

8 Conclusions

This work is a contribution to the improvement of techniques and derivatives of chitosan for the recovery of precious metals from diluted solutions.

Glutaraldehyde-crosslinked chitosan flakes are very efficient at removing palladium from dilute solutions. Though sorption performances depend on the composition of the solution, and especially the acid used to control the pH, maximum uptake occurs around pH 2. The predominance of chloro-anionic species is found to be favourable. The Freundlich equations fit sorption isotherms well with both hydrochloric and sulphuric acid solutions, though hydrochloric solutions allow a better affinity to be obtained for sorption on chitosan.

Sorption kinetics are controlled by particle size, crosslinking ratio, and palladium concentration. Kinetics curves are modelled with simple external and intraparticle diffusion relationships allowing a good fit of experimental data for systems in sulphuric acid solutions or with low sorbent dosage.

Sorption capacities as high as 190-200 mg·g⁻¹ have been obtained for palladium sorption on crosslinked chitosan in batch systems. The same sorption levels are reached with fixed-bed column systems. The favourable sorption breakthrough curves are obtained. The breakthrough curves are characterized by steep slopes.

The breakthrough curves are controlled by several experimental parameters such as the column depth, the superficial flow velocity, the metal concentration, and also the size of the sorbent particles. Although the effect of these parameters cannot be neglected, the differences are not so marked as with other sorbent/sorbate systems. In the case of palladium, the ready diffusion of mononuclear metal species is not sterically hindered as with systems involving the diffusion of polynuclear hydrolyzed species (molybdate, vanadate).

The complete recovery of palladium from exhausted sorbent was not achieved, a concentrated solution of hydrochloric acid (11 M) allows more than 85 % of sorbent palladium to be eluted.

Though cross-linked chitosan is efficient at removing palladium from synthetic and pure acidic solutions, its sorption properties are strongly decreased by the presence of competitor anions. The modification of the ion exchange resin to a chelating resin, resulting from the grafting of sulphur compounds, improves sorption capacity and reduces the influence of pH and competitor anions.

The grafting of sulphur compounds through glutaraldehyde linkage reveals an interesting way to improve sorption properties against platinum group metals. The thiourea derivatives of chitosan has been used for palladium and platinum recovery, the results showed that the enhancement of sorption properties is more significant in the case of platinum.

Other important parameter in the design of chitosan adsorbents is the diffusion resistance. Several studies dedicated to diffusion in chitosan gel beads confirm the interest of expansion of the polymer network resulting from the gel formation. In this work gel beads with optimum crosslinking-ratio (CR:1) here been used for the study of platinum and palladium sorption. The results showed the improvement on sorption capacities and sorption kinetics.

However, for large-scale use, chitosan gel beads containing high water percentage cannot be easy handled and transported.

The drying process has shown that sorption rates for the platinum and palladium are greatly reduced. Preliminary re-hydration of the beads partly restores diffusion properties, however since the drying is irreversible, kinetics are still affected by intraparticle diffusion limitations. The drying results in a strong irreversible reduction in the size of the beads, which may result in a decrease in the porous volume, pore size and in a re-establishment in the polymer crystallinity.

The saccharose pre-treatment prevents the collapse of the structure and limits the volume variation. Sorption kinetics and isotherms are thus maintained at a level close to that of raw beads.

The incorporation of PEI in chitosan gel beads is assumed to produce new primary, secondary and tertiary amine functions that increase the reactivity of the sorbent for metal ions. After re-hydration, the influence of PEI on sorption kinetics is similar to the effect to the presence of saccharose in the beads during the drying step: it maintains the structure of the polymer, it prevents the collapse of the porous network and improves diffusion properties.

The grafting of thiourea makes the polymer less sensitive to the presence of chloride ions.

Derivatives of chitosan are effective at removing iridium and osmium from dilute solutions. Iridium and osmium can be sorbed on chitosan derivatives including glutaraldehyde crosslinking, PEI-grafted and thiourea-grafted chitosan gel beads. Experiments were performed at pH 2 using HCl for controlling the pH.

Desorption was very efficient for iridium using hydrochloric acid due to weak interaction between cross-linked chitosan and this metal. In the case of osmium the strength of the interaction between the metal and the sorbent makes the desorption significantly less efficient.

Similar experiments were performed on rhenium, ruthenium and rhodium, with diluted standard solutions. The sorption levels were so low that the sorption capacities remained below $10 \text{ mg Me}\cdot\text{g}^{-1}$.

