



Selective recovery of palladium using an innovative functional polymer containing phosphine oxide

Q. Ricoux^{a,b}, V. Bocokić^b, J.P. Méricq^{a,*}, D. Bouyer^a, S.v. Zutphen^b, C. Faur^a

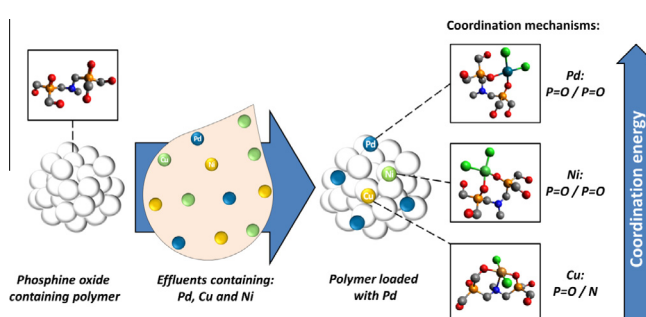
^aIEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université Montpellier 2 cc47, Place E. Bataillon, 34095 Montpellier Cedex 5, France

^bMagpie Polymers, 108 avenue Carnot, 77140 Saint Pierre Les Nemours, France

HIGHLIGHTS

- Palladium sorption on innovative polymer containing phosphine oxide groups.
- Sorption with high capacities, fast kinetics and high selectivity toward palladium.
- High palladium recovery by elution.
- Investigation of metals sorption mechanisms via experiments and molecular modeling.

GRAPHICAL ABSTRACT



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ABSTRACT

A new polymeric sorbent powder (MP-102) containing phosphine oxide groups was developed for the selective recovery of palladium by sorption from acidic effluents containing base metals such as nickel and copper. Experiments show an interesting affinity of MP-102 to palladium species with sorption capacity up to 1 mmol g^{-1} at pH 2, fast kinetics and up to 96% selectivity for Pd in presence of Cu and Ni at pH 1. It was found that 99% of the sorbed palladium can be stripped by elution with an acidified solution of thiourea. The influence of various operating parameters (pH, chloride concentrations and temperature) on Pd sorption equilibria was studied in presence of copper and nickel in order to investigate their influence on the sorption selectivity of the palladium species and to investigate the metal binding mechanisms. Experiments, supported by DFT calculations, suggest a coordination of Pd and Ni by the phosphine oxide groups, preferably in a bidentate mode (chelation), whereas Cu appears to bind to both amine and phosphine oxide groups. The sorption selectivity for palladium is likely due to the energy gain upon palladium coordination to MP-102 which is at least 40 kJ mol^{-1} higher than upon copper and nickel coordination.

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1. Introduction

Platinum group metals (PGM), including platinum and palladium, are used in many applications due to their remarkable properties (high conductivity, thermal stability, catalytic

properties) [1]. They are widely used in electronic devices but their main application is as catalysts in chemical process industries and in catalytic converters for automotive industries [2].

PGM production generally comes from the mining of huge volumes of copper–nickel ores containing traces of PGM (less than 1 g t^{-1}). Because of the low concentration of PGM in the ores and the depletion of resources, the cost of metal extraction progressively increases. In this context, PGM recycling from manufactured

* Corresponding author. Tel.: +33 467 14 91 88; fax: +33 467 14 91 19.

E-mail address: jean-pierre.mericq@univ-montp2.fr (J.P. Méricq).

materials such as catalytic converters provide a growing production source of PGM [2].

Hydrometallurgical processes are commonly employed to extract precious metals from ores and catalytic wastes. After concentration of metals from ores by flocculation and/or pyrometallurgical processes, they are dissolved in aqua regia or in mineral acids like hydrochloric acid under oxidizing conditions (Cl_2 , H_2O_2) [3–5]. Metals are then extracted from these acidic multicomponent solutions by conventional extraction techniques, such as chemical precipitation and solvent extraction. However, chemical precipitation presents the drawbacks of incomplete recovery and low selectivity while solvent extraction provides excellent selectivity but requires the use of high quantities of toxic solvents for the complete recovery of metals [6]. Consequently, sorption and ion exchange processes present substantial advantages compared to other recovery methods in the case of dilute effluents to extract and concentrate precious metals [7–10]. New and innovative sorption processes are increasingly studied [11–14].

A wide range of sorbents have already been studied for palladium recovery, a key PGM. This includes strongly basic ion exchange materials [15,16], weakly basic ion exchangers [17,18] and chelating polymers allowing sorption by coordination mechanisms [19,20]. For ion exchangers, sorption capacity and selectivity for palladium are the key properties that allow the materials to extract the palladium so that it can be further refined. The sorption performance of ion exchangers depends on chemical functional groups, degree of functionalization and physical structure of the sorbent [16].

Most of the commercially available strong base ion exchangers used for the recovery of PGM are ammonium salts [16,21], which are able to capture chloro-complexes of palladium via unselective electrostatic interactions. Chelating and cation exchange resins are polymers functionalized with ligands such as amines, thiols or phosphine sulfides [17,19,22]. Sorption onto such materials occurs via two different mechanisms: (i) interactions between negatively charged metal chloro-complexes and protonated ligands (NH^+ , $=\text{S}-\text{H}^+$, $\text{P}=\text{S}-\text{H}^+$) at low pH and high chloride concentrations; (ii) coordination interactions between free electron lone pairs and metal center. This binding mode gives selectivity for the PGM with respect to metal cations such as Al^{3+} , Zn^{2+} and Na^+ [23].

