

Synthesis and Characterization of a Thiourea Derivative of Chitosan for Platinum Recovery

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ABSTRACT: Chitosan is effective at removing platinum from dilute solutions, but sorption properties are significantly affected by the presence of competitor anions, such as chloride and, especially, sulfate anions. Sorption capacities in such complex solutions are enhanced by grafting thiourea through glutaraldehyde linkage. The influence of the amount of glutaraldehyde and thiourea in the impregnation bath was investigated and optimized with special attention to the composition of the solution and the type of acid used for pH control. This modification involves a change in the sorption mechanism: While glutaraldehyde-crosslinked chitosan adsorbs platinum through an ion-exchange mechanism, the thiourea derivative of chitosan acts as a chelating resin, less sensitive to ionic strength and competitor anions. Platinum sorption is also less sensitive to pH, and increasing the sulfate anion concentration has a limited effect on platinum sorption in comparison with the crosslinked sorbent. Thiourea grafting seems to increase sorption kinetics, especially in solutions controlled with sulfuric acid. SEM-EDAX techniques as well as FTIR analyses were used to characterize chemical modifications of the sorbent. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 119–134, 2000

Key words: chitosan; thiourea; glutaraldehyde; platinum; sorption isotherms; sorption kinetics; competitor anion effect; pH effect; FTIR; SEM-EDAX

INTRODUCTION

Chitosan, a natural heteropolymer constituted of glucosamine and acetylglucosamine monomers, is efficient at removing metal ions from solutions. Sorption of metal ions proceeds from several mechanisms including ion exchange, owing to the cationic behavior of this polymer in acid media, and complexation, which takes advantage of the high nitrogen content of the sorbent. The free electronic doublet of nitrogen involves the effi-

cient binding of metal cations to amine groups. These properties have been used to recover several metal ions such as copper,¹ mercury,² uranium,³ lead and chromium,⁴ molybdenum and vanadium,⁵ as well as noble metals: platinum and palladium.^{6,7}

Chitosan is a low porous material allowing for diffusion control of the sorption kinetics and the equilibrium. Several parameters control these diffusion limitations, especially the crystallinity of the sorbent.^{8,9} Physical modifications may increase the sorption properties: gel formation decreases the crystallinity of the sorbent and involves an expansion of the porous network.^{9–12} Chemical modifications also offer a wide spec-

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trum of tools to enhance the sorption properties of chitosan for metals. They may increase the chemical stability of the sorbent in acid media and, especially, decrease the solubility in most mineral and organic acids. They also increase its resistance to biochemical and microbiological degradation.¹³ Moreover, chemical grafting of new functional sites improves extraction selectivity as well as maximum sorption capacities and pH sensitivity.

Several options have been investigated such as the single grafting of new functional sites, while more sophisticated processes involve the formation of cluster sites.^{6,14,15} These techniques include the sorption of the targeted metal followed by a crosslinking step and a further metal desorption allowing the specific metal ion volume to be protected. This technique involves a specific topographic recognizing efficiency for the sorbent. The selectivity and the recognizing efficiency is conditioned by the analogy between the targeted metal and the metal used for the impregnation/crosslinking step. Using the targeted metal is expensive for precious metals, while substituting common heavy metals in replacement decreases the selectivity of the sorbent. Thus, the grafting method has been selected for further study.

While in previous studies the grafting of organic acids on a chitosan backbone was discussed for uranium(VI)^{16,17} and vanadium(IV) sorption,¹⁸ for precious metals, this kind of substitution is not effective at removing metals such as platinum or palladium. Platinum sorption occurs in acid media; it is necessary to reinforce chitosan stability by a crosslinking treatment. Glutaraldehyde is one of the crosslinks which has been used for metal ion recovery with chitosan in acid media.^{7,19,20} For platinum sorption on glutaraldehyde-crosslinked chitosan (GC), the sorption efficiency is controlled by the composition of the solution and, especially, by the presence of competitor ions (chloride, nitrate) due to ion-exchange competition mechanisms. For treatment of industrial effluents, the selectivity of the sorbent might be increased. To address this objective, it is necessary to modify the sorption mechanism and the properties of the sorbent by grafting new functional groups. This substitution is assumed to transform the ion-exchange resin into a chelating resin.

The introduction of donor P atoms has been extensively studied for the last 10 years for selective ion-exchange resins and extractant-impregnated resins, while the grafting of donor S groups

is less documented. Argüelles-Monal and Peniche-Covas investigated the grafting of mercapto groups on chitosan for mercury removal.²¹ More recently, Binman et al. studied the fabrication of sulfur-chlorinated compounds derived from jojoba wax bound to polystyrene beads for mercury and chromate recovery.²² They showed that the grafting of these sulfur derivatives is characterized by an enhanced selectivity and efficiency for metal recovery from brines and complex solutions.

This study was dedicated to the optimization of the synthesis of a new chitosan derivative, on which sulfur groups have been grafted through the binding on a chitosan backbone of an intermediary product resulting from the chemical reaction of thiourea and glutaraldehyde. Glutaraldehyde is a dialdehyde which is able to react with one or two groups of the chitosan polymer, thus strengthening the polymer network in acid media and preventing its dissolution in such aggressive media. The bifunctional reagent can also interact with amine groups on thiourea and amine groups on chitosan. In this case, glutaraldehyde acts as a linking spacer between a chitosan backbone and sulfur-containing compounds. Preliminary studies showed that the grafting of new functional sulfur groups on a chitosan backbone through glutaraldehyde linkage is enhanced when glutaraldehyde and thiourea were previously reacted together and then added to chitosan rather than carrying out the thiourea reaction on GC. In this study, the production of the thiourea derivative sorbent was studied in order to optimize sorption properties for platinum recovery in several types of matrices including chloride and sulfate solutions. The influence of the components of the solution was investigated in relation to the differences in structure between glutaraldehyde-crosslinked and sulfur-derivative sorbents.

EXPERIMENTAL

Materials

Chitosan flakes were purchased from Aber Technologies (Plouvien, France, Lot No. A17G28). The samples were previously characterized⁹: The deacetylation percentage and molecular weight were found to be 87% (using Fourier-transform infrared spectroscopy analysis) and 125,000 (using size-exclusion chromatography), respectively. Samples were used as received without any additional treatment except for crushing and sieving

operations to separate the chitosan samples into several fractions. The fraction 125–250 μm was used in this study.

Reagents were purchased from Fluka AG (Switzerland) as pure reagents: glutaraldehyde (50% v/v aqueous solution) and thiourea. Dihydrogen hexachloroplatinate was purchased from ChemPur (Germany). Infrared-grade KBr was purchased from Carlo Erba (Milano, Italy).

Chemical Modification of Chitosan

To optimize thiourea grafting, 48 samples were prepared with varying thiourea and glutaraldehyde amounts introduced in 20 mL of demineralized water and reacted for 3 h. Thiourea amounts were chosen among eight values: 0 (reference), 0.1, 0.25, 0.5, 0.75, 1, 2, and 3 g. A glutaraldehyde solution (50% v/v in water) was added at the following levels: 0.1, 0.25, 0.5, 0.75, 1, and 2 mL. After the reaction between the thiourea and glutaraldehyde, 1 g of chitosan was added to the solution, then placed under agitation for 16 h. Finally, the solid was separated by filtration and rinsed several times with water and dried at about 50°C overnight. The following nomenclature was used for the description of the sorbents:

GC-a:b: GC prepared with “a” mL of glutaraldehyde (50% in water) and “b” g of chitosan (in 20 “b” mL of water).

TGC-a:b:c: Thiourea derivative of chitosan prepared with “a” mL of glutaraldehyde (50% in water) and “b” g of thiourea and “c” g of chitosan (in 20 “c” mL of water).

In the second step of the study, for the exhaustive investigation of optimized chitosan derivatives, the contact time was increased for both the prereaction time (between thiourea and glutaraldehyde) from 3 to 16 h and the contact time of the intermediary product with chitosan which was increased to 72 h. It is noticeable that the sorbent particle size does not significantly change after chemical modification.

Sorbent Characterization

FTIR Analysis

Solid samples were ground with infrared-grade KBr in an agate mortar. An aliquot of 400 mg of this was taken with a 0.1% w/w biosorbent content. The ground powder was pressed with a Specac press (under a pressure of 6.6×10^{11} Pa)

for 5 min. The translucent discs obtained by this procedure were analyzed by transmission with a Nicolet FTIR spectrophotometer 510 (32 scans, background: air; resolution: 4 cm^{-1}).

