A. Assunção), [amcosta@ualg.pt](mailto:amcosta@ualg.pt) (A.M.R. da Costa), [candeias@uevora.pt](mailto:candeias@uevora.pt) (A. Candeias), [mcorada@ualg.pt](mailto:mcorada@ualg.pt) (M.C. Costa).

species which are extractable into the organic phase (Butler, 2012; Rao and Reddi, 2000) with various reagents. Di-*n*-octyl sulphide or hydroxyoxime are examples of selective extractants for Pd while tributyl phosphate (TBP) and amines are frequently mentioned for Pt (Rydberg et al., 2004) among others (Harjanto et al., 2006; Barakat et al., 2006; Komjarova and Blust, 2006; Costa et al., 2013).

Recently, Costa et al. (2013) proposed a new promising extractant *N,N'*-dimethyl-*N,N'*-dicyclohexyltetradecylmalonamide, DMDCHTDMA, for the recovery of Pt(IV) from hydrochloric acid media. The Pt can be easily and quantitatively stripped to a new aqueous phase by simple contact with a 1 M HCl solution. Furthermore, this extractant showed a good loading capacity towards Pt(IV) and it can be reutilized several times without losing its extraction ability (Costa et al., 2013). In addition, the same research group has very recently discovered the extraction ability of *N,N'*-dimethyl-*N,N'*-dicyclohexylsuccinamide, DMDCHSA, for the extraction on both Pt(IV) and Pd(II) from hydrochloric acid media (Costa et al., 2016). Taking into account the good performance of these two extractants they were both selected and used in the present investigation, DMDCHTDMA for Pt(IV) and DMDCHSA for Pd(II) extraction.

The PGM stripping from the loaded organic phase and the subsequent recovery is not so much studied. The metals' recovery from the loaded organic phase by stripping methods is usually a difficult process, especially when the metal concentration is low, which is normally the case of PGM. The use of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Nowotny et al., 1997) or thiourea (Lee et al., 2009b; Kumar et al., 2008; Lee et al., 2009a) as stripping agents for Pt in a single stage has been explored (Marinho et al., 2010), but the replacement of these chemicals by more environmentally friendly and low-cost alternative stripping agents still remains a relevant issue.

The use of biological methods mainly based on the use of bacterial strains and communities for PGM recovery from aqueous solutions has also been investigated (Martins et al., 2013). The PGM biorecovery processes have some advantages compared to the chemical methods, since the biorecovery strategies are cleaner and more attractive from an economic point of view and particularly suitable for metal recovery at low concentrations (Macaskie et al., 2010).

Several studies have shown the potential of pure bacterial cultures for biological reduction of Pd(II) to Pd(0), such as *Desulfovibrio desulfuricans* (Yong et al., 2002) and *Shewanella oneidensis* (De Windt et al., 2005) and Pt bioreduction by *Shewanella algae* (Konishi et al., 2007), cyanobacteria (Lengke et al., 2006; Brayner et al., 2007) and *Desulfovibrio* sp. (Rashamuse and Whiteley, 2007; Rashamuse et al., 2008). Although the use of bacterial communities presents considerable recognized advantages over the use of pure strains (Mukred et al., 2008), few studies are reported. A sulphate-reducing bacteria (SRB) community was mentioned as having the ability to reduce Pt(IV) to Pt(0) via the intermediate cation Pt(II) (Riddin et al., 2009). Other authors demonstrated the ability of a Pd(II)-resistant mixed bacterial culture to recover Pd (II) from an aqueous medium, leading to the formation of Pd(0) nanoparticles (Martins et al., 2013). Pd and Pt biorecovery mechanisms, such as the bioaccumulation of Pd by *Desulfovibrio fructosivorans* (Mikheenko et al., 2008) and the bioabsorbance of Pd and Pt by *Desulfovibrio* (Vargas et al., 2004) have been reported.

The aim of this study was to test the potential of metabolic products (MP) from the growth of an anaerobic bacterial community, enriched for SRB, for Pd and Pt removal from aqueous solutions, namely those resulting from the stripping stage of SX processes. The use of MP presents advantages in comparison to the biorecovery techniques that occur in the presence of live bacterial cells, since the process does not require the utilization of metal-resistant bacteria.

The combination of both chemical (SX) and biological methods may have potential for PGM recovery, taking into account that after the stripping stage of a solvent extraction process, the metals remain soluble in the purified aqueous phase, and thus a subsequent method

is required for its recovery. Hence, this research explores for the first time, to our knowledge, the possibility of combining the use of liquid–liquid extraction with a biological process for the recovery of Pt and Pd from aqueous media.

