

7 Results and Discussion

7.1 Palladium sorption on glutaraldehyde-crosslinked chitosan (flakes)

7.1.1 Batch system

- pH optimisation

The influence of the pH on palladium sorption was studied with respect to the acid used for the pH control (HCl and H₂SO₄). With hydrochloric acid solutions the maximum sorption capacity is obtained at a pH 2, above pH 2, sorption capacity strongly decreases. With sulphuric acid solutions, the maximum sorption capacity remains almost unchanged in the range of pH 1.5 to 3. Sorption capacity is significantly higher in the optimum pH range for hydrochloric acid solutions than for sulphuric acid solutions.

To describe the differences in palladium sorption the following mechanism is proposed: in hydrochloric acid solutions, a small chloride excess involves formation of ionic chloro-palladate species, which can be adsorbed and exchanged on protonated amino groups. Increasing the pH (and decreasing the hydrochloric acid concentration) decreases the competitor effect between chloride ions excess and palladate species. On the other hand, in sulphuric acid solutions, palladate species are less reactive with sulphate anions and do not form favourable ionic forms. Sulphate is free in solution to be electrostatically attracted to protonated amino groups where, in excess, they directly compete with palladate species.

- Influence of the chloride concentration

The increase in chloride concentration significantly decreases sorption efficiency, thus the favourable effect of chloride is only a relative effect in comparison with sulphate anions, mainly related to the association of chloride with palladium to form

anionic species. Moreover, the strong influence of chloride competitors anions confirms the proposed ion-exchange mechanism.

- Influence of the acid used for pH control

The sorption isotherms of hexachloropalladate anions on cross-linked chitosan has been proved to be strongly influenced by the acid used to control the pH of the solutions. While with hydrochloric acid the adsorption isotherm is highly favourable, in the case of sulphuric acid solutions the shape of the sorption isotherm, indicates a less favourable sorption. This results confirmed the influence of this parameter on palladium sorption.

One of the possible reasons for this unfavourable trend can be attributed, to the predominance of less favourable palladium species due to the lack of chloride in solutions controlled with sulphuric acid.

- Influence of particle size

The size of sorbent particles has been shown to be a key parameter in the control of sorption performances of several metal ions on chitosan. In the case of palladium sorption this parameter hardly influence the sorption performance. The weak influence of particle size in the case of palladium sorption in comparison with other metals may be explained by the low ionic radius of the mononuclear chloro-palladate species. Though the hydration of metal ions increases the ionic size of chloro-palladate species, this parameter has no influence in the case of mononuclear palladate species.

As expected, decreasing the sorbent particle size involves a decrease in the time required to reach the equilibrium and a strong increase in the initial sorption velocity.

- Influence of crosslinking ratio

Increasing the crosslinking ratio leads to a significant decrease in equilibrium performance and kinetics.

Increasing a crosslinking ratio, between 0.42 and 4.15, induces a decrease in the maximum sorption capacity by almost 20 %. In the kinetics, the equilibrium time increases with the crosslinking.

The glutaraldehyde crosslinking involves: (a) the formation of new interchain linkages, and thus some restriction at the entrance in the polymer network, and (b) a loss in the chain flexibility.

- Influence of palladium concentration

The influence of palladium concentration on sorption kinetics was studied changing the type of acid used for controlling the pH at 2. In sulphuric acid solutions, at low sorbent dosage ($50 \text{ mg}\cdot\text{L}^{-1}$), increasing the initial concentration involves a decrease in sorption efficiency at equilibrium.

For HCl solutions, at sorbents dosage ($150 \text{ mg}\cdot\text{L}^{-1}$), decreasing palladium concentration allows equilibrium to be reached faster with final concentration tending to 0. In this case is difficult to compare these experiments accurately, because the level of saturation can be different.

7.1.2 Dynamic System

- Influence of palladium concentration on breakthrough curves

As expected, increasing the metal concentration reduces the breakthrough curves volume significantly, however, this reduction is not proportional to that of the metal

concentration: It seems that increasing the metal concentration makes the system more efficient.

