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PLATINUM AND PALLADIUM SORPTION ON CHITOSAN DERIVATIVES

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ABSTRACT

Chitosan is a unique biopolymer due to its cationic properties in acidic solutions. Protonation of the amino groups induces ion-exchange properties that can be used for anion recovery. As this sorbent is soluble in acidic media, it may be necessary to reinforce its chemical stability using a glutaraldehyde cross-linking treatment. Sorption properties are strongly influenced by the pH of the solution and the presence of competitor anions, especially sulfate anions. This competitor effect may be decreased by the grafting of sulfur derivatives on the chitosan backbone using glutaraldehyde as a linker between the polysaccharide chains and the substituent. Several techniques such as FTIR and SEM-EDAX were used for the chemical characterization of chitosan substitution and for the location of PGM sorption on the sorbent. Sorption isotherms and kinetics were investigated and compared for cross-linked materials and substituted polymers, and special attention was given to the influence of competitor anions. The grafting of sulfur compounds increased sorption capacities and decreased the competition of sulfate and chloride anions. While cross-linked materials sorbed platinum and palladium through anion exchange, the grafting of sulfur moities gave chelating functionalities to the ion-exchange resin.

INTRODUCTION

Palladium and platinum are some of the most expensive metals; however, because of their special properties in catalytic processes, they are widely used in industry. Many processes have been developed to recover these metals in complex solutions, or are aimed at their recovery from spent catalysts (1). Ion-exchange processes as well as liquid/liquid extraction techniques have been investigated. The latest developments in the recovery of platinum group metals (PGMs) have involved the use of impregnated resins (2); however, these processes are usually efficient at removing PGMs only from medium-concentration to high-concentration solutions. The research of alternative sorbents remains a priority in this field of hydrometallurgy. These new sorbents might be (a) efficient at removing PGMs in complex and dilute solutions, (b) available at low cost, or (c) easy to recycle.

Chitosan is an aminopolysaccharide extracted by a deacetylation procedure from chitin, the most abundant biopolymer in nature except for cellulose (3). It is characterized by its high nitrogen content, which explains, in turn, its ability to uptake several metal ions through different mechanisms such as ion-exchange or chelation processes, depending on the metal and the pH of the solution (4-6). Chitosan is also characterized by its ready dissolution in many dilute mineral acids, with the remarkable exception of sulfuric acid. Thus necessary its chemical stabilization is necessary for the recovery of metal ions in acidic solutions. Several processes have been developed to reinforce its stability using cross-linking treatments, which can be accomplished with chemicals such as epichlorhydrin or glutaraldehyde. Glutaraldehyde has been used by several groups for cadmium recovery on chitosan beads (7), as well as for molybdenum and vanadium sorption (8). Glutaraldehyde cross-linking occurs through a Schiff's base reaction between the aldehyde ends of the cross-linking agent and the amine moities of chitosan to form imine functions (3). However, depending on the extent of the cross-linking reaction and the concentration of glutaraldehyde in the cross-linking bath, some unreacted aldehyde groups remain free on the sorbent in a pendant fashion. Chitosan has been widely used in experiments for the sorption of noble metals either in its original form or after chemical modification (9-11). However, these investigations have mainly focused on general studies of sorption performances at equilibrium or on the synthesis of new derivatives of chitosan obtained through complex chemical modification.