SEM-EDAX Analysis

Dry samples of free or saturated polymers were embedded in a synthetic resin Epotek 301: 4 parts glue and 1 part lubricant. After a drying phase, of 24 h at mild temperature, the sections were polished with several abrasive GEOPOL disks of decreasing grain size (6/12, 2/6, and 0.5/3 μm). The section between each pair of abrasive disks was rinsed with water after each polishing. Finally, sections were polished with a fine tissue disk using a DP emulsion lubricant and a diamond spray HQ (successive sizes: 6, 3, and 1 μm). After this polishing step, the sections were coated with carbon in order to increase the sample conductivity. Samples were observed through a scanning electron microscope (JEOL JEM 35.CF). Element distributions were estimated on each section by an X-ray energy-dispersive analysis with a Kevex spectrometer and a Delta Quantum detector (Si/Li detector and beryllium aperture) with an accelerating voltage of 25 kV. The K_α bands of carbon, oxygen, chlorine, and sulfur were detected at 0.27, 0.53, 2.62, and 2.31 keV, respectively; the M_α band of platinum was detected at 2.07 keV.

Metal-sorption Procedure

Preliminary studies on GC showed that platinum sorption is strongly influenced by the kind of mineral acid used for pH control. Hydrochloric acid enhanced platinum sorption in comparison with sulfuric acid. These results have lead us to compare systematically the behavior of both GC and thiourea–glutaraldehyde (TGC), according to the acid used for pH control.

For optimization of the modification operations, platinum sorption was compared for the 48 samples using a standard procedure: mixing 10 mg of sorbent with 100 mL (or 300 mL) of the platinum solution with a concentration equal to 20 mg L^{-1} (or 15 mg L^{-1}) controlled H_2SO_4 (or HCl, respectively) for 72 h.

Sorption isotherms were obtained by mixing known amounts of the sorbent with known volumes of the solution controlled at pH 2 with HCl or H_2SO_4 for 72 h. Samples were filtrated at equilibrium and analyzed for the determination of the

residual platinum concentration. Concentration in the sorbent was obtained by a mass balance between the liquid and solid phases.

Sorption kinetics were performed in a jar test, at a rotation speed of 240 rpm, by mixing 50 mg (or 100 mg) of the sorbent with 1 L of the hexachloroplatinate solution (concentration 10 mg L⁻¹) controlled at pH 2 with HCl (or H₂SO₄, respectively), at a temperature of 20 ± 1°C. Samples were steadily withdrawn, filtrated, and analyzed.

The platinum concentration in single synthetic solutions was obtained by a visible spectrophotometric procedure deduced from Charlot,²³ consisting of the reaction of platinum ions with stannous chloride in a HCl concentrated solution and absorbance measurement at 406 nm on a Shimadzu UV-1601 spectrophotometer (Japan). Alternatively, for complex solutions, the analysis was performed on an ICP Jobin-Yvon JY-35 (France) spectrophotometer for calibration and control.

Kinetic Modeling

Mass transfer involves several steps including (i) bulk diffusion, (ii) film diffusion, (iii) intraparticle diffusion, and (iv) a sorption and/or ion-exchange process. Providing sufficient agitation to avoid particle and solute gradients in the batch reactor allows the bulk diffusion to also be neglected. Sorption processes can be considered as instantaneous processes and the kinetic control is attributed mainly to film and intraparticle diffusion. Simplified models have been developed, such as the homogeneous diffusion model (HDM) and the shrinking core model (SCM), with special definitions for film diffusion, intraparticle diffusion, and chemical reaction control, respectively.²⁴ Several models exist, which include both external, intraparticle diffusion, and sorption isotherm characteristics.^{25,26} Except for the case of linear isotherms, these models cannot be solved analytically and numerical analysis is required. The first approach in this work will involve the separation of external and intraparticle diffusion steps to obtain the order of magnitude of the external and intraparticle diffusion coefficient, respectively.

To obtain the external mass-transfer coefficient, a simplified procedure previously described by Findon et al. was used.²⁷ Coupled mass-transfer equations and boundary and initial conditions can be solved algebraically to give the following equation:

$$\ln\left(\frac{C(t)}{C_0}\right) = -k_f St \quad (1)$$

where k_f is the external mass-transfer coefficient, and S , the outer surface of sorbent particles per unit of volume of particle-free solution (m⁻¹), which is obtained using the following equation:

$$S = \frac{6m}{d_p \rho (1 - \varepsilon)} \quad (2)$$

where m represents the sorbent dosage (g L⁻¹); d_p , the mean particle diameter (m); ρ , the density of sorbent particles (kg m⁻³); and ε , the porosity of the sorbent particles. The true density was measured using a pycnometer at 1.36 kg L⁻¹. It appears that the density as well as the porosity are of the same order for both sorbents: The outer surface per unit of volume was determined at 5.6 m⁻¹.

Crank proposed a model whereby diffusion is controlled only by intraparticle mass transfer for a well-stirred solution of limited volume (V), assuming the solute concentration to be always uniform and the sorbent sphere to be initially free from the solute.²⁸ Under these conditions, the total amount of solute M_t (mg g⁻¹) in a spherical particle after time t , expressed as a fraction of the corresponding quantity after infinite time (M_∞ , mg g⁻¹), is given by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp(-Dq_n^2 t/d_p^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (3)$$

where D is the intraparticle diffusion coefficient (m² min⁻¹). The fractional approach to equilibrium (FATE) may be used to estimate the intraparticle diffusion coefficient D , when the external diffusion coefficient is neglected. α is the effective volume ratio, expressed as a function of the equilibrium partition coefficient (solid/liquid concentrations ratio) and is obtained by the ratio $C_{eq}/(C_0 - C_{eq})$; q_n represents the nonzero solutions of the equations

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad \text{and} \quad \frac{M_\infty}{VC_0} = \frac{1}{1 + \alpha} \quad (4)$$

The infinite sum terms are summed until the summation does not vary. In this study, eqs. (4) were used to determine the overall intraparticle

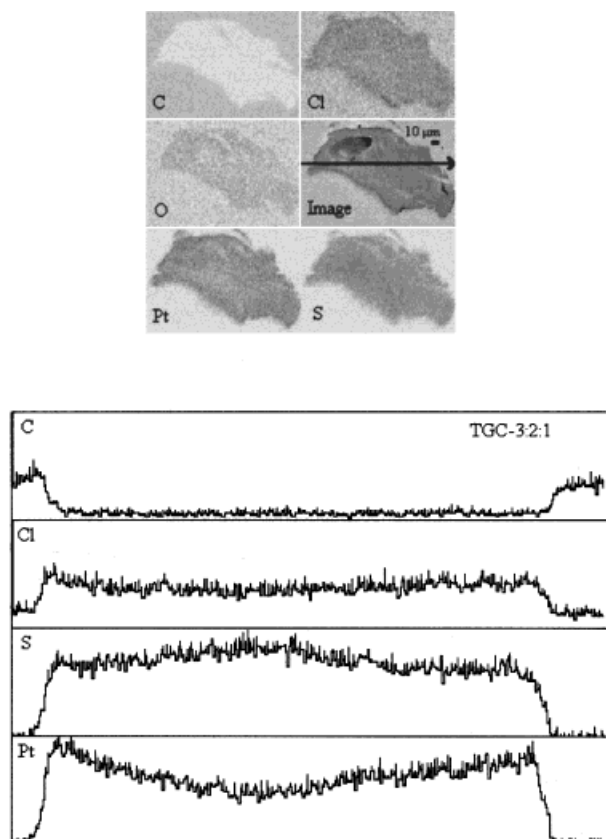


Figure 1 (Top figure, $\times 600$) Cartography of chemical elements (C, S, O, Cl, and Pt) in a particle of TGC-3:2:1 after saturation with platinum solution at pH 2 and (bottom figure) distribution of elements along a cross section of this particle (cross section in the direction of the arrow).

diffusivity which best fitted the experimental data.

RESULTS AND DISCUSSION

Characterization of the Sorbents and Interactions with Platinum

SEM-EDAX

The SEM-EDAX technique allows the distribution of C, O, Cl, S, and Pt to be observed in the sorbent particle, making it possible to draw a qualitative cartography of these elements or to detect these elements along a cross section of the particle. Figure 1 shows typical analyses of TGC-3:2:1 after platinum sorption. It appears that the Cl and C elements are homogeneously distributed around the sorbent. Platinum distribution is also

homogeneous and the cross section shows that the profile of platinum and chloride diffusion in the sorption is almost constant, perhaps slightly less adsorbed in the center of the particle (Fig. 1). The similarity in the profiles can be easily explained: Platinum sorption occurs through the uptake of hexachloroplatinate anions, so both Pt and Cl are similarly distributed along the cross section. On the contrary, it seems that sulfur groups are distributed slightly more densely in the center of the sorbent, following a reciprocal trend in comparison with platinum. A reference experiment, using TGC:3:2:1 before platinum sorption, showed that the C, O, and S elements are homogeneously distributed in the sorbent, while both Cl and Pt are absent. An X-ray diffractogram (not shown) confirmed that the Cl element is not significantly present in the sorbent free of platinum. Although chitosan is known to be a low porous material, it seems that the modification procedure allows a complete and homogeneous grafting of the sulfur moieties inside the chitosan particle. This result contrasts with the study of heterogeneous glutaraldehyde crosslinking of chitosan, for which Hsien and Rorrer showed that the crosslinking kinetics may be described by the shrinking core model¹² and can be characterized as a slow phenomenon requiring about 2 days to reach equilibrium.

