OSMIUM AND IRIDIUM SORPTION ON CHITOSAN DERIVATIVES

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ABSTRACT

Glutaraldehyde cross-linked chitosan exhibits a great affinity for osmium at pH 2: the sorption capacity can reach up to 3 mmol Os g^{-1} and the initial slope of the isotherm curve confirms that strong interactions exist between the biopolymer and osmium ions. In the case of iridium sorption, the affinity and the maximum sorption capacities are considerably lower than the levels we reached with osmium. The modification of the sorbent by grafting new amine groups (poly(ethyleneimine)) allows the sorption capacities to be increased while the grafting of thiourea did not significantly change sorption capacities. Sorption kinetics are fast but in the case of iridium after 12 hours of contact a significant release of metal is observed, it confirms that the interactions of the polymer with iridium are significantly weaker than those established between chitosan and osmium ions. Rhodium, rhenium, ruthenium are not significantly adsorbed indicating that a kind of sorption selectivity may be expected in the uptake of osmium, iridium but also platinum and palladium against rhodium, ruthenium and rhenium.

INTRODUCTION

The growing demand on platinum group metals (PGM) due to their exponential use in catalysts production has stimulated research on the development of separation and recovery processes focused on the treatment of low concentration acid solutions resulting from the exploitation of low grade minerals or the recycling of waste materials (1). Though synthetic ion exchange and chelating resins have been developed for the recovery of PGM from medium to high concentration solutions, (2-5) there is still a need for low cost sorbents aimed at the treatment of dilute solutions. Biosorption has recently received a great deal of attention due to the low cost of the materials used in these applications and for the environmental friendly impact of the treatment of exhausted sorbents. Several types of biomass have been tested for the recovery of precious metals, including fungal biomass (6), algal biomass but also polymers of biological origin (7-16) . Chitosan (hetero polymer constituted by glucosamine and a fraction of acetylglucosamine residues) is a well-known biopolymer characterized by its high sorption properties due to its high nitrogen content. Amine groups on the polymer are responsible for the sorption of metal cations through chelation mechanisms in near neutral solutions (14-17). Metal anions can be also removed through a different mechanism involving ion exchange and electrostatic interactions on protonated amine functions (8,10,13,18). Indeed, chitosan has a unique property among biopolymers to be protonated in acidic solutions. This property has been used to develop metal anions sorption processes including molybdate and vanadate anions (18-19), but also metal cations chelated by ligands to reach in acidic solutions global anionic charges (20). PGM in solution are frequently characterized, under selected experimental conditions (pH and chloride concentration), by the predominance of anionic chloro-complexes, which renders very efficient their sorption on chitosan (19). The most of the studies dedicated to PGM have been aimed at the recovery of platinum, palladium and rhodium (,21). The literature is substantially less abundant on the recovery of other PGM such as ruthenium, rhenium, osmium and iridium (12).

Chitosan is soluble in the most of the mineral and organic acids, sulfuric acid excepted. For the treatment of hydrochloric acid solutions containing PGM a preliminary cross-linking treatment is required. Glutaraldehyde can be used to improve chitosan resistance in acidic solutions (22). The reaction of glutaraldehyde with chitosan proceeds through a Schiff's base reaction between aldehyde groups of the cross-linker and amine functions of the biopolymer. This reaction produces an imine linkage that can be easily reduced by reaction with sodium borohydride to re-hydrogenate the double linkage.

On the other hand, chitosan is characterized by a low porosity that can reduce its efficiency for the sorption of metal ions, especially under respect of kinetics. To reduce this resistance to mass transfer (and more specifically to intraparticle diffusion) chitosan gel beads have been developed (18,21-22). This treatment allows the structure of the polymer to be expanded and its crystallinity to be reduced, favoring sorption rate. However, these treatments results in either a decrease of the number of available sorption sites (cross-linking treatment) (22), or the volumetric sorption capacity (the percentage of water in the gel beads can reach 95 %). Previous investigations have shown that the uncontrolled drying of chitosan gel beads reduces the beneficial effect of gel bead formation (23). For this reason, some processes have been developed to increase the volumetric density of sorption sites, for example by grafting supplementary amine groups (24-26). Poly(ethyleneimine) (PEI) reveals a very interesting substitute (24-25). Beads were impregnated with a solution of PEI before being mixed with glutaraldehyde that induces the linkage of PEI to chitosan backbone. It allows the volumetric density of chitosan to be significantly increased (23). Thiourea has been used for the grafting on chitosan in order to reduce the influence of competitor ions (such as chloride ions) on platinum sorption (27). The grafting of thiourea is expected to bring chelating facilities to the ion exchange resin and then to decrease the competitor effect of the matrix (26-27). This derivative of chitosan was obtained by contact of thiourea with glutaraldehyde prior to the contact

with chitosan. Schiff's base reactions allow on each side of glutaraldehyde the formation of imine linkage with alternatively thiourea and amine groups of chitosan.