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Muzzarelli and Tanfani (12) have prepared the dithiocarbamate chitosan and tested its metal sorption properties; although sorption properties are improved by sulfur grafting, the sorbents are unstable. Peniche-Covas and Argüelles-Monal have investigated the grafting of mercapto groups on chitosan for mercury removal (13). More recently, Binman et al. have studied the fabrication of sulfur-chlorinated compounds derived from jojoba wax bound to polystyrene beads for mercury and chromate recovery (14). They have shown that the grafting of these sulfur derivatives is characterized by an enhanced selectivity and efficiency for metal recovery from brines and complex solutions. The present study was focused on the testing of a new chitosan derivative, which wasobtained by grafting thiourea onto chitosan through glutaraldehyde linkage. This bi-functional reagent can interact with amine groups on both thiourea and chitosan. The chitosan derivative was studied in order to optimize sorption properties for the recovery of PGMs in several types of matrices, including chloride and sulfate solutions. To achieve a better understanding of the sorption mechanism and optimization of experimental conditions, modified chitosan has been used in experiments on platinum and palladium recovery in solutions where the pH was controlled by either sulfuric acid or hydrochloric acid. The study was performed through optimization of the pH, determination of sorption isotherms, and observation of the influence of competitor anions. The influence of diffusion mechanisms was investigated through the study of sorption kinetics, by examining the influence of particle size and type of acid used for pH control.

EXPERIMENTAL SECTION

Materials

Chitosan was supplied by ABER-Technologie (France) as a flaked material, with a deacetylation of 87% as defined by FTIR spectrometry (8). The mean molecular weight was measured at 125,000 using a size exclusion chromatography method coupled with a differential refractometer and a multi-angle laser light-scattering photometer (6). The moisture content of sorbent particles was determined to be 10%; sorbent masses are expressed on a wet basis.

Chitosan Modification

Chemical cross-linking of chitosan was performed by reacting chitosan flakes with glutaraldehyde aqueous solutions with differing concentrations for 24 h. The cross-linked chitosan particles were rinsed extensively with demineralized water. This general procedure was applied to prepare cross-linked chitosan flakes at four particle sizes: G1 $< 125\ \mu m <$ G2 $< 250\ \mu m <$ G3 $< 500\ \mu m <$ G4 $< 710\ \mu m$.

The thiourea grafting was performed in a two-step procedure: (a) thiourea was reacted with glutaraldehyde for 16 h, and (b) then the mixture was contacted with chitosan for 72 h. After filtration, the sorbent was rinsed several times with water and dried at about 50°C overnight.

The following nomenclature was used for the description of the sorbents:

GCC-a:b → Glutaraldehyde cross-linked chitosan 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), “b” g of thiourea, and “c” g of chitosan (in 20 · “c” mL of water).

Experimental Procedure for Metal Ion Sorption

Palladium and platinum solutions were prepared from palladium chloride ($PdCl_2$) and dihydrogen hexachloroplatinate (H_2PtCl_6) purchased from ChemPur (Germany). For the studies of the influence of chloride/sulfate ions, NaCl and Na_2SO_4 salts were added in solid form to these solutions. The pH of each solution was controlled using either hydrochloric acid or sulfuric acid, and sodium hydroxide concentrated solutions (5 M). The pH was kept constant during the sorption step, with the exception of the studies on the optimization of the sorption pH.

For sorption isotherms, known volumes of metal ion solutions (100 mL) at fixed concentrations were contacted with varying sorbent quantities (5 to 30 mg, wet mass) at room temperature (20°C ± 1°C). After 3 days of agitation in a reciprocal shaker, the solutions were filtered through 1.2-μm membranes and the filtrates were analyzed using the $SnCl_2$/HCl spectrophotometric method (using a SHIMADZU 1601 UV-Visible spectrophotometer, Japan) (15) or alternatively, by using inductively coupled plasma analysis (JOBIN-YVON JY36, France). Control experiments showed that no sorption occurred on either the glassware or the filtration systems. The sorption capacity, or metal ion concentration in the sorbent, was obtained using a mass balance equation and was expressed as milligrams of metal per gram of sorbent, without reference to actual chitosan content in the sorbent, which is, in turn, dependent on the cross-linking ratio and the degree of substitution.

A standard procedure was applied for the study of sorption kinetics (8). One liter of metal ion solution at fixed pH was mixed with a fixed amount of sorbent in a jar-test agitated system (240 rotations per minute). Five-milliliter samples were then withdrawn at specified times and filtered through a 1.2-μm membrane and analyzed as previously specified.