Infrared Spectroscopy

The influence of increasing glutaraldehyde and thiourea grafting was studied through FTIR analysis. Chitosan, being a heteropolymer made up of glucosamine and acetylglucosamine units, is characterized in FTIR spectra by several bands: (a) 1580–1605 cm^{-1} : amine band (free form) which is shifted to 1550–1480 cm^{-1} when protonated; (b) 1650 cm^{-1} : amide I band; (c) 1550–1590 cm^{-1} : amide II band; and (d) 1300 cm^{-1} : amide III band.

The reaction between aldehyde groups and amine moieties on glutaraldehyde and chitosan, respectively, involves the formation of ceto-imine linkage: $>\text{C}=\text{N}$ bonds, identified by bands (1690–1640 cm^{-1}).²⁰ Aldehyde grafting on the amine functions confers to these groups a structure similar to that of the amide II band (1560–1520 cm^{-1}). The band at around 1709–1714 cm^{-1} is attributed to the $-\text{C}=\text{O}$ carbonyl groups of unreacted aldehyde functions.

Zhang et al. cited some thiocarbonyl derivatives of chitosan characterized with FTIR and

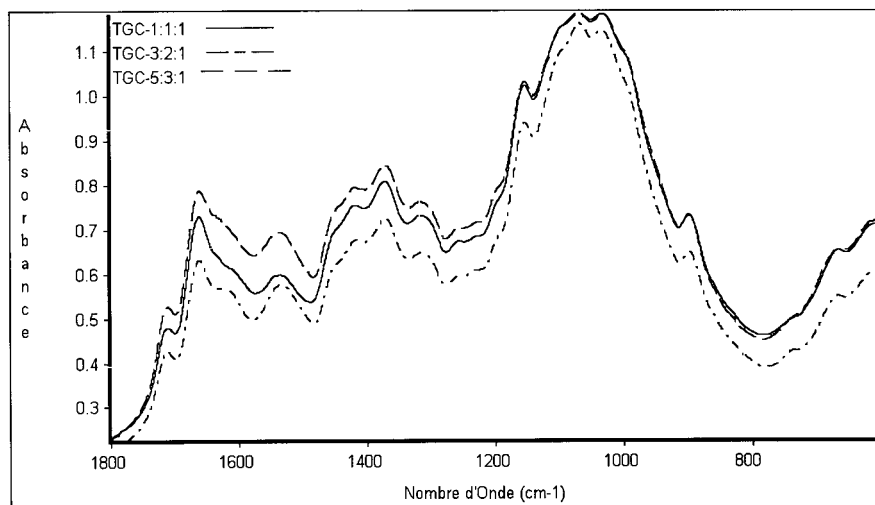


Figure 2 FTIR spectra of TGC at several extents of modification (nombre d'onde: wavenumbers).

^{13}C -CP/MAS NMR techniques.²⁹ Argüelles-Monal and Peniche-Covas prepared a mercaptan derivative of chitosan, using thiourea and epichlorhydrin, the spectra of this mercaptan derivative are similar to that of raw chitosan.²¹ Spectra of the compounds in which the $>\text{C}=\text{S}$ group is attached to a nitrogen atom show an absorption band in the general $>\text{C}=\text{S}$ stretching region ($1050\text{--}1300\text{ cm}^{-1}$). Several other bands in the broad region, $1563\text{--}700\text{ cm}^{-1}$, can be attributed to (a) vibrations involving interaction between $>\text{C}=\text{S}$ stretching and $\text{—}>\text{C}\text{—}\text{N}\text{—}$ stretching ($1590\text{--}1420\text{ cm}^{-1}$)³⁰ and (b) the $>\text{C}\text{—}\text{S}$ group. These bands are superimposed to amine/amide bands and the glucose ring, respectively. So, the sulfur-type vibrations are difficult to detect, and the changes in the spectra resulting from chemical modification are observed mainly on amine/amide regions.

The glutaraldehyde-crosslinked sorbents (GC-1:1, GC-2:1, and GC-3:1) and the thiourea derivatives (TGC-1:1:1, TGC-3:2:1, and TGC-5:3:1) were analyzed using FTIR spectrophotometry, as they were produced. In glutaraldehyde-crosslinked sorbents (spectra not shown), increasing the glutaraldehyde concentration involves an increase in the absorbance of the $>\text{C}=\text{O}$ band around 1710 cm^{-1} .²⁰ The change in amide bands is not very significant, suggesting that the excess of glutaraldehyde involves a greater proportion of free (unreacted) aldehyde groups. Thiourea derivatives present significant changes when increasing both glutaraldehyde and thiourea in compar-

ison with GC sorbents: The same amount of glutaraldehyde (with reference to GC sorbents) was added to chitosan in order to measure the sulfur contribution with a standard crosslinking level (Fig. 2). Increasing both reagent concentrations does not change significantly the absorbance of the $>\text{C}=\text{O}$ band: The reaction between aldehyde groups of the crosslinking agent with amine groups of thiourea decreases the number or proportion of free (unreacted) aldehyde groups in comparison with thiourea-free derivatives.

Figure 3 shows the FTIR spectra of GC and the thiourea derivative of chitosan after being mixed with solutions controlled with sulfuric and hydrochloric acids, respectively, as well as the chitosan and thiourea spectra. The thiourea derivatives, obtained in this study, exhibit FTIR spectra very similar to that of GC, when treated with sulfuric acid solutions, while significant differences appear when treated with hydrochloric acid solutions. The figure shows that the carbonyl group band is less marked for GC conditioned with sulfuric acid solutions than in hydrochloric acid solutions. The same observation can be made on the band $>\text{C}=\text{N}\text{—}$ around 1666 cm^{-1} , well resolved for HCl media conditioning, while for GC conditioned in sulfuric acid solutions, this band is combined with that of amine groups at around 1590 cm^{-1} to give a broad band. When treated with sulfuric acid solutions, the crosslinked chitosan spectrum also presents a broad band around 1536 cm^{-1} , which may be attributed to a structure similar to that of the amide II band, perhaps due