The present work, based on previous finding 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. Previous investigations have shown that the optimum pH with glutaraldehyde cross-linked chitosan was close to pH 2: below pH 2, competitor anions compete for protonated amine functions with PGM anions, while above pH 3 the speciation of metal ions is less favorable to interactions with chitosan. Indeed, the most highly charged species are required to strongly interact with the sorbent. Sorption isotherms and uptake kinetics have been studied. Complementary experiments where performed on ruthenium, rhenium and rhodium under comparable experimental conditions. The sorption levels reached for the later metals were almost negligible an attempt to explain this low efficiency will be proposed.

MATERIAL AND METHODS

Material

Chitosan was supplied by Aber Technologie (France) as a flaked material, with a deacetylation percentage ca. 87 %, defined by FTIR spectrometry. The mean molecular weight was measured at 125,000 g mol^{-1}, using a size exclusion chromatography (SEC) method coupled with a differential refractometer and a multi-angle light scattering photometer. Moisture content of chitosan was determined at ca. 10 %.

Metal solutions were prepared by dilution from AAS standards supplied by Fluka (Switzerland): These standards were obtained from dilution of $(NH_4)_2(OsCl_6)$, $RhCl_3$ and $RuCl_3$ in HCl (1 M), while rhenium standard was prepared from dissolution of Re in HNO_3 (1 M). In order to check the influence of the state of oxidation on iridium sorption, 2 different salts have been tested: tri-valent

form: $IrCl_3$ from an AAS standard (Fluka, Switzerland), and tetra-valent form: $H_2OsCl_6,6H_2O$ in HCl (1 M). Other reagents (Glutaraldehyde (50 % w/w in water), PEI, thiourea, NaOH, HCl, acetic acid) were purchased from Fluka AG (Switzerland).

Chitosan Gel Bead Preparation

The procedure for the fabrication of gel beads was previously described (18). It consisted in a two-step procedure: chitosan flakes were ground and dissolved in acetic acid solution (a small of excess of acetic acid was used in order to protonate the totality of amine groups and decrease the viscosity of the solution). The viscous solution was then pumped and distributed dropwise through a thin nozzle (diameter 0.6 mm) in an alkaline solution (NaOH 2.5 M). In order to control the size of particle beads it is possible to inject an airflow, at a controlled flow rate, in an appropriate system (constituted by concentric tube around the nozzle to drive air flow at its basis). The airflow makes the chitosan drops fall down before they fall by their own weight. Chitosan drops coagulated in the alkaline solution and gave perfect spherical beads, which diameter was measured. After 24 hours of contact with the alkaline solution, beads were removed and rinsed several times with demineralized water till the pH did not vary.

Preparation of glutaraldehyde cross-linked chitosan gel beads

The cross-linking was performed by mixing for 16 hours the appropriate amount of chitosan beads (calculated using the dry weight) with an aqueous solution of glutaraldehyde at an equimolar concentration (compared to the number of free amine groups in chitosan). The beads were then rinsed several times with water to remove un-reacted glutaraldehyde. At each stage of the fabrication, samples (100 or 250 beads, depending on the size of the beads) were collected and dried at 105 °C overnight, to compare water content and measure the weight of the bead for each fabrication procedure. The mean diameter of the beads was also determined on the final products.

These determinations were performed in triplicate. Main characteristics of these beads are summarized in Table 1.

Preparation of thiourea grafted chitosan gel beads

Thiourea derivative of chitosan was produced using a procedure similar to the method previously used for the synthesis of thiourea derivatives of chitosan flakes (27). The 3:2:1 thiourea derivative was prepared by mixing 14.4 mL of glutaraldehyde (50 % w/w, 8.5 mmol) with 9.6 g of thiourea (12 mmol) and 96 mL of demineralized water for 3 hours. Chitosan wet beads were then added (4.8 g, dry weight, 29 mmol $-NH_2$) and agitated for 16 hours. The modified beads were then removed from the solution, rinsed several times and stored in water. Samples of these preparations were submitted to the hydrogenation procedure to prepare 3:2:1 BH. The hydrogenation of imine functions was performed by dissolving 1 g of sodium borohydride in 100 mL of demineralized water. 10 g of wet beads were then added to the solution and the slurry was agitated for 6 hours. The beads were then removed from the solution and rinsed several times with demineralized water.

