Thesis Outline

Platinum group metals (PGMs) are rare metals with remarkable physical properties (high conductivity, thermal stability) and rich chemistry. Palladium, platinum, rhodium and iridium are used in diverse applications such as electronic devices, glass and ceramics, medical applications and pharmaceuticals, and their main usage is as catalysts in chemical process industries and in catalytic converters in order to minimize cars and trucks exhaust emissions.Their natural abundance is very low, with mines in South Africa and Russian Siberia accounting for 90% of all PGMs produced worldwide. It is therefore not surprising that recycling is becoming an increasingly important source for these metals. The recycling of domestic industrial and electronic waste (urban mines) represents about 40% of the annual needs and thus does not manage on its own to secure the supplies of the developed countries. Highly efficient recycling and refining processes exist and are able to recover the major part of PGMs from scraps. However, in the wastewaters of such refining processes, concentrations of PGMs between 2 and 100 mg/l are not uncommon. PGMs have similar properties and reactivities,which makes their separation and purification particularly delicate and expensive. Moreover, they are generally extracted as by-products from copper, nickel or cobalt ores with which they also share similar physicochemical properties. Conventional methods for the removal of low metal ion concentration from wastewater such as solvent extraction; chemical precipitation and ion exchange have been found to possess significant disadvantages. Prominent among the disadvantages are: incomplete metal removal, high capital costs, high reagent and/or energy requirements, and generation of toxic sludge or other waste products that require disposal.Materials containing functional coordinating groups are numerous and can be applied for selective extractions for an array of metals in a large range of applications. Many functionalities were successfully applied in PGMs extraction, among them being those based on sulfur (in the form of organic sulfides, thiols, thioureido, and similar functionalities) which belong to the group of those most suitable for PGMs capture, and they are found in many applications in the industry. However, there are a number of effluents for which the application of such coordinating/chelating materials is limited due to the incompatibility between the resin and the dissolved chemical compounds such as strong, concentrated acids and/or oxidizing agents. Such solutions are, for example, nitric acid, which is widely used as solvent in the silver refining industry. In this context of high demand and economic tensions, the profitability of extractive processes is largely conditioned by their efficiency characterized by a high recovery rate and their selectivity Founded in 2011, Magpie Polymers has introduced innovative organophosphorus resins with high specificity and efficiency, intended for solid / liquid extraction by direct sorption of the targeted metals. This first-rate technological breakthrough has been the subject of several industrial developments in partnership with operators in the hydrometallurgy sector,particularly in Germany, Italy and South Africa, with to date several industrial installations containing hundreds of liters of Magpie resins for the treatment of refinery waste. Protected by several patents, the innovation is based on the judicious choice of the functional groups (phosphine or phosphine oxide) which have much better affinities and selectivities with regard to PGMs than the generic ion exchange resins commonly used, allowing them to recover the species ions of interest from complex solutions, strongly acidic and oxidizing, with high efficiency. This thesis is focused on PGMs recovery using targeted resins. The basic objective of the study in this thesis is to contribute to the understanding and modelling of the equilibria and kinetics of PGMs adsorption processes from chloride media. It aims to evaluate the performance of some of the Magpie current products in terms of relative affinity to the different PGMs and determining the thermodynamic and kinetic parameters describing the metal-resin interactions.Moreover, other commercially available resins were included in the experiments and examined in the same conditions for their ability to recover PGMs. A second objective is to develop an industrial process for Pd and Pt recovery from silver refining effluents. The recovery of palladium and platinum from the silver refining processes is important for two reasons: to produce high quality silver and to recover the valuable precious metals.

This manuscript is composed of four chapters.

The first chapter consists of a state-of-the-art review presenting the platinum group metals, their extraction methods and their various refining processes. Moreover, an insight on silver refining and the challenges of obtaining high purity silver is given. Various methods for PGMs recovery and PGMs speciation are also reviewed. Theoretical aspects of chemisorption and the most common models used to describe the adsorption equilibria and kinetics are presented.

Chapters 2 to 4 present the authors' original contributions to the PGMs recovery using adsorption processes.

The second chapter presents the thermodynamic and kinetic studies of PGMs recovery from mono-component chloride effluents. Two Magpie products were evaluated against three commercially available resins. In order to understand the acid (HCl) and ionic strength (controlled by NaCl concentration) influence on the PGMs capture, the studies were carried on in six different effluents. The experimental data was modelled using non-linear regressions. The isotherms data were modelled using three isotherms models: Langmuir, Freundlich and Sips, while the kinetics were fitted with the most used models: pseudo-first order and pseudosecond order models.

The third chapter is focused on the PGMs recovery experimental results of the two best performing resins, determined in the 2nd chapter, from multi-element synthetic acid solutions.

Moreover, similar to the previous chapter, the effect of acid concentration and solution ionic strength, addition were evaluated. The isotherms data were modelled using two extended isotherms models: Langmuir and Sips

The fourth chapter presents the development of two adsorption processes for Pd and Pt recovery from silver refining effluents. The lab testing in batch and flow experiments from different industrial effluents, followed by pilot evaluation are given. Moreover, a risk assessment of using organic resins in nitric acid was performed in collaboration with external laboratories and the results are presented in this chapter.

The final chapter is dedicated to the overview of the work presented in this thesis, making a short assessment of the main findings.