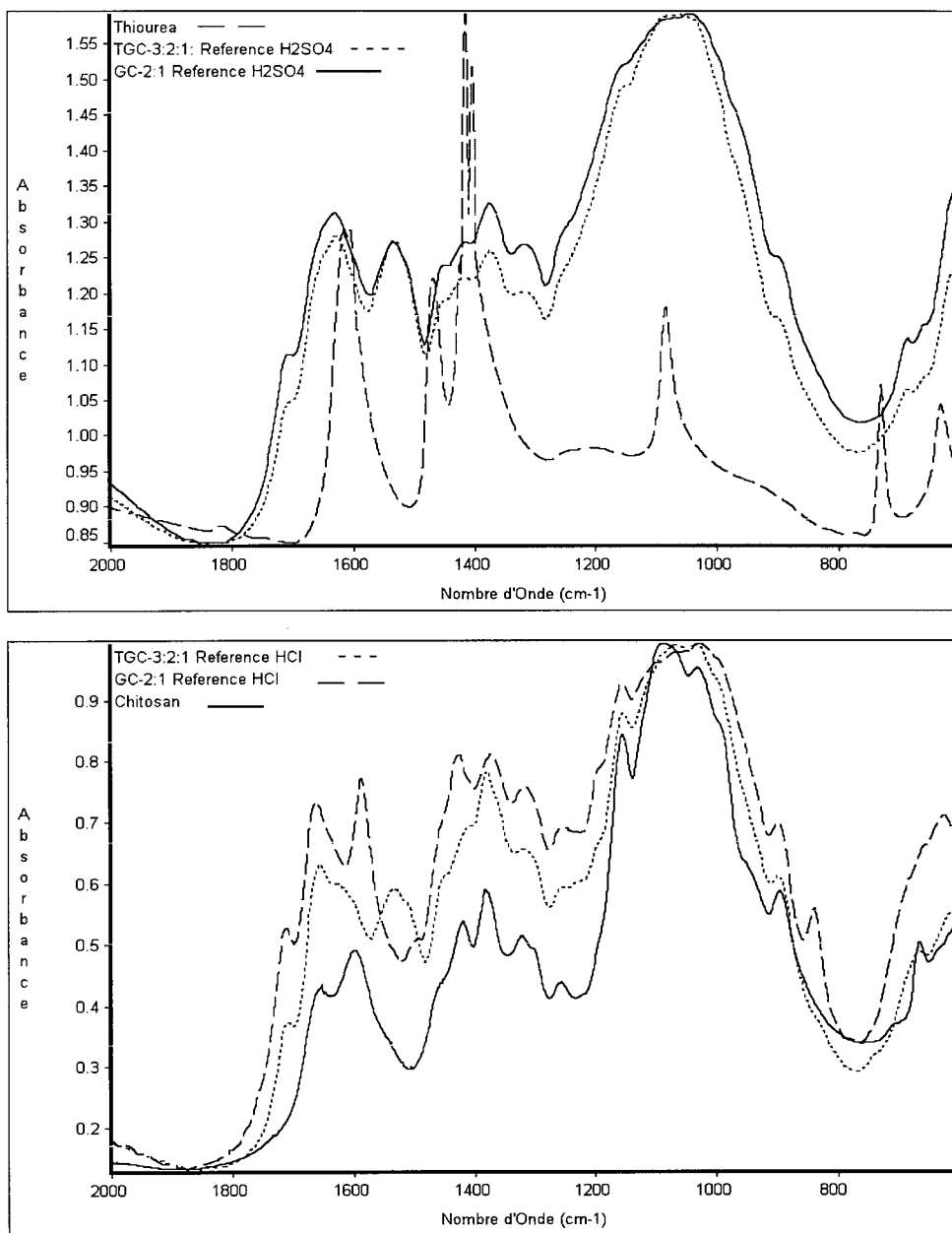


Figure 3 FTIR spectra of chitosan, thiourea, GC-2:1, and TGC-3:2:1 (after treatment at pH 2 with either sulfuric or hydrochloric acid solution) (nombre d'onde: wavenumbers).

to sulfate binding. On the spectra of modified and grafted chitosan, a decrease in the absorbance of bands related to carbonyl groups can be noticed, whatever kind of acid conditioning is performed. The free amine band also decreases in hydrochloric acid-treated sorbent and is replaced by a broad amide II-like transition.

Platinum sorption hardly influences the FTIR spectra of these chitosan derivatives (spectra not

shown). With sulfuric acid-treated sorbents, FTIR spectra are quite similar for glutaraldehyde-crosslinked sorbents and thiourea-derivative chitosan. On the other hand, when treated with hydrochloric acid, the major differences between the sorbents correspond to the significant decrease in the adsorption of the carbonyl groups and the decrease in the intensity of the amide II band. Moreover, for the thiourea derivative, treated

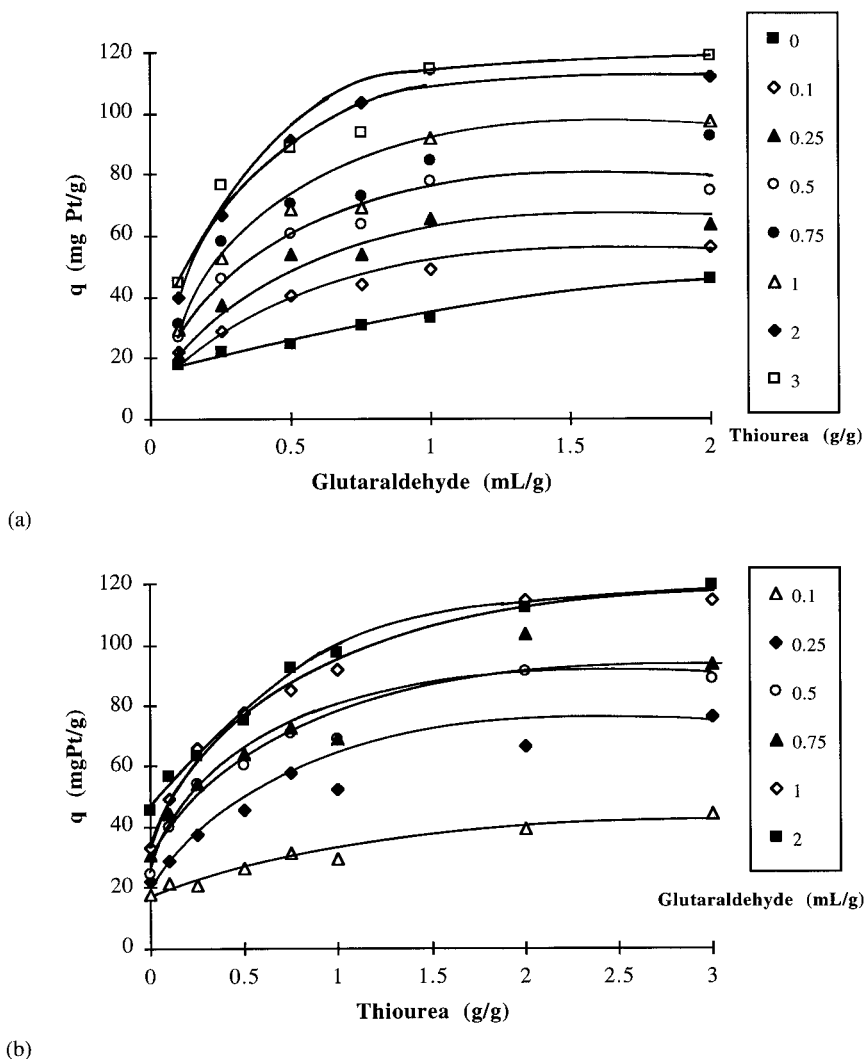


Figure 4 Influence of (a) glutaraldehyde proportion or (b) thiourea on platinum sorption at pH 2 (pH controlled with sulfuric acid).

with hydrochloric acid solutions, the shoulder appearing at around 1630 cm^{-1} is slightly weakened. So, platinum sorption hardly changes the FTIR spectra of either sorbent, whatever the acid used for pH control, although sorption capacities in these experimental conditions tends to $50\text{--}60$ and $200\text{--}250\text{ mg Pt g}^{-1}$ for sulfuric acid and hydrochloric acid solutions, respectively.

Synthesis Optimization

The proportions of glutaraldehyde and thiourea are varied and the sorption of platinum in both sulfuric and hydrochloric acids is carried out at pH 2. With solutions in which pH was controlled with hydrochloric solutions, the sorption capacity

varies between 280 and 330 mg Pt g^{-1} . While increasing the amounts of both thiourea and glutaraldehyde seems to decrease the sorption capacity for similar experimental conditions, the calculation of the χ^2 -test gives a high value equal to 40.7 . Moreover, the mean value of the sorption capacity (mean) equals 318.65 mg g^{-1} with a standard deviation (sdev) of 28.59 , and 17 data are out of the range of $[\text{mean} - \text{sdev}, \text{mean} + \text{sdev}]$. Thus, it is possible to conclude that the proportion of glutaraldehyde and thiourea does not have a significant effect on the platinum sorption capacity in solutions controlled at pH 2 with hydrochloric acid. Conversely, Figure 4 shows the influence of glutaraldehyde and thiourea on the platinum sorption capacity in solutions with the

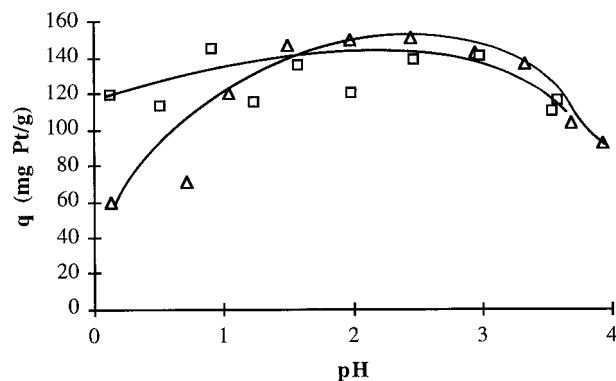


Figure 5 pH optimization for TGC-3:2:1 in (Δ) hydrochloric acid and (\square) sulfuric acid (initial concentration Co: 10 mg L^{-1} ; sorbent dosage: $15 \text{ mg}/240 \text{ mL}$).