Preparation of PEI-grafted chitosan gel beads

PEI-grafted beads (PEI GA) were prepared according to the following procedure. 5 g of PEI (M_w: 600,000-1000,000) were dissolved in 100 mL dimethylacetamide, 5 g (dry weight) of wet chitosan beads were then added under agitation for 16 hours. The impregnated beads were then separated from the solution and rinsed with 30 mL of dimethylacetamide. 3 g of glutaraldehyde (50 % w/w in water) were dissolved in dimethylacetamide and then mixed with impregnated beads for 6 hours. Finally, the beads were rinsed several times with water.

The characteristics of the beads are given in Tables 1 and 2.

Sorption Procedure

The pH of the solutions was controlled at pH 2 with hydrochloric acid. The pH of the solutions did not vary significantly during the sorption (by less than 0.1 unit). For sorption isotherms, known

increasing numbers of beads were brought into contact with a fixed volume of solution at a known concentration (ca. 23 mg Metal L^{-1}) for four days. Filtrates were collected and analyzed using an inductively coupled plasma atomic emission spectrometer, ICP-AES JY 2000 (Jobin-Yvon, France). The metal content in the beads was calculated using the mass balance equation, and the sorption capacity was determined in function of the actual mass of chitosan in the sample: unless specified, the increase in weight resulting from glutaraldehyde cross-linking was not taken into account. To take into account the total mass of the sorbent, the sorption capacity (on chitosan weight basis) should be multiplied by 0.73 (mg Metal g^{-1} sorbent). For the study of sorption kinetics a standard procedure was applied (13). One liter of solution at pH 2 was mixed with 229 beads corresponding to a constant weight of chitosan, ca. 100 mg, (independently of the increase in weight resulting from the modification of the biopolymer). The initial metal concentration was 10 mg Metal L^{-1}.

Desorption Procedure

The study of osmium and iridium desorption was performed on loaded cross-linked chitosan beads collected from the sorption kinetics at 10 mg Metal L^{-1}. 10 beads were mixed with 4 mL of hydrochloric acid solutions at 0.2 M, 0.4 M, 0.6 M, 1 M, 5 M and 11 M for 16 hours. The initial contents of osmium and iridium in these samples of beads were 0.81 mg and 0.60 mg, respectively. Desorption was performed in two steps and the metal concentration was systematically determined in the acid solution, the mass balance equation was used to get the desorption efficiency at each step.

RESULTS AND DISCUSSION

Sorption isotherms

Figure 1 presents the sorption isotherms for osmium and iridium at pH 2 using glutaraldehyde cross-linked chitosan. Experimental data have been modeled using both the Langmuir and the

Freundlich equations, but the figure only presents the equation that fits better experimental data: the Langmuir equation for osmium recovery and the Freundlich equation for iridium uptake.

Osmium – Langmuir equation:

$$q = \frac{q_m \, b \, C_{eq}}{1 + b \, C_{eq}} = \frac{3.26 * 0.105 \; C_{eq}}{1 + 0.105 \, C_{eq}}$$

where q and q_m (mmol Os g^{-1}) represents the concentration of the metal ion the solid in equilibrium with the concentration in the liquid phase Ceq (μmol Os L^{-1}) and the maximum sorption capacity, respectively. The coefficient b (L μmol^{-1}) is the affinity coefficient.

Iridium – Freundlich equation

$$q = k \, C_{eq}^{1/n} = 0.0674 \, C_{eq}^{1/1.619}$$

where k and n are the parameters of the Freundlich equation

Under selected experimental conditions, osmium was quite well adsorbed on glutaraldehyde cross-linked chitosan: maximum sorption capacity tended to 3 mmol Os g^{-1} (550 mg Os g^{-1}); while the initial slope of the curve was very steep: this initial slope is representative of the affinity of the sorbent for the solute. Osmium sorption can be considered very favorable (almost irreversible). On the opposite hand, iridium sorption capacity hardly exceeded 1 mmol Ir g^{-1} (220 mg Ir g^{-1}) and the initial slope is significantly lower than that obtained in the case of osmium. Moreover, it appeared that the sorption capacity was strongly decreasing even with residual concentrations as high as a 2-3 mg Ir L^{-1}. Similar shapes of isotherms where obtained in the sorption of other metal anions such as molybdate and vanadate ions (28-29) depending on the pH; or palladium at pH 2 depending on the concentration of chloride anions (19). Metal anions are adsorbed through electrostatic attraction mechanisms involving the exchange of the counter ions fixed on protonated amine sites. Depending on the experimental conditions (pH, chloride concentration, total metal concentration), metal ion speciation may change and affect the charge of metal species in solution, and consequently their ability to be sorbed on the sorbent.