Increasing metal concentration, the slope of the breakthrough curves increases, indicating a better mass transfer in the column. Palladium concentration at the column exhaustion increases with the initial concentration, reaching 150, 178, and 198 $\text{mg}\cdot\text{g}^{-1}$ for 5, 25, and 50 $\text{mg}\cdot\text{L}^{-1}$, respectively. These values are close to those obtained for the sorption isotherms: 155, 170 and 182 $\text{mg}\cdot\text{L}^{-1}$, respectively.

Dynamic sorption capacities range from 160 and 200 $\text{mg}\cdot\text{g}^{-1}$, values close to those obtained in batch systems.

- Influence of superficial flow velocity on breakthrough curves

The influence of this parameter is almost negligible. This result may be related to the fast sorption kinetics obtained in batch systems.

- Influence of column depth (sorbent amount) on breakthrough curves

For differing column depths (2.4, 4.5, and 6.6 cm), the sorption capacities at exhaustion are comparable (from 195 to 199 $\text{mg}\cdot\text{g}^{-1}$).

The BV of the solution for half-exhaustion ($C_s/C_o = 0.5$) would be expected to be almost identical for different amounts of sorbents (and different column depth), while the slope of the breakthrough curves would change with the column depth: Increasing the depth of the column increases the contact time between the sorbent and the sorbate.

The results are in concordance with this prediction for 4.5 and 6.6 cm column depth. However, with a short column, the breakthrough occurs at lower BV number and the slope of the curve is reduced, it seems that the short column is a critical column

depth. The results obtained in the study of the influence of column diameter confirms this opinion.

- Influence of column diameter on breakthrough curves

The change in the column diameter does not change the breakthrough curves for a similar column depth.

Breakthrough curves obtained with the same column depth and different column diameter (10 mm – 2.3 cm, and 7 mm – 2.4 cm) shown a overlap, but the comparison with the same amount of sorbent (10 mm – 2.3 cm and 7 mm – 4.5 cm) with the same superficial flow rate, shown that the lowest column depth used for the experiment with a column diameter of 10 mm is less favourable to sorption, perhaps due to a contact time too brief and dispersion effects. This finding is consistent with previous results on the effect of column depth. For the same, amount of sorbent, enlarging the column results in a diminution of column depth. As a consequence, the resistance to diffusion may limit the overall mass transfer and the sorption efficiency.

- Influence of sorbent particle size on breakthrough curves

The influence of this parameter is not restricted to diffusion properties, increasing the particle size of the sorbent may result in a significant drop in the column. The optimisation of the process should take into account both hydraulic and mass-transfer properties.

- Influence of competitor ions on breakthrough curves

The presence of competitor anions involves a strong decrease in palladium-sorption performance.

Considering the volume at 50% of the exhaustion (BV_0), the competitor effect may be clearly classified following the sequence sulphate > chloride > nitrate.

The sorption mechanism is assumed to be an anion exchange process involving the exchange of the counterion near the protonated amine groups or the electrostatic attraction of metal anions to these protonated amine groups.

7.2 Grafting of Thiourea on Chitosan Backbone for the Study of Platinum and Palladium Sorption

The grafting of sulphur compounds through glutaraldehyde linkage reveals an interesting way to improve sorption properties against platinum group metals. However, the thiourea derivatives of chitosan seems to be more interesting for platinum recovery than for palladium sorption: the enhancement of sorption properties is more significant for Pt, especially in the competitor effect of the ions.

7.3 Gel Beads

The effect of diffusion properties may be diminished using chitosan gel beads. The following results shown the study doing for the platinum, palladium, iridium, osmium, rhodium, ruthenium and rhenium sorption on chitosan gel beads.

7.3.1 Platinum and Palladium Sorption on Crosslinking Chitosan Gel Beads

- Sorption kinetics

The size of the beads and the initial metal concentration were varied. As expected, sorption kinetics for Pd and Pt were faster with small particle size than with the largest beads. However, the difference between small and large beads increased with the initial concentration.