pH controlled with sulfuric acid. Sorption capacities are significantly lower than those obtained with hydrochloric acid: The sorption levels are decreased two to four times. A significant increasing trend clearly appears with increasing amounts of both reagents. In this case, the χ^2 -test gives a lower value equal to 9.45. Increasing the concentration of glutaraldehyde and thiourea enhances the sorption efficiency in unfavorable conditions, such as in solutions controlled with sulfuric acid. However, Figure 4 shows that the sorption capacity tends to reach a plateau when glutaraldehyde and thiourea levels exceed 1 mL and 2 g, respectively. Thus, further experiments concerning the sorption behavior were carried out with GC-2:1 (2 mL glutaraldehyde 50% per gram of chitosan) and TGC-3:2:1 (3 g thiourea and 2 mL glutaraldehyde per gram of chitosan).

pH Optimization with TGC-3:2:1

Platinum sorption was previously studied in HCl-controlled pH solutions with GC.⁷ This study showed that the optimum pH ranges are between 2 and 2.5. Figure 5 shows the influence of the pH equilibrium on the platinum sorption capacity for the thiourea derivative of chitosan. The figure clearly demonstrates that in solutions controlled with sulfuric acid the sorption capacity and efficiency are independent of the pH of the solution if it is between 0 and 4 (the sorption capacity varies slightly between 100 and 140 mg g^{-1}), while in solutions controlled with hydrochloric acid, the optimum sorption occurs around pH 2, the sorption capacity being increased twofold. It is possible to notice that at a pH lower than 1 sorption

capacities are almost identical for solutions controlled by both sulfuric and hydrochloric acids.

Previous results obtained on GC have shown that decreasing the pH strongly diminishes the sorption capacity: At a pH lower than 1, the sorption capacity is lower than 40 mg g^{-1} . Thiourea grafting increases the sorption ability of chitosan for platinum and decreases the sensitivity to pH. These differences may be explained by the difference in the mechanism of platinum sorption: In the case of glutaraldehyde-crosslinked sorbents, adsorption occurs through ion-exchange reactions, while in the case of thiourea derivatives, sorption results from the combination of ion-exchange and complexation reactions. Chelating resins are assumed to be characterized by their intrinsic complexation constants, which, according to the Gibbs–Donnan model, are related to the complexation constants in solutions with ligands having a similar structure to that of the active groups in the resin.³¹ Thiourea, being a weak base, is totally deprotonated in the pH range carried out in this study; moreover, in these conditions, hydrolyzed species are negligible, and for metal ions such as Ag^+ and Hg^{2+} , Ringbom showed that their complexation by thiourea is independent of the pH.³² Similar trends may be suggested for thiourea and platinum interactions and the low effect of pH on platinum sorption was expected in comparison with pure ion-exchange resins as obtained by single glutaraldehyde grafting. A comparison of sorption capacities for HCl- and H_2SO_4 -controlled solutions shows that for extrema pH (lower than 1 or greater than 3) sorption is similar for both solutions, while around pH 2, hydrochloric acid enhances platinum sorption.

Figure 6 shows the distribution coefficient, de-

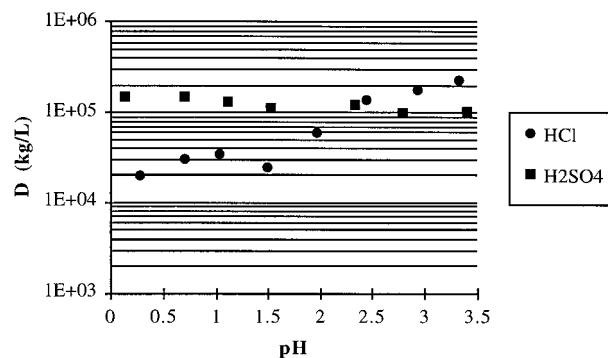
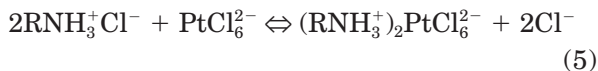


Figure 6 Influence of pH on the distribution coefficient D for platinum sorption on TGC 3:2:1 as a function of the acid used for pH control.

defined as the ratio of the amount of metal ion adsorbed by the dry adsorbent (mg kg^{-1}) to its equilibrium concentration in the aqueous solution (mg L^{-1}). The distribution coefficient for TGC 3:2:1 in sulfuric acid solutions is almost constant and equal to 10^5 L kg^{-1} , while in hydrochloric solutions, it increases from 2×10^4 to $2 \times 10^5 \text{ L kg}^{-1}$. These values are significantly higher than those cited by Inoue et al. using crosslinked copper-complexed chitosan sorbents,³³ but lower than the sorption capacities cited by Baba and Hirakawa using N-(2-pyridylmethyl)chitosan, a complex and expensive derivative of chitosan.⁶

Influence of Competitor Anions

The influence of the type of acid on hexachloroplatinate anion sorption can be explained by the competitor effect of other anions (brought by the acid) and their affinity for sorption sites. The sorption mechanism on GC is assumed to be an anion-exchange mechanism through the formation of an ion pair as suggested by the following equations^{7,33}:



Thus, the presence of an excess of anions involves a competition which can be improved by their affinity for sorption sites. For example, sulfate anions, being divalent, may be involved in stronger linkage with the sorbent, decreasing the availability of the sorbent sites for hexachloroplatinate anions and increasing the actual ionic strength of the media.

In the case of thiourea-substituted sorbents, the introduction of sulfur moieties may involve changes in sorption mechanisms or superimposition of two mechanisms: (a) anion exchange through ion-pair formation and (b) binding on sulfur moieties (alone or in conjunction with amine sites). Thus, the sensitivity of the sorption mechanism to competitor anions may be reduced: The ionic strength, and, more generally, the concentration of competitor anions, has a more marked effect on ion-exchange mechanisms than on complexation.

To verify these assumptions, the effect of increasing the concentrations of salts was carried out using both sulfuric and hydrochloric acids,

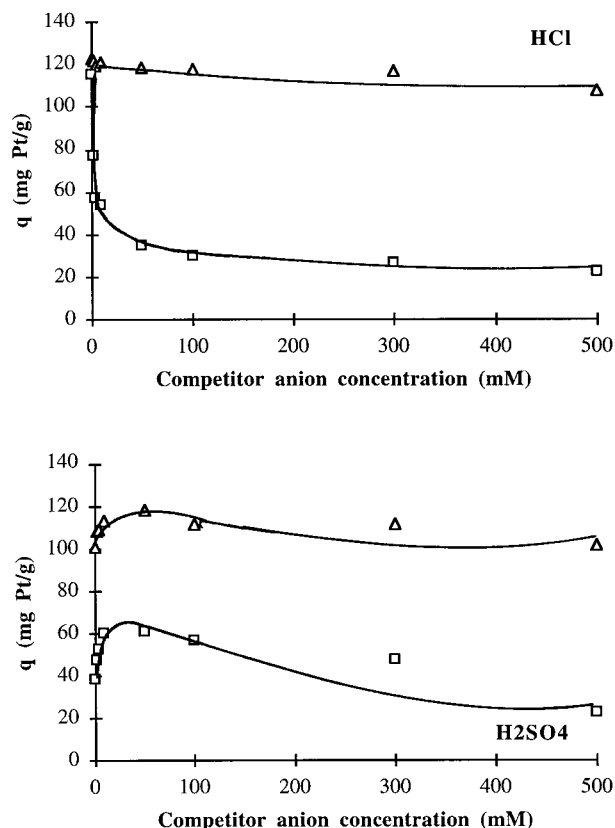


Figure 7 Influence of competitor anion Na_2SO_4 (respectively, NaCl) on platinum sorption at pH 2 in HCl -controlled pH solutions (respectively, H_2SO_4 -controlled pH solutions) using (Δ) TGC-3:2:1 and (\square) GC-2:1 (sorbent dosage: $15 \text{ mg}/200 \text{ mL}$; Co : 9.4 mg L^{-1}).

completed by addition of sodium chloride (to a H_2SO_4 -controlled pH solution) and sodium sulfate (to a HCl -controlled pH solution) at the level of 2, 5, 10, 50, 100, 300, and 500 mM . Figure 7 reports the results obtained with several experimental sets at pH 2 with low metal concentration (10 mg L^{-1}). For solutions whose pH is controlled with hydrochloric acid, and completed with sodium sulfate, the sorption capacity decreases continuously with increasing concentration of the competitor ion. However, the differences observed between reference conditions (free of competitor ions) and complex media are not similar for TGC-3:2:1 and GC-2:1. While for thiourea-grafted chitosan the sorption capacity decreases from 120 to 100 mg g^{-1} , for GC platinum, sorption is strongly decreased from 120 to 20 mg g^{-1} between the competitor-free ion medium and a solution containing 500 mM of sodium sulfate. Sulfate interaction with chitosan involves a change in the crystallinity of chitosan. Several studies have shown

that sorption efficiency for metals such as copper, uranium, and molybdenum is significantly reduced when increasing the crystallinity of the sorbent.^{9,34,35}