## 2. Material and methods

### 2.1. Synthesis and characterization of the extractants

The structures of the malonamide and succinamide derivatives synthesized and used in this research work, *N,N'*-dimethyl-*N,N'*-dicyclohexyltetradecylmalonamide (DMDCHTDMA) and *N,N'*-dicyclohexyl-*N,N'*-dimethylsuccinamide (DMDCHSA), are presented in Fig. 1.

DMDCHTDMA was synthesized according to the procedure already described by Costa et al. (2013) and its characterization was in accordance with the data previously reported.

The reagents used for the DMDCHSA synthesis were succinyl chloride (Sigma-Aldrich, 95%), *N*-methylcyclohexylamine (Sigma-Aldrich, 99%), and dichloromethane (DCM, Absolve, ≥99%) and were used without further purification. Succinyl chloride (7 g, 5 mL, 0.044 mol) was dissolved in 75 mL of DCM in a two neck round bottom flask, and cooled down in a cold bath (ice/CaCl<sub>2</sub>-15 °C). *N*-methylcyclohexylamine (20.83 g, 24 mL, 0.184 mol) was dissolved in 25 mL of DCM, in an addition funnel. The amine solution addition was performed dropwise under stirring. The reaction was monitored by Fourier Transform Infrared Spectroscopy (FTIR) in a Bruker (Tensor 27) spectrophotometer, placing an aliquot into NaCl discs. The disappearance of the band at 1783 cm<sup>-1</sup> (acyl chloride carbonyl group) and the appearance of the amide carbonyl band at 1639 cm<sup>-1</sup> were monitored. After 48 h, the reaction was completed and the obtained mixture was transferred to a separatory funnel, washed three times with HCl solution (4% w/w), once with distilled water and, finally, dried over anhydrous magnesium sulphate and filtered to a round bottom flask. The DCM was evaporated in a rotary evaporator, yielding a yellow solid that was recrystallized from *n*-hexane and dried in a vacuum oven at 30 °C overnight. The yield of the product (DMDCHSA) was 80%, corresponding to 11.14 g of compound. DMDCHSA was characterized by melting point (86–88 °C), FTIR (KBr: 1639 cm<sup>-1</sup> (ν C = O), 1591 cm<sup>-1</sup> (Amide II)), <sup>1</sup>H NMR(CDCl<sub>3</sub>: 4.44 (1 H, broad singlet, CH cyclohexyl), 3.69 (1 H, broad singlet, CH cyclohexyl), 2.88 (3 H, s, N-CH<sub>3</sub>), 2.81 (3 H, s, N-CH<sub>3</sub>), 2.73–2.65 (4 H, m, O=C-CH<sub>2</sub>-CH<sub>2</sub>-C=O), 1.85–1.05 (20 H, m, CH<sub>2</sub> cyclohexyl), and LC-MS (*m/z*: 309 ([M + H]<sup>+</sup>)), the spectroscopic data being consistent with the expected structures.

### 2.2. Solvent extraction and stripping experiments

All reagents and solvents were used without further purification. Feed aqueous phases containing 102 mg·L<sup>-1</sup> Pd(II) or 163 mg·L<sup>-1</sup> Pt(IV) in HCl 6 M (prepared from a hydrochloric acid, 37% (w/w) solution, ACS reagent, Acros Organics) were prepared from their respective atomic absorption spectroscopy standards (1 g·L<sup>-1</sup> Pd(II), Pd standard solution, CertiPUR, Merck or 1 g·L<sup>-1</sup> Pt(IV), Platinum Standard solution, Acros Organics) and were dissolved in the required volumes of the hydrochloric acid solution.

The organic phases containing 0.05 M DMDCHSA and 0.05 M DMDCHTDMA were prepared in 1,2-dichloroethane (1,2-DCE, VWR Prolabo BDH chemicals). The aqueous phases containing Pd(II) or Pt(IV) were then placed in contact with the organic phases. Seawater and 1 M hydrochloric acid solution were used as agents to strip Pd and Pt from the respective loaded organic phases.

The extraction and stripping experiments were carried out at room temperature and the organic and aqueous phases were placed in contact with equal volumes (A/O = 1) for 30 min, by mechanical shaking, adopting a rotation speed between 900 and 1000 rpm. The two phases

Download English Version:

<https://daneshyari.com/en/article/211853>

Download Persian Version:

<https://daneshyari.com/article/211853>

[Daneshyari.com](https://daneshyari.com)