In the case of Pd, the affinity of the sorbent for the metal was so high that even with a low concentration of sorbent (as low as $0.1 \text{ g}\cdot\text{L}^{-1}$, dry weight) the residual concentration tended to 0. With small beads more than 95% of the metal was

sorbed within the first 4 hours, while increasing the initial concentration resulted in a progressive increase in the time required to reach the same level of extraction.

In the case of Pt sorption, small beads obviously reached equilibrium faster than middle and large size beads, but the differences were not so marked as they were with Pd sorption. Whatever the initial concentration the equilibrium was reached earlier than in the case of Pd sorption. It is also noticeable that independently of the initial concentration the residual concentration did not tend to 0: it seems that under selected experimental condition a fraction of metal ions is not adsorbable.

For constant initial Pd and Pt concentrations, the kinetic parameters were larger for small than for large beads, while the parameter related to the external diffusion resistance increased with the size of the beads. It appeared that the variation in the sorption rates was proportional to the variation in the external sorbent surface for the different particle sizes. This indicates that intraparticle mass transfer resistance plays a significant part in the kinetic control of the sorption. According to Helfferich's rules, the weak effect of metal concentration confirms that sorption kinetics is mainly controlled by diffusion within the polymer beads, though the contribution of film mass transfer can not be totally ruled out.

When the experiments were carried out with different concentrations of chitosan, the independence of the sorption kinetics from the change in chitosan concentration and the external sorbent surface confirms that the film mass transfer resistance was not the main controlling step. On the other hand, the results shown that the intraparticle mass transfer resistance was not influenced by density parameter of the beads.

The drying procedure strongly influences palladium and platinum extraction rates. This may be explained by several reasons, including (a) a restriction in the porous volume of the beads; (b) a decrease in the size of the pores, which may control the diffusion of the metal ions; (c) an increase in the crystallinity of the material.

Re-hydration allows the sorption kinetics to be increased, however, under the condition selected in the experiments, it was not sufficient to compensate for the diffusion restriction.

In the case of beads that were pre-treated with saccharose the kinetic curves were improved. The incorporation of saccharose during the drying step allowed the beads to partly maintain their structure: the network was not so shrunk as occurred in absence of the sugar. In the absence of saccharose, new bonds may be formed between the chains of the polymer during the shrinking, which made re-hydration impossible.

- Sorption Isotherms

The maximum sorption capacities for Pd and Pt were ca. 360 mg Pd·g⁻¹ chitosan (266 mg Pd·g⁻¹ sorbent), and 530 mg Pt·g⁻¹ chitosan (392 mg Pt·g⁻¹ sorbent), respectively. On the basis of molar units, the maximum sorption capacities were 3.4 mmols Pd·g⁻¹ chitosan (2.5 mmol Pd·g⁻¹ sorbent), and 2.7 mmol Pt·g⁻¹ chitosan (2.0 mmol Pt·g⁻¹ sorbent). Based on the deacetylation degree of the chitosan used in this study (87%), 1 g of chitosan contained ca; 6 mmol -NH₂, neglecting the fraction of amino groups involved in imine linkages with glutaraldehyde, the maximum molar ratio between Pd/Pt and -NH₂ groups was 0.57 and 0.45, respectively.

For Pd sorption the residual concentration was below 1 mg Pd·L⁻¹, while for Pt the residual concentration was above 1 mg Pt·L⁻¹. This is consistent with the above results on kinetics, which have shown that the equilibrium concentration was usually higher than 1 mg Pt·L⁻¹. Depending on the speciation, which in turn depends on metal concentration and pH, the metal ions can be present in solution in either non- or less-adsorbable ionic forms. As a consequence, at low metal concentration the predominance of non adsorbable species leads to a very low sorption level, while an increase in the residual concentration results in the formation of more adsorbable species, and the sorption capacity increases.