Conversely, for solutions for which the pH is adjusted with sulfuric acid, increasing the concentration of sodium chloride involves a discontinuous trend in sorption capacity: Below a 10–50 mM concentration of NaCl, the sorption capacity increases from 40 to 60 mg g⁻¹ for the glutaraldehyde-crosslinked sorbent and from 100 to 120 mg g⁻¹ for a thiourea derivative of chitosan. Above a competitor ion concentration of 50–100 mM, the sorption decreases again to 20 and 100 mg g⁻¹ for GC-2:1 and TGC-3:2:1, respectively. Obviously, the thiourea derivative allows the sorbent to be less influenced by the composition of the solution in comparison with the GC: Depending on the concentration of the competitor ions, the sorption capacity may be increased twofold or more. Similar trends are obtained with higher platinum concentration solutions (not shown), and the differences observed between TGC and GC compounds is much more marked than that obtained at low concentration. While sulfate ions strongly compete with hexachloroplatinate anions for sorption on the glutaraldehyde-crosslinked sorbent, chloride ions cause the effect of sulfate (and sulfuric acid) on platinum sorption to be decreased, up to a limit concentration, above which chloride ions become competitor ions again.

Helfferich discussed the scaling of affinity for ion exchange³⁶ and showed that ion-exchange resins tend to prefer the counterion of (a) higher valence, (b) smaller solvated equivalent volume, (c) greater polarizability, (d) higher affinity for the fixed ionic groups or the components of the solution, and (e) lower reactivity for complexation with the co-ions. He stated that for usual anion-exchange resins the selectivity for sulfate is higher than that for chloride. According to Marcus,³⁷ these anions may be classified under the scope of polarizability and solvated equivalent volume:

$$\text{Polarizability } (\text{\AA}^3) = 3.964 \times 10^{-25} R_{\infty}; \text{Cl}^- \text{ (3.42)}$$

$$< \text{SO}_4^{2-} \text{ (5.47)} < \text{PtCl}_6^{2-} \text{ (20.69)}$$

where R_{∞} is the molar refractivity:

$$\text{Ionic volume } (\text{cm}^3 \text{ mol}^{-1}): \text{Cl}^- \text{ (23.3)}$$

$$< \text{SO}_4^{2-} \text{ (25)} < \text{PtCl}_6^{2-} \text{ (161)}$$

Chloride and sulfate ions have similar trends regarding these ionic properties. In terms of polarization, sulfate should be exchanged more easily than is chloride, while the ionic volume factor is more favorable to chloride ion bonding. The increase in platinum sorption capacity in sulfuric acid pH-controlled solutions, resulting from the introduction of low chloride concentrations, tends to indicate that chloride ions are easily sorbed to form ion pairs which are exchanged with hexachloroplatinate anions according to eqs. (6). Another parameter useful for the description of electrostatic effects involved in ion-exchange mechanisms refers to the ratio between the charge and the ionic radius of the ion. It appears that hexachloroplatinate anions are closer to chloride than are sulfate anions, as a possible explanation for better results observed with hydrochloric acid-controlled solutions³⁷:

$$\text{Ionic radius (pm): Cl}^- \text{ (181)}$$

$$< \text{SO}_4^{2-} \text{ (230)} < \text{PtCl}_6^{2-} \text{ (313)}$$

Ionic charge/ionic radius (10³ pm⁻¹):

$$\text{Cl}^- \text{ (5.5)} < \text{PtCl}_6^{2-} \text{ (6.4)} < \text{SO}_4^{2-} \text{ (8.7)}$$

The presence of sulfate thus involves a strong competition with hexachloroplatinate anions for uptake on glutaraldehyde-crosslinked sorbents, while this effect is reduced with thiourea derivatives due to complexation reactions on thiourea moieties. It appears that for similar global concentrations of both sulfate and chloride in solutions with pH controlled by either sulfuric or hydrochloric acid, sorption performances are not identical. It indicates that the control of sorption performances is not only due to the global concentration of competitor ions, but also to its affinity for sorption sites, or for hexachloroplatinate ions, and it seems that it depends on the form in which it is added to the solution (salt or acid). Ringbom observed that for some metal ions the complexation strength significantly increases when the ligand is provided as hydrochloric acid rather than as alkaline chloride.³²

Sorption Kinetics

Figure 8(a) shows the general trend followed by platinum sorption kinetics for sulfuric and hydrochloric acid solutions for both TGC-3:2:1 and GC-

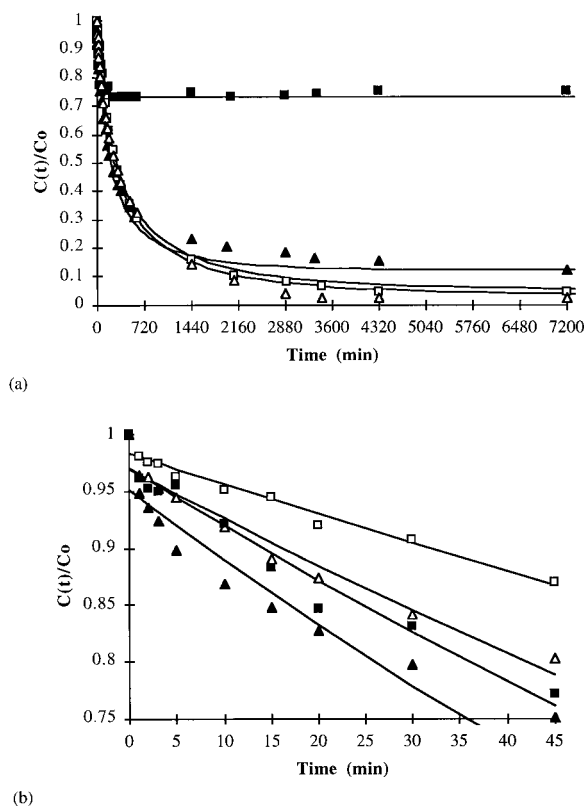


Figure 8 Platinum sorption kinetics using (Δ/\blacktriangle) TGC-3:2:1 and (\square/\blacksquare) GC-2:1. C_0 : 10 mg L^{-1} ; sorbent dosage: (open symbols) 50 mg L^{-1} for HCl-controlled pH solution and (closed symbols) 100 mg L^{-1} for H_2SO_4 -controlled pH solutions at pH 2. (a) Complete sorption kinetics [solid lines: modeling of intraparticle diffusion according to eq. (3)]; (b) initial sorption step [solid lines: modeling of external diffusion according to eq. (6)].

2:1 sorbents. It appears that the time required to reach equilibrium greatly changes according to the experimental system. While a pseudoequilibrium is reached within a few hours of contact for GC in sulfuric acid media, with an equilibrium concentration greatly higher than that obtained in hydrochloric acid or with the thiourea derivative of chitosan, a larger contact time is required for other systems. The final equilibrium is obtained after 3–4 days, although about 85–90 % of the total sorption occurs within the first 24 h of contact. Kinetic curves are quite close for TGC-3:2:1 in both sulfuric and hydrochloric acid solutions, as well as for GC-2:1 in hydrochloric acid solutions, within the first 10 h of contact. For a greater time of contact, it appears that sulfuric media is less favorable to sorption in terms of both kinetic and equilibrium criteria, while in

hydrochloric acid solutions, TGC-3:2:1 and GC-2:1 follow the same kinetic trend during the second step corresponding to the control of sorption by intraparticle diffusion.

The overlapping of kinetic curves in hydrochloric acid solutions demonstrates that the diffusion properties are not significantly affected by the grafting of thiourea groups. The modification of the sorbent is carried out in a heterogeneous mode by contact between free aldehyde groups (not bound to amine groups of thiourea in the intermediary compound) and amine groups of chitosan. Enhancement of sorption and diffusion properties has been cited using physical or chemical modifications of chitosan: It usually includes the dissolving and the reprecipitation of chitosan, which involves a further modification of the polymer network opening or the decrease of the crystallinity of the sample.^{3,5,7,38}

In the present case, the grafting of thiourea has a limited effect on the accessibility to internal sites by comparison with glutaraldehyde-crosslinked sorbents. The chitosan modification is suspected to change the mechanism of sorption from an ion-exchange process to a mixed ion exchange (on free nonsubstituted amine groups) and chelating resin (on sulfur moieties). This change has no significant effect on the sorption kinetics: The complexation rate could control overall sorption kinetics²⁴; however, it is not the case for platinum sorption using the thiourea derivative of chitosan, the sorption curves being overlapped in the HCl media.