The maximum sorption capacity for osmium uptake was 3 mmol Os g^{-1} chitosan. In the case of raw chitosan 1 g of chitosan corresponds to 6 mmol of $-NH_2$ groups, on the basis of a deacetylation degree of 87 %. After glutaraldehyde a significant fraction of these amine groups has been reacted and did not remain free. This decrease in the number of free amine groups represents an important parameter in the case of metal ion chelation. It seems that the degree of cross-linking is not so important in the case of ion exchange processes (19). In a first approach, we can approximate the number of sorption sites to amine content in the sorbent: 6 mmol g^{-1} chitosan. Comparing the maximum sorption capacity to the "concentration" of sorption sites, we can assume the stoichiometry between amine groups and Os to be 2:1. On the opposite hand, in the case or iridium, the sorption isotherm curve did not exhibit a clear asymptotic curve and the maximum sorption capacity could be greater than 1.2 mmol g^{-1}. It is thus difficult to discuss the stoichiometric ratio between iridium anions and amine group. However, taking into account the large differences in the experimental data for each system it seems that other mechanisms are involved in the control of iridium sorption: effect of metal speciation, competitor effect, accessibility to internal sites…

Figure 2 shows the distribution coefficient (defined by the ratio of equilibrium concentration in the solid to the residual concentration in the solution, L kg^{-1}) in function of the residual concentration (Scatchard plot) for the uptake of both osmium and iridium. For both Ir and Os sorption, the distribution coefficient decreased at increasing the residual metal concentration. However the order of magnitude is significantly higher for osmium than for iridium. The higher affinity of osmium (than iridium) for chitosan is confirmed and may be explained by several causes as cited above.

It should be noted that the sorption capacities have been given in function of the actual mass of chitosan contained in the beads. To get the actual sorption capacity, relative to the mass of sorbent used, it is necessary to multiply the data by 0.73: this coefficient includes the increase in the weight of chitosan beads resulting from glutaraldehyde reaction.

Influence of chemical modification of chitosan on osmium and iridium sorption kinetics

Figures 3 and 4 present the sorption kinetics for osmium and iridium, respectively, using glutaraldehyde cross-linked chitosan beads, PEI-grafted chitosan beads and thiourea-grafted chitosan beads. The concentration of the sorbent was quite low, about 100 mg chitosan L^{-1} (229 beads), which corresponds to137 mg GA-beads L^{-1}, .192 mg PEI-grafted beads L^{-1}, and 169 mg TU-grafted chitosan beads L^{-1}. With higher sorbent dosage faster kinetics would be expected but the objective of this part of the work was to evaluate the relative efficiency of the sorbents and this comparison is only possible if the residual concentration does strictly tend to 0. Initial sorption rates (contact time lower than 60 minutes) seems to be hardly influenced by the kind of sorbent and by the metal. Usually the initial step is mainly controlled by external diffusion. This result was expected since the superficial area of the sorbents is almost independent of the modification of the sorbent and that the number of beads used for the kinetic experiments was independent of the experimental series. Slight differences appeared in the second stage of the process: the late stage is usually controlled by intraparticle diffusion. It is possible to suggest that the grafting of new functional groups change the diffusion properties of the sorbent, alternatively, the grafting of new functional groups involves an increase in the density of sorption sites, which makes easier the interaction of metal anions with the sorbent. The differences between the different sorbents were not very marked with iridium, while in the case of osmium the changes were significant. The sorbents may be ranked in the following order: PEI-grafted beads > glutaraldehyde cross-linked beads > thiourea grafted beads. In the case of osmium sorption on PEI grafted beads, the residual concentration in the solution tended to 0 after 6-8 hours, it is thus difficult to accurately compare the series and the difference between PEI-grafted beads and the other sorbents is suspected to be greater. The most surprising results were obtained with the thiourea derivative, since the grafting reduced the sorption velocity, though sulfur sorption sites have been added. It is also interesting to observe that for both osmium and iridium a slight increase in the concentration of the metal was

observed in the aqueous phase after one day of contact with glutaraldehyde cross-linked chitosan gel beads. Both thiourea and PEI derivatives of chitosan appeared to be more stable than the reference material (glutaraldehyde cross-linked chitosan gel beads).