For the study of sorption in continuous sytems, a column with an internal diameter of 7 mm and a column depth of 43 mm was filled with 0.5 g of sorbent and was fed with 5 L of a palladium solution (inlet concentration, 49 mg Pd L^{-1}) at pH 2 (controlled with hydrochloric acid). The flow rate was 59 mL/h (corresponding to a superficial velocity of 1.5 m h^{-1}, or 0.9 bed volume (BV) h^{-1}).

Sorbent Characterization

FTIR Analyses

Solid samples were ground with infrared-grade KBr in an agate mortar. An aliquot of 400 mg of this material was taken with a 0.1 wt % sorbent 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; and resolution 4 cm^{-1}).

SEM-EDAX Analyses

Dry samples of free or saturated polymers were embedded in a synthetic resin, EPOTEK 301 (four parts glue and one 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 μm, 2/6 μm, 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 an emulsion lubricant, DP, 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_a bands of carbon, oxygen, chlorine, and sulfur were detected at 0.27, 0.53, 2.62, and 2.31 keV respectively; the M_a bands of platinum and palladium were detected at 2.07 and 2.84 keV, respectively.

RESULTS AND DISCUSSION

Characterization of Modified Sorbents

FTIR Analyses

Chitosan is a heteropolymer made up of glucosamine and acetylglucosamine units, and its FTIR spectrum is characterized by several amine andamide bands in the 1200-1800 cm^{-1} range of wavenumbers. These bands are the most representative among several other bands (glucose ring for example) (16). The >N-H stretching band of amine that is detected at 1580-1605 cm^{-1} is shifted to 1550-1480 cm^{-1} when amine functions are protonated. The amide I band (conjugation of →C-O stretching mode with -N-H deformation mode) is detected at 1650 cm^{-1}, while the amide II band (conjugation of >N-H deformation mode with >C=N- deformation mode) appears at 1550-1590 cm^{-1}. The amide III band which is identified at 1300 cm^{-1}, represents the conjunction of the >N-H deformation mode with >C=O and >C=N stretching modes. The glutaraldehyde cross-linking of chitosan results from a Schiff's reaction between amine functions and aldehyde groups, and this reaction is followed by the appearance of new bands. The unreacted C=O carbonyl groups appear at 1730-1710 cm^{-1}, while the imine bond, -C=N, which is representative of the chemical reaction, is identified in the 1690-1640 cm^{-1} region. The glutaraldehyde cross-linking involves a decrease in the number of free amine groups, while the amide II band appears under the form of a small shoulder.

Thiourea grafting is obtained by a first reaction between the amine groups of the sulfur compound and aldehyde moities of the cross-linker. The reaction of this intermediary compound with chitosan through the chemical reaction between aldehyde ends and amine groups of the biopolymer is thus expected to give a polymer with similar bands: aldehyde, amine and imine function, in addition to the typical sulfur bands, which are usually detectable at 1300-1050 cm^{-1} (>C=S stretching) and1590-1420 cm^{-1} (combination of >C=S and →C-N stretching vibrations) (17). However, these bands are superimposed over that of the raw material and that of glutaraldehyde cross-linked chitosan, and thus are difficultly detectable. Figure 1 shows some FTIR spectra obtained with these sorbents (GCC and TGC) after being in contact with either hydrochloric or sulfuric acids. As expected, the superimposition of sulfur-type bands and that of imine and carbonyl groups over those of the raw material makes the chemical modifications difficult to detect. For the thiourea derivative, the intensity of the carbonyl band at 1715 cm^{-1} is decreased as a result of the reaction between aldehyde moities and amine groups of thiourea; the number of free carbonyl groups is diminished. When the sorbents are treated with H_2SO_4, the protonated amine groups for both TGC and GCC are detected, while after HCl treatment, their bands appear only with TGC compounds.