It is also noticeable that platinum sorption is slower in solutions whose pH is controlled by sulfuric acid in comparison with hydrochloric acid. Several hypotheses can be proposed to explain the role of sulfuric acid in the restriction of diffusion properties. Sulfate anions are known to involve a change in the crystallinity of chitosan and thus cause a decrease in the accessibility to intraparticle sorption sites, which results in diffusion limitations. Moreover, sulfate anions act as competitor anions for the attribution to ion-exchange sites; the presence of these large anions is suggested to induce a steric hindrance for the sorption of hexachloroplatinate anions on the bordering binding sulfur sites.

Figure 8(b) shows kinetic curves for the first minutes of contact. The platinum sorption by the thiourea derivative of chitosan seems to be faster than is glutaraldehyde-crosslinked material, whatever acid is used for pH control. During the initial sorption step, the kinetic curve with HCl-

Table I Sorption Kinetics for Platinum Using TGC-3 : 2 : 1 and GC-2 : 1 (pH 2)

Sorption System		External Mass Transfer			Intraparticle Mass Transfer	
Sorbent	Acid	k_f (m min ⁻¹)	α_0	R^2	D (m ² min ⁻¹)	SSR
TGC-3 : 2 : 1	HCl	8.2×10^{-4}	-0.031	0.96	8.0×10^{-13}	0.010
GC-2 : 1	HCl	5.0×10^{-4}	-0.017	0.97	1.3×10^{-12}	0.008
TGC-3 : 2 : 1	H ₂ SO ₄	11.9×10^{-4}	-0.051	0.89	5.8×10^{-12}	0.064
GC-2 : 1	H ₂ SO ₄	9.6×10^{-4}	-0.030	0.96	1.6×10^{-10}	0.162

SSR: Sum of squared residuals according to $SSR = \sum_{i=1}^n (F_{\text{exp}}(t_i) - F_{\text{calcd}}(t_i))^2$, with F the function representative of the diffusion equation [fractional approach to equilibrium (FATE) according to the intraparticle diffusion eq. (3)].

controlled solutions almost overlaps with that of the thiourea derivative in the sulfuric acid solutions. For this initial period, intraparticle diffusion is usually considered as nonlimiting and differences cannot be interpreted as for the final sorption step. Thiourea grafting is assumed to give chitosan the structure of a chelating resin. It can be suggested that surface binding might be enhanced with chemical reaction in comparison with single ion-exchange reactions: The initial slope of the kinetic curve is thus higher, while for a larger contact time, intraparticle diffusion limitations involve slower sorption kinetics.

External diffusion, which controls sorption in the initial sorption phase, is modeled using eq. (1). Actually, the linearization of experimental data according to the logarithm transform of $C(t)/C_0$ versus time gives a linear rather than a directly proportional equation according to the following equation:

$$\ln\left(\frac{C(t)}{C_0}\right) = -k_f St + \alpha_0 \quad (6)$$

where α_0 corresponds to a fast decrease in the concentration of the solution in the first seconds of contact, as it appears in Figure 8(b). Table I shows the external diffusion coefficients and the corresponding correction factor. The external diffusion coefficients vary between 5×10^{-4} and 11.9×10^{-4} m min⁻¹: In hydrochloric acid solutions, the film mass transfer appears to be slightly slower than in sulfuric acid solutions, while for both acids, thiourea grafting involves a slight increase in the external diffusion coefficient. These values are of the same order of magnitude as those cited by Findon et al.²⁷ and Guibal et al.⁵ The α_0 coefficients may be converted to a correction factor [$\exp(\alpha_0)$] by the inverse trans-

form of eq. (6) and show that sorption kinetics occur in the first minutes of contact, as if the initial concentration was instantaneously decreased by 2–5%, depending on the experimental conditions.

Table I reports the values of the intraparticle mass-transfer coefficients. Except for the glutaraldehyde-crosslinked sorbent in sulfuric acid media, other systems are characterized by intraparticle diffusion coefficients ranging from 8×10^{-13} to 5.8×10^{-12} m² min⁻¹, quite lower than copper diffusivity in alginate gel beads,³⁹ but higher than values obtained with molybdate ions using glutaraldehyde-crosslinked sorbents.⁵ The intraparticle diffusion coefficient is not significantly affected by the grating of thiourea: The change in the sorption mechanism (chelating versus ion-exchange resin) has no significant effect on the mass-transfer performance.

Sorption Isotherms

Sorption isotherms give complementary information on the association between the sorbent and the targeted metal ions. Figure 9 presents the results obtained in H₂SO₄ and HCl media.

The equilibrium is described by standard isotherm equations, such as those described by Freundlich, Langmuir, Brunauer Emmett and Teller, and Sips.⁴⁰ A preliminary screening of the corresponding equations showed that the Langmuir and Freundlich models best fit the experimental data, and the following standard equation is used for the modeling of results:

$$\text{Langmuir model} \quad q = \frac{q_m b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (7)$$

$$\text{Freundlich model} \quad q = k_F C_{\text{eq}}^{1/n} \quad (8)$$

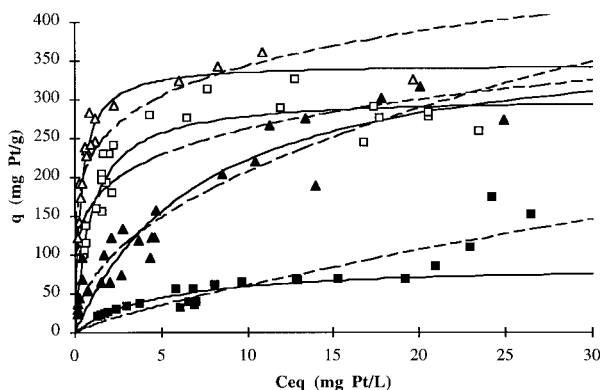


Figure 9 Platinum sorption isotherms using (Δ/\blacktriangle) TGC-3:2:1 and (\square/\blacksquare) GC-2:1 with (open symbols) HCl and (closed symbols) H_2SO_4 -controlled pH solutions, at pH 2; (solid lines) Langmuir modeling; (dashed lines) Freundlich modeling.

where q_m is the maximum sorption capacity for monolayer coverage (mg g^{-1}) and b is the affinity coefficient (L mg^{-1}), while q (mg g^{-1}) and C_{eq} (mg L^{-1}) represent the sorption capacity and metal concentration in the solution at equilibrium, respectively; k_F and n represent the Freundlich coefficients (n , dimensionless; k_F : $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$). The model parameters q_m , b , n , and k_F are obtained by nonlinear regression analysis to avoid statistical bias.⁴⁰

Maximum sorption capacity, corresponding to the sorption level at monolayer coverage, in the Langmuir model, is significantly increased when the pH is controlled by hydrochloric acid and for sorbent modified with thiourea. While the sorption capacity is of the same order of magnitude for hydrochloric solutions, in the case of sulfuric acid-controlled solutions, the thiourea derivative exhibits a sorption capacity as high as twice the maximum sorption obtained with the glutaraldehyde-crosslinked sorbent. It is noticeable that for

less favorable experimental conditions (glutaraldehyde-crosslinked sorbent and sulfuric acid) the sorption isotherm is described by the Henry model, defining a partition coefficient for the sorbate between the liquid and solid phases, in the first section of the curve, while increasing the metal concentration involves a strong increase in sorption capacity, giving the isotherm curve the shape of the BET isotherm.²⁶ The differences between the four experimental systems are also remarkable for the initial slope of the curve: At a low residual platinum concentration, sorption capacities are of the same order, with the remarkable exception of GC in sulfuric acid solution which is much more unfavorable. The differences relative to the platinum sorption capacity increase with increasing residual concentration. It also appears with the affinity coefficient, which is significantly increased for the thiourea derivative, as well as with pH controlled by hydrochloric acid. While the difference is not large for hydrochloric solutions for TGC and GC compounds, with sulfuric acid-controlled solutions, the grafting of sulfur compounds involves a significant enhancement of the sorption properties.