Figure 5 compares the sorption kinetics for palladium, platinum, osmium and iridium under comparable experimental conditions with glutaraldehyde cross-linked chitosan. The sorption rates were comparable: 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.

Influence of the oxidation state on iridium sorption kinetics and isotherms

Figure 6 compares the sorption kinetics and isotherms for iridium under the oxidation states +III and + IV using glutaraldehyde cross-linked chitosan beads. Sorption kinetic curves are perfectly overlapped: the oxidation state of iridium does not influence the diffusion properties though the metal is not under the same ionic form. After reaching a minimum at 12 hours of contact time, the residual concentration increased again at increasing the time of contact. Small differences were observed in the isotherms but they are not representative of great differences in the sorption performance. It seems that the initial slope was as low as that obtained with Ir(III): the affinity of the sorbent for the metal was not changed by changing its oxidation state. On the other hand the maximum sorption capacity was slightly higher with the most oxidized salt (Ir(IV)), however the experiments corresponding to high residual concentrations have been performed with a low number of beads and a small difference in the weight of sorbent (due to some heterogeneities in the preparation of the beads and to the high content of water in these beads that makes sometimes the determination of the dry masses less accurate) may cause significant fluctuations in the sorption capacities.

Influence of initial concentration on osmium and iridium sorption kinetics on chitosan

Figure 7 presents the sorption kinetics at pH 2 for different initial osmium and iridium concentrations using glutaraldehyde cross-linked chitosan. Whatever the initial metal concentration, after 12 hours of contact iridium concentration increases; and it seems that the "release" of iridium increases with increasing the initial metal concentration. In the case of osmium, the release of the metal is less pronounced. This metal release can be a source of discrepancies in the determination of sorption isotherms since the sorption capacities will depend on the sampling time.

The weak stability of iridium on the sorbent at large contact time suggests that a kind of selectivity may be expected against other PGM: platinum, palladium and to a lesser extent osmium. This weak stability could be attributed to a reduction of iridium on the sorbent. Previous studies have shown that the cross-linked chitosan beads are able to reduce some metal ions due to the presence of reducing ends on the polymer and to the presence of free aldehyde functions (some aldehyde functions from the dialdehyde may remain free and non involved in the formation of the cross-links. The reducing efficiency depends on the metal and more specifically its redox potential: chromate ions are more efficiently reduced than molybdate ions while cupric ions are not influenced by the sorption on cross-linked chitosan beads.

Osmium and iridium desorption from loaded glutaraldehyde cross-linked chitosan beads.

Figure 8 shows the desorption efficiency for osmium and iridium using hydrochloric acid solutions at different conenrations. Obviously iridium was more efficiently desorbed from the sorbent than osmium. 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. This result can be correlated to the strength of the interactions between the sorbent and the metals. Indeed, Figures 1 and 2 have shown that the sorbent has a greater affinity for osmium than for iridium: the initial slope of the isotherm and the distribution ratios clearly establish that osmium is strongly bound to the polymer. This strength may explain that higher concentrations of acid are required, and that the complete

desorption cannot be achieved in the case of osmium. With a 11 M HCl solution, iridium is completely recovered from the sorbent after 2 desorption steps. During the first desorption step at the highest HCl concentration, the metal concentration was 140 mg Ir L^{-1} (only 87 mg Os L^{-1}, in the case of osmium despite a greater metal concentration in the beads).

Ruthenium, rhenium and rhodium interactions with chitosan derivatives.

Experiments have also been performed on rhodium with diluted standard solutions, under experimental conditions similar to those used for osmium and iridium solutions (not shown). The sorption levels were so low that the sorption capacities remained below 10 mg Me g^{-1}. These results are consistent with those presented by Inoue et al. for the recovery of rhodium using chitosan derivatives (10). Alam et al. enhanced rhodium sorption on modified chitosan using an original chitosan derivative produced by the template cross-linking method using Fe(III) as a template ion (21). However, they showed that the improvement of sorption performance was tributary to the presence of thin. They attributed the positive effect of tin on rhodium sorption by the reduction of trivalent rhodium species (RhCl$_6^{3-}$ and RhCl$_5$(H$_2$O)$^{2-}$) to monovalent species (Sn(II) being simultaneously oxidized to Sn(IV)), and their subsequent complexation with tin chloride anions to form Rh(SnCl$_3$)$_5^{4-}$. These complexes bear higher anionic charge and they are more labile than other kinetically inert chloride complexes of rhodium due to the strong π acid nature of SnCl$_3^-$. They also observed that the selectivity order against platinum and copper was reversed after oxime grafting and stannous chloride addition.