The drying of chitosan beads resulted in similar Pd sorption isotherms, but for Pt sorption capacity was halved. This can be explained by the very long sorption

kinetics, which require a long contact time. Since the contact time for sorption isotherms was limited for 4 days, the equilibrium was not really reached but such a large decrease in sorption capacity may be related to difficult access to internal sorption rates, resulting from uncontrolled drying.

In the case of re-hydrated beads the same behaviour was observed and can be explained by the same reason. On the other hand, in the case of saccharose-treated beads, the sorption isotherms overlapped perfectly with that of the raw beads. Saccharose-treated beads were less sensitive to diffusion limitations and the equilibrium was reached within the contact time selected for sorption isotherms. Drying in presence of saccharose significantly improved sorption performance.

7.3.2 Platinum and Palladium Sorption on PEI-grafted Chitosan Beads

- Sorption kinetics

While in the case of the Pt sorption the same sorption level was achieved that in the case of glutaraldehyde cross-linked beads, in the case of Pd sorption the grafting of PEI significantly increased the sorption rate, especially in the second stage of the process, which is usually controlled by intraparticle diffusion or reaction velocity. This can be explained by the presence of extra sorption sites due to PEI chains inside the porous structure of the beads: increasing the number of sorption sites increases the velocity of metal removal. Moreover, these functions (from PEI chains) may be less sterically hindered than the sorption sites in the porous chitosan structure. The sorption rate for Pd and Pt are of the same order for PEI grafted beads: 6-7 hours were necessary to reach 90 % of the equilibrium sorption for both Pd and Pt, while a large contact time was required to reach the same sorption level in the case of glutaraldehyde cross-linked beads.

- Sorption isotherms

For the Pd uptake, the grafting of PEI led to an increase in sorption capacity from 360 mg Pd·g⁻¹ chitosan to 810 mg Pd·g⁻¹ chitosan. On the basis of the actual total mass of sorbent the increase in sorption capacity was slightly lower: the maximum

sorption capacities was increased from 270 mg Pd·g⁻¹ sorbent to 420 mg Pd·g⁻¹ sorbent.

In the case of Pt uptake, the grafting of PEI also led to an increase in sorption capacity but it was slightly lower than that observed in the case of Pd sorption. The sorption capacity, on the basis of chitosan content was increased from 550 mg Pt·g⁻¹ chitosan to 1000 mg Pt·g⁻¹ chitosan. When calculated on the basis of total sorbent mass, the sorption capacity was only increased from 400 mg Pt·g⁻¹ sorbent to 520 mg Pt·g⁻¹ sorbent.

7.3.3 Platinum and Palladium Sorption on Thiourea-grafted and Hydrogenated Chitosan Beads

- Sorption kinetics

Kinetic curves overlapped for both Pd and Pt sorption with simply cross-linked beads and thiourea derivatives, while in the case of the beads treated with sodium borohydride the sorption was significantly slowed down, especially during the second stage of the sorption process (intraparticle and chemical reaction controls).

- Isotherms

Based on total sorbent mass the grafting of thiourea slightly increased sorption capacity at high residual palladium concentration from 266 mg Pd·g⁻¹ sorbent to 330 mg Pd·g⁻¹ sorbent, while at low initial concentration sorption capacity was decreased. Relative to actual chitosan mass the increase in sorption capacity is more significant (360 mg Pd·g⁻¹ chitosan to 560 mg Pd·g⁻¹ chitosan).

In the case of Pt sorption, thiourea-grafting slightly decreased sorption capacity from 400 mg Pt·g⁻¹ sorbent to 380 mg Pt·g⁻¹ sorbent. On the basis of chitosan content, the sorption capacity was slightly increased from 500 mg Pt·g⁻¹ chitosan to 640 mg Pt·g⁻¹ chitosan.