Table II reports the coefficients of the Langmuir and Freundlich models for the sorption of platinum with both TGC-3:2:1 and GC-2:1 in sulfuric and hydrochloric acid solutions (at pH 2). The Langmuir model fits the experimental data better than does the Freundlich model in hydrochloric acid solutions, while in sulfuric acid solutions, the Freundlich model gives a more accurate prediction of experimental points. This difference can be explained by some heterogeneities on the sorbent: Some specific sites, being more sensitive to the presence of sulfate, can interact differently with platinum through ion-exchange and chelating mechanisms. In hydrochloric acid solutions, the thiourea derivative shows a sorption capacity

Table II Sorption Isotherms for Platinum Using TGC-3 : 2 : 1 and GC-2 : 1 (pH 2)

Sorption System		Langmuir Model			Freundlich Model		
Sorbent	Acid	q_m (mg g^{-1})	b (L mg^{-1})	MSR	k_F	n	MSR
TGC-3 : 2 : 1	HCl	346.2	3.00	23.7	229.2	5.68	35.0
GC-2 : 1	HCl	304.1	1.08	23.7	166.7	5.08	36.4
TGC-3 : 2 : 1	H_2SO_4	386.9	0.135	31.9	69.0	2.09	28.1
GC-2 : 1	H_2SO_4	288.1	0.208	28.4	9.87	1.26	16.7

k_F : $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$. MSR: mean sum residuals according to $\text{MSR} = \sqrt{[\sum_{i=1}^n (F_{\text{exp}}(C_i) - F_{\text{calcd}}(C_i))^2]/n}$, with F the function representative of the isotherm equation (Langmuir or Freundlich equation).

about 10 % higher than that of the glutaraldehyde-crosslinked sorbent, while, simultaneously, the thiourea-grafting allows the affinity coefficient to be two or three times that of a crosslinked sorbent. In sulfuric acid solutions, both the k_F and n Freundlich coefficients are increased with thiourea grafting.

CONCLUSIONS

The modification of chitosan by grafting of thiourea groups results in increase in the sorption capacities in both hydrochloric and sulfuric acid solutions. The enhancement of the sorption properties is more specifically significant in sulfuric acid-controlled solutions. The improvement of sorption characteristics is also noticeable in the optimization of pH: While the platinum sorption capacity strongly decreases out of the optimum pH range (between 2 and 3), with glutaraldehyde-crosslinked sorbents, the thiourea derivative seems to be less influenced by the pH of the solution, especially for sulfuric acid solutions.

The addition of chloride allows the sorption capacity and efficiency to be increased up to a limit value, at which chloride anions become competitors. Conversely, in hydrochloric solutions, the addition of sulfate anions involves a strong decrease in sorption properties. Thus, the influence of these anions is not solely due to the increase of ionic strength, but also to specific interactions between the sorbent and the sulfate anions. The influence of competitor ions can be balanced by the complexation effect of chloride on platinum ions: It allows the influence of sulfate anions to be reduced. It seems that the influence of competitor anions is also controlled by the form used to introduce these anions (salt or acid forms).

The grafting of thiourea on the chitosan backbone, through glutaraldehyde linkage, changes the structure of the biopolymer and the metal-uptake mechanism: While platinum sorption occurs via ion-exchange mechanisms on GC, thiourea groups give the sorbent the properties of chelating resins. These changes in structure and mechanism explain the less sensitive behavior of the new derivative to pH and competitor ion effects.

Sorption capacities can be described by the Langmuir equation. The affinity coefficient is also increased by thiourea grafting, whatever the pH. Sorption kinetic curves give similar general trends. It seems that in the initial part of the curve the thiourea derivative adsorbs platinum

faster than does crosslinked sorbent, while in the second part of the curve, controlled by intraparticle diffusion, the trend seems to be reversed. However, the differences are not very marked: We can conclude that the grafting of thiourea groups hardly changes the diffusion properties.

The differences in the behavior of these sorbents with the type of acid used for pH control may be correlated to the influence of these acid solutions on the chemical modification of the sorbents as highlighted by the FTIR spectra. The differences between glutaraldehyde-crosslinked sorbents and the thiourea derivative are not very important, but depend on the type of acid used for pH control, the most significant differences being located in the 1550–1650 cm^{-1} wavenumber range, where absorbance bands of amine, amide, and sulfur groups can be superimposed. Platinum sorption also has a very limited effect on the FTIR spectra.

SEM–EDAX analyses showed that sulfur compounds are homogeneously distributed in the particle. Platinum is also homogeneously distributed over the particle, and the small ionic size of hexachloroplatinate anions may explain that sorption occurs in the whole mass of chitosan flakes, in contrast with previous results on molybdate or uranyl sorption.

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REFERENCES

1. Wan Ngah, W. S.; Isa, I. M. *J Appl Polym Sci* 1998, 67, 1067.
2. Peniche-Covas, C.; Alvarez, L. W.; Argüelles-Monal, W. *J Appl Polym Sci* 1992, 46, 1147.
3. Guibal, E.; Jansson-Charrier, M.; Saucedo, I.; Le Cloirec, P. *Langmuir* 1995, 11, 591.
4. Eiden, C. A.; Jewell, C. A.; Wightman, J. P. *J Appl Polym Sci* 1980, 25, 1587.
5. Guibal, E.; Milot, C.; Tobin, J. M. *Ind Eng Chem Res* 1998, 37, 1454.
6. Baba, Y.; Hirakawa, H. *Chem Lett* 1992, 1905.
7. Guibal, E.; Larkin, A.; Vincent, T.; Tobin, J. M. *Ind Eng Chem Res* 1999, 38, 401.
8. Piron, E.; Accominotti, M.; Domard, A. *Langmuir* 1997, 13, 1653.
9. Milot, C.; McBrien, J.; Allen, S. J.; Guibal, E. *J Appl Polym Sci* 1998, 68, 571.

10. Rorrer, G. L.; Hsien, T.-Y.; Way, J. D. *Ind Eng Chem Res* 1993, 32, 2170.
11. Kawamura, Y.; Mitsuhashi, M.; Tanibe, H.; Yoshida, H. *Ind Eng Chem Res* 1993, 32, 386.
12. Hsien, T.-Y.; Rorrer, G. L. *Ind Eng Chem Res* 1997, 36, 3631.
13. Yamamoto, H.; Amaike, M. *Macromolecules* 1997, 30, 3936.
14. Inoue, K.; Baba, Y.; Yoshizuka, K.; Noguchi, H.; Yoshizaki, M. *Chem Lett* 1988, 1281.
15. Baba, Y.; Masaaki, K.; Kawano, Y. *React Funct Polym* 1998, 36, 167.
16. Muzzarelli, R. A. A. *Carbohydr Polym* 1985, 5, 85.
17. Saucedo, I.; Guibal, E.; Roulph, Ch.; Le Cloirec, P. *Environ Technol* 1992, 13, 1101.
18. Jansson-Charrier, M.; Saucedo, I.; Guibal, E.; Le Cloirec, P. *React Funct Polym* 1996, 27, 209.
19. Masri, M. S.; Garcia Randall, V.; Pittman, A. G. *Polym Prepr ACS Div Polym Chem* 1978, 19, 483.
20. Guibal, E.; Milot, C.; Eterradosi, O.; Gauffier, C.; Domard, A. *Int J Biol Macromol* 1999, 24, 49.
21. Argüelles-Monal, W.; Peniche-Covas, C. *Makromol Chem* 1993, 207, 1.
22. Binman, S.; Belfer, S.; Shani, A. *J Appl Polym Sci* 1997, 63, 625.
23. Charlot, G. *Dosages Absorptiométriques des Éléments Minéraux*; Masson: Paris, 1978.
24. Juang, R.-S.; Lin, H. C. *J Chem Tech Biotechnol* 1995, 62, 132, 141.
25. Tien, C. *Adsorption Calculations and Modeling*; Butterworth-Heinemann: Boston, 1994.
26. Weber, W. J., Jr.; DiGiano, F. A. *Process Dynamics in Environmental Systems*; Wiley: New York, 1995.
27. Findon, A.; McKay, G.; Blair, H. S. *J Environ Sci Health A* 1993, 28, 173.
28. Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1975.
29. Zhang, M.; Hisamori, H.; Yamada, T.; Hirano, S. *Biosci Biotech Biochem* 1994, 58, 1906.
30. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.
31. Pesavento, M.; Biesuz, R. *React Funct Polym* 1998, 38, 135.
32. Ringbom, A. *Les Complexes en Chimie Analytique*; Dunod: Paris, 1967.
33. Inoue, K.; Baba, Y.; Yoshizuka, K. *Bull Chem Soc Jpn* 1993, 66, 2915.
34. Kurita, K.; Koyama, Y.; Chikaoka, S. *Polym J* 1988, 20, 1083.
35. Piron, E.; Domard, A. *Int J Biol Macromol* 1997, 21, 327-335.
36. Helfferich, F. *Ion Exchange*; Dover: New York, 1995.
37. Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.
38. Piron, E.; Domard, A. *Int J Biol Macromol* 1998, 22, 33.
39. Chen, D.; Lewandoski, Z.; Roe, F.; Surapaneni, P. *Biotechnol Bioeng* 1995, 41, 755.
40. Kinniburgh, D. G. *Environ Sci Technol* 1986, 20, 895.