Rhenium and ruthenium sorption was also studied through kinetic experiments under similar experimental conditions, and as in the case of rhodium, sorption remained negligible. No literature has been found on the sorption of these metals on chitosan or chitosan derivatives. The speciation of these metal ions may be considered as a limiting parameter as well as the weak affinity of the amine groups of chitosan. The grafting of other functional groups, ca. different nitrogen-bearing groups or other chelating functions could enhance sorption properties.

Sorption experiments have been performed with these metal ions with addition of chloride anions (up to a concentration 0.3 M) in order to verify if the addition of chloride, that may result in a change in the distribution of the metal species, could enhance sorption capacities. Actually a very small increase in the sorption capacities was observed with an addition of chloride anions of 0.15-0.2 M, but in any case the sorption was below 10 mg Me g^{-1}.

CONCLUSION

These preliminary informations have confirmed that iridium and osmium can be readily sorbed on chitosan derivatives including glutaraldehyde cross-linked, PEI-grafted and thiourea-grafted chitosan gel beads. Experiments were performed at pH 2 using HCl for controlling the pH. The sorption capacity for osmium (3 mmol Os g^{-1} chitosan) was comparable to those obtained with platinum and palladium under similar experimental conditions, but significantly higher than that of iridium (1.1 mmol Ir g^{-1}), while ruthenium, rhodium and rhenium were not adsorbed under selected experimental conditions. The decrease in the sorption capacity may be correlated to the speciation of these metal anions in solution: the lack of chloride may displace the complexation equilibrium to the formation of less adsorbable species.

Sorption kinetics for osmium and iridium were comparable to those of platinum and palladium: under selected experimental conditions, more than 90 % of the total sorption was achieved within the first six hours. Compared to other systems involving polynuclear species (vanadate, molybdate) it is a fast sorption phenomenon. The time required to reach the equilibrium would be decreased at increasing the amount of sorbent but the objective of the kinetic section of this work was to check the influence of intraparticle diffusion. This diffusion mechanism is usually predominant in the later stage of the sorption process and the residual concentration should not tend to zero in order to be able to compare intraparticle diffusion rates.

Desorption was very efficient for iridium using hydrochloric acid due to the 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.

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Table 1: Characteristics of PEI-chitosan gel beads [a].

Sample	DWC	PW	GW	CLR	D	S_{exc}	Characteristics
B	59.3	-	15.6	0.60	3.36 (±0.12)	8.1	Glutar. Cross-linked beads
PEI	62.5	18.8	-	-	n.d.		PEI-impregnated beads
PEI GA	83.8	18.8	21.3	0.81	3.50 (±0.15)	8.8	PEI-grafted beads (with GA)

DWC: Dry weight of cross-linked beads (with PEI or without PEI) (mg)

PW: PEI weight (mg)

GW: Glutaraldehyde weight (mg)

CLR: Cross-linking ratio (mol glutaraldehyde / mol $-NH_2$)

D: Diameter of beads (mm).

S_{exc}: External sorbent surface for kinetic experiment (m^{-1}).

(a): For 100 beads.

n.d.: not determined.

Table 2: Characteristics of thiourea-chitosan gel beads and beads treated with sodium borohydride[a].

Sample	DWC	G+T	D	S_{exc}	Characteristics
B	59.3	15.6	3.36 (±0.12)	8.1	Glutaraldehyde Cross-linked beads
3:2:1 BH	73.85	30.15	3.47 (±0.12)	8.7	Thiourea grafted beads after hydrogenation[c]

G+T: Weight of glutaraldehyde and thiourea (mg).

Other symbols are described in Table 1.

(a): For 100 beads.

(b): low thiourea grafting

(c): high thiourea grafting.

Figure 1: Osmium and Iridium sorption isotherms at pH 2 (symbols: experimental data; lines: modeling using either the Langmuir equation (Osmium) or the Freundlich equation (Iridium)).