Phosphines and its derivatives are widely used as ligands in coordination chemistry, and as scavengers in solvent extraction of metals. For instance, tri-*n*-octylphosphine oxide (TOPO) is not only used in solvent extraction procedures in the recovery of PGM [24–26], but also for the selective removal of PGM from acidic media [27]. Water soluble aminophosphines are excellent ligands [28–33] used in various homogeneous catalysts. The oxidized form of the excellent phosphine ligand 1,3,5-triaza-7-phosphaadamantane (PTA), $\text{PTA}=\text{O}$, displays weaker ligation properties, but higher selectivity toward PGM than PTA. Indeed, $\text{PTA}=\text{O}$ preferably coordinates to Pd in a mixture of Pd, Ni, and Cu, while PTA would indiscriminately bind to all three metals. Interactions between PGM and aminophosphine-oxides can therefore occur through coordination by phosphine oxide and ion exchange with the amine groups. However, surprisingly, the strategy of PGM-recovery by sorption on aminophosphine [34] and aminophosphine-oxide [35] containing materials has been very little studied and reported in the literature, despite their great potential.

This work concerns an application of a novel functional polymer containing aminophosphine-oxide as complexing group (MP-102) developed by Magpie Polymers in selective palladium sorption. The main goal of this paper lies in the investigation of the sorption mechanisms of the MP-102 material and its modus operandi. In order to achieve this objective, binding kinetics, binding equilibria and the selectivity towards Pd in the presence of metals as Cu and Ni were studied. The feasibility of recovering the Pd bound MP-102

by elution was investigated. In addition, supported by a DFT-study in which the most favorable coordination modes were calculated, the mechanism of Pd sorption onto MP-102 was modeled to explain the experimentally observed selective sorption in presence of copper and nickel.

2. Materials and methods

2.1. Material

The aminophosphine oxide polymer (MP-102) was synthesized by Magpie Polymers. All solutions were prepared using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 97%, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Thermo Fisher Scientific, Waltham, MA, USA) and PdCl_2 99.9% (Strem Chemicals, Newburyport, MA, USA) in deionized water. Acidity was adjusted with HCl, HNO_3 or NaOH (Sigma Aldrich, St Louis, MO, USA). Pd elution was carried out using thio-urea, potassium thiocyanate, sodium metabisulfite, urea, sodium EDTA and sodium thiosulfate (Sigma Aldrich).

2.2. Analysis

Dried particle size was estimated using a scanning electron microscope (SEM) Hitachi S4800 (Hitachi, Japan). The EDX analysis was made using a SEM Hitachi S4500 equipped with an EDX analysis system (Thermo Scientific System Seven, NSS 212; Thermo Fisher Scientific). FTIR spectra were recorded with a Nicolet FTIR 710 (Thermo Fisher Scientific) equipped with a ZnSe ATR crystal. MALDI-TOF mass spectrometry was performed with a Bruker UltraFlex TOF/TOF instrument (Bruker, Billerica, MA, USA), equipped with Nd-YAG laser (355 nm wavelength at 100 Hz), an electrostatic reflector and using a DCTB matrix. Mass spectra were acquired from 500 laser shots with ion sources set to 25 kV and 21.50 kV, and a lens voltage of 9.6 kV.

2.3. Metal sorption

Sorption isotherms of Pd were performed with 0.030 g of polymer placed in a 50 mL solution magnetically stirred at 500 rpm, containing from 0.15 to 6 mmol L^{-1} of Pd, 3 mmol L^{-1} of Ni and Cu and 0.01 mol L^{-1} of HCl, monitored during 1 week. It was verified that this duration was long enough to reach equilibrium.

The influence of pH and chloride concentration was studied on batch equilibria at 0.3 mmol L^{-1} of initial concentration of Pd, Cu and Ni at 287 K, 298 K and 310 K. pH was modified by addition of HCl at a fixed chloride concentration (0.1 mol L^{-1} , i.e. pCl 1, fixed by addition of NaCl). Chloride concentration was changed by NaCl addition at pH 2 (adjusted with HCl). Samples were filtered with 0.2 μm syringe filters in cellulose acetate (Fisher Scientific), to determine metal concentrations using an atomic absorption spectrometer Perkin Elmer AAnalyst 400 for Pd and Ni (Perkin Elmer, Waltham, MA, USA) and a Varian SpectrAA 220FS for Cu (Varian, Palo Alto, CA, USA). The metal uptakes Q (the amounts of metal sorbed (mmol) per unit of sorbent mass (g)) were determined by mass balance (Eq. (1)):

$$Q = \frac{(C_i - C_t) \cdot V}{m} \quad (1)$$

where C_i and C_t (mmol L^{-1}) are metal concentrations in solution at $t = 0$ and at time t , V is the solution volume (L) and m (g) is the mass of sorbent. To investigate the influence of the experimental parameters on sorption capacity, palladium speciation was calculated as a function of pH and chloride concentration, using data from literature [36], for $[\text{Pd}^{2+}] = 0.3 \text{ mmol L}^{-1}$.

Sorption isotherms were described by Langmuir and Freundlich equations (Eqs. (2) and (3)):

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