The hydrogenation procedure, resulting from the reaction of sodium borohydride, did not significantly change the sorption capacity and affinity for both Pd and Pt uptake. The chemical modification is expected to transform imine functions into amine

functions, and to stabilize the sorbent. Primary amines are very efficient in the case of cation complexation (chitin affinity for metal cations is drastically lower than that of chitosan), in the case the hydrogenation of imine functions is expected to increase sorption capacity, however, in the case of anion-exchange process, the effect of the parameter is less significant.

The results obtained for the influence of chloride ions on Pt sorption isotherm chitosan beads confirm previous studies that have shown that an excess of chloride ions leads to high levels of competition for metal sorption. The influence of chloride ions may be also related to a change in the speciation of metal ions.

In the study of the influence of chloride ions on Pd sorption using thiourea derivatives of chitosan results shown that while increasing chloride concentration to 0.3 M only reduced the sorption capacity by 30%, but for glutaraldehyde cross-linked beads the sorption capacity was reduced by a factor of more than 3. This confirms the interest of thiourea derivatives for the sorption of palladium in complex media.

7.4.4 Osmium, Iridium, Rhodium, Ruthenium and Rhenium Sorption on Chitosan Beads

- Isotherms

For the osmium, under selected experimental conditions, maximum sorption capacity on glutaraldehyde crosslinked chitosan tended to 3 mmol Os·g⁻¹ chitosan (550 mg Os·g⁻¹). Osmium sorption can be considered very favourable. On the opposite hand, iridium sorption capacity hardly exceeded 1 mmol Ir·g⁻¹ chitosan (220 mg Ir·g⁻¹).

- Kinetics

The kinetics for osmium and iridium were carried out using different sorbents: glutaraldehyde cross-linked chitosan beads; PEI-grafted chitosan beads and thiourea-grafted chitosan beads. The differences between the different sorbents

were not very marked with iridium, while in the case of osmium the changes were significant. The sorption kinetics may be ranked for the different sorbents in the following order: PEI-grafted beads > glutaraldehyde cross-linked beads > thiourea grafted beads.

The comparison of sorption kinetics for palladium, platinum, osmium and iridium shown comparable sorption rates: during the first hour of contact the curves were perfectly overlapped, in the second stage it appeared that osmium and iridium sorption were slightly faster than those of platinum and palladium.

Experiments have also been performed on rhodium, rhenium, ruthenium with diluted standard solutions, under experimental conditions similar to those used for osmium and iridium solutions, and under different chloride concentrations (from 0.01 M to 0.3 M), but in any case the sorption was below 10 mg Me·g⁻¹.

7.4 Desorption

- Palladium desorption from loaded cross-linked chitosan beads

The use of the HCl concentrated solutions (2, 5 and 11 M) has shown that mixing 0.5 g of exhausted sorbent (containing ca. 200 mg Pd·g⁻¹) with 4 ml of eluent for 16 h in agitated systems allows after two desorption steps to achieve a desorption yield of 71, 79 and 85 % respectively. When the eluent was a concentrated solution of NH₃ the level of desorption was 40 %.

- Platinum, Palladium, Iridium and Osmium desorption from loaded cross-linked chitosan beads

The desorption was performed on loaded cross-linked chitosan beads collected from the sorption kinetics.

The study of platinum and palladium desorption has shown that mixing 0.1 g of loaded sorbent (containing between 100 and 300 mg of Pt or Pd·g⁻¹) with 4 ml of concentrated HCl for 48 h in agitated systems allows after two desorption steps to achieve a desorption yield of 60 % for both metals. When ammoniac solution (2 M) was used the desorption yield was 0.7 % for platinum desorption and 45 % for palladium desorption.

The desorption efficiency for Osmium and Iridium using hydrochloric acid solution at different concentrations (0.2 M, 0.4 M, 0.6 M, 1 M, 5 M and 11 M) has shown that while a molar solution of hydrochloric acid is sufficient to reach a desorption efficiency greater than 95 % for iridium in two steps, in the case of osmium, even with a 11 M solution the extraction efficiency did not exceed 48 % after two desorption steps. In the other hand, with a 11 M HCl solution iridium is completely recovered from the sorbent after two desorption steps.