Figure 2: Distribution coefficient for Os and Ir sorption on glutaraldehyde cross-linked chitosan gel beads at pH 2.
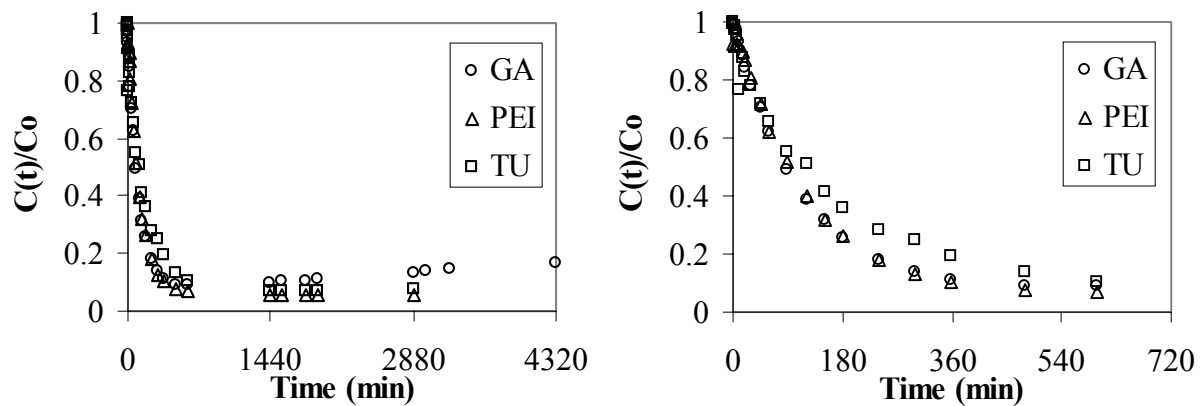
Figure 3: Osmium sorption kinetics at pH 2, using glutaraldehyde cross-linked chitosan beads (GA),

PEI-grafted chitosan beads (PEI), Thiourea-grafted hydrogenated chitosan beads
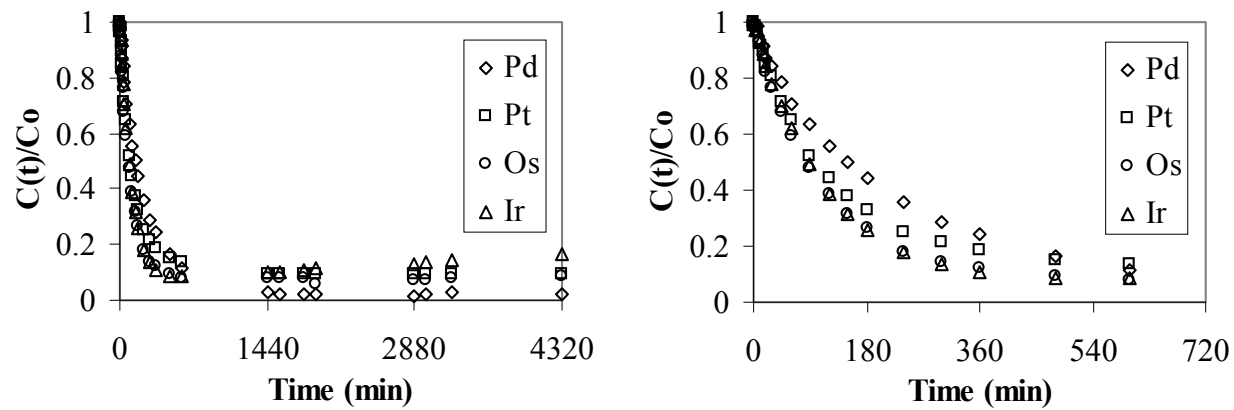
(TU).(experimental conditions).

Figure 4: Iridium sorption kinetics at pH 2, using glutaraldehyde cross-linked chitosan beads (GA),

PEI-grafted chitosan beads (PEI), Thiourea-grafted hydrogenated chitosan beads

(TU).(experimental conditions).

