

4 The Scope of this Work

This study is focused on the recovery of precious metals from hydrochloric acid solutions by techniques based in sorption on natural polymers.

Due to the high value and scarcity of precious metals, the need of developing and consolidating new separation and concentration processes is very important.

The work presented in this thesis has been planified and based on the contribution given by the research of the properties of chitosan in the sorption of metals, realized in the "Laboratoire Génie de l'Environnement Industrial de l'Ecole des Mines d'Alès" and by the research of the behaviour of the precious metals in solution, realized in the Department of Chemical Engineering, Universitat Politècnica de Catalunya.

The result of this cooperation has been the thesis that is being presented here and which has been organized in the following manner:

■ Paper 1

Glutaraldehyde-crosslinked chitosan was studied for palladium recovery in acidic medium (around pH 2). The influence of several parameters such as pH and competitor anions, was studied with respect to sorption equilibrium. Sorption isotherms were obtained and modelled using the Langmuir and Freundlich models. This study also examines the effect of palladium concentration, particle size, sorbent dosage, the influence of the acid used to control the pH of the solution, and the extent of crosslinking on sorption kinetics. Kinetic curves are modelled using single diffusion model equations to evaluate the predominance of either external or intraparticle mass transfer resistance.

■ Paper 2

Palladium sorption on glutaraldehyde-crosslinked chitosan was studied in fixed-bed column systems. Sorption performances were controlled mainly by the presence of competitor anions in the solution.

■ Paper 3

Paper 3 was dedicated to the optimization of the synthesis of a new chitosan derivative, on which sulphur groups have been grafted through the binding on a chitosan backbone of an intermediary product resulting from the chemical reaction of thiourea and glutaraldehyde.

The production of the thiourea derivative sorbent was studied in order to optimize sorption properties for PGMs recovery in several types of matrices including chlorine and sulphate solutions. To achieve a better understanding of the sorption mechanism and optimization of experimental conditions, modified chitosan has been experimented for platinum and palladium recovery in solutions whose pH were controlled by either sulphuric acid and hydrochloric acid. The study has been performed through the optimization of the pH, the determination of sorption isotherms, and the observation of the influence of competitor anions. The influence of diffusion mechanisms has been investigated through the study of sorption kinetics, examining the influence of particle size and type of acid used for pH control.

This study also included the desorption of Pd from samples used previously in fixed-bed column system (Paper 2).

■ Paper 4

This study shows the equilibrium and kinetic performances of glutaraldehyde chitosan for palladium recovery in batch systems and the influence of palladium concentration on breakthrough curves.

■ Paper 5

Chitosan gel beads was used for the study of the palladium and platinum sorption. The main problem for a large scale application using chitosan gel beads is the high water content of the beads (about 94-96 %), which makes the transport, handling and scaling up the process economically non-competitive. For this reason the study focused on the influence of the drying process on sorption performance (sorption isotherms and uptake kinetics). The influences of the re-hydration of the beads and the adsorption of saccharose (before drying) were studied.

■ Paper 6

In this paper, several methods have been tested for chitosan modification including PEI-grafting (poly(ethylene imine)), hydrogenation of imine function on glutaraldehyde-cross-linked chitosan, and thiourea-grafting. Depending on the modification technique, the improvement in sorption performances may consist in an increase in sorption capacity (PEI-grafted chitosan), a change in the stability of the sorbent (hydrogenation of imine linkage) or an increase in the selectivity of sorption in presence of co-ions (thiourea derivatives of chitosan). The influence of drying and re-hydration of the beads are studied too for some of these chitosan derivatives whit regard to their diffusion properties.

■ Paper 7

This work is focused on the study of the influence of drying process (oven-drying at 60 °C) on Pt and Pd sorption performance. The influence of the rehydration of the beads and the influence of the adsorption of saccharose (before the drying) has been studied on sorption isotherms and kinetics.

■ Paper 8

This paper, based on previous work on platinum and palladium recovery, is focused on the recovery of osmium and iridium, using glutaraldehyde cross-linked chitosan gel beads, PEI-grafted chitosan gel beads and re-hydrogenated glutaraldehyde cross-linked chitosan gel beads. Complementary experiments has been performed on ruthenium, rhenium and rhodium under comparable experimental conditions.