Figure 5: Comparison of sorption kinetics on glutaraldehyde cross-linked chitosan gel beads for Pt, Pd, Os and Ir at pH 2.
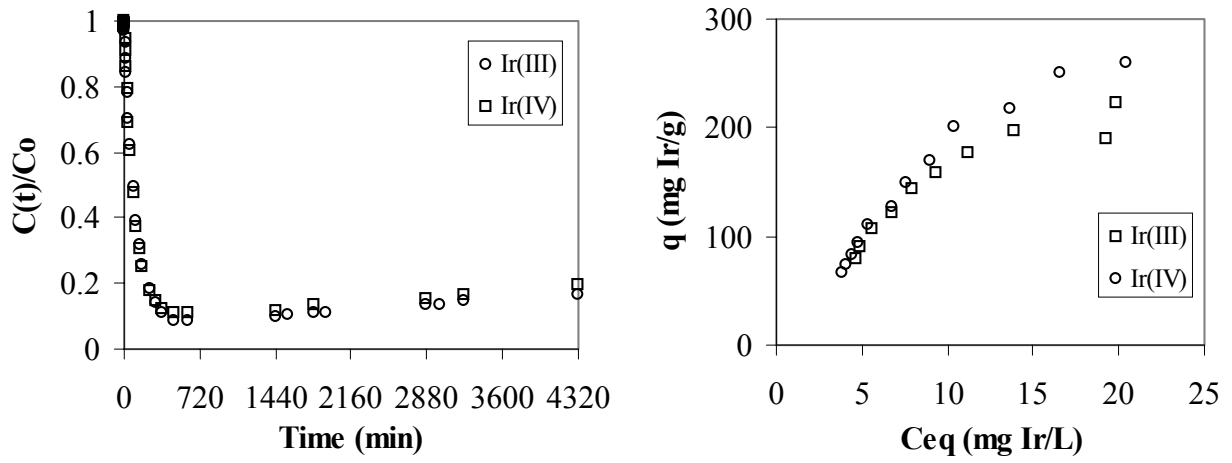
Figure 6: Influence of the oxidation state of iridium on its sorption properties (kinetics: left panel; isotherms: right panel) at pH 2.
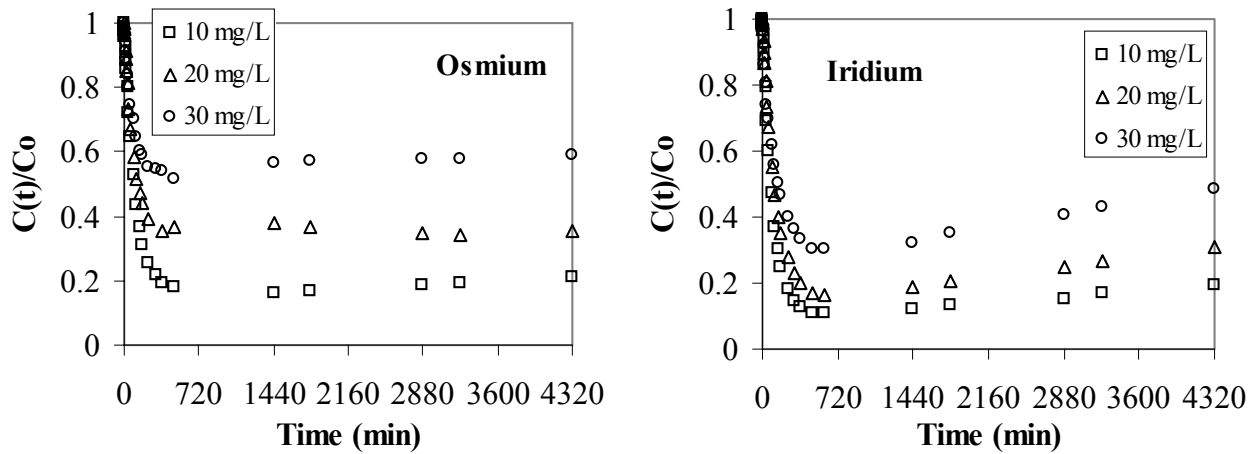
Figure 7: Influence of metal concentration on osmium and iridium sorption on cross-linked chitosan at pH 2.
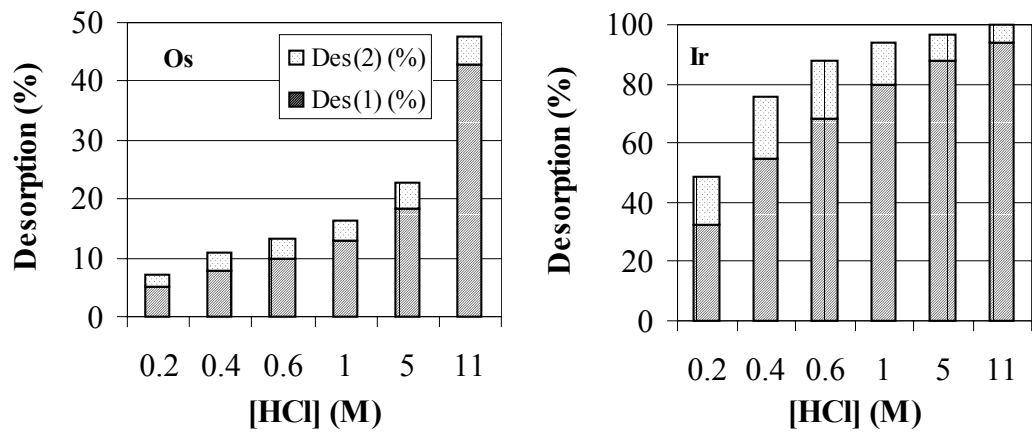
Figure 8: Influence of hydrochloric acid concentration on the desorption of osmium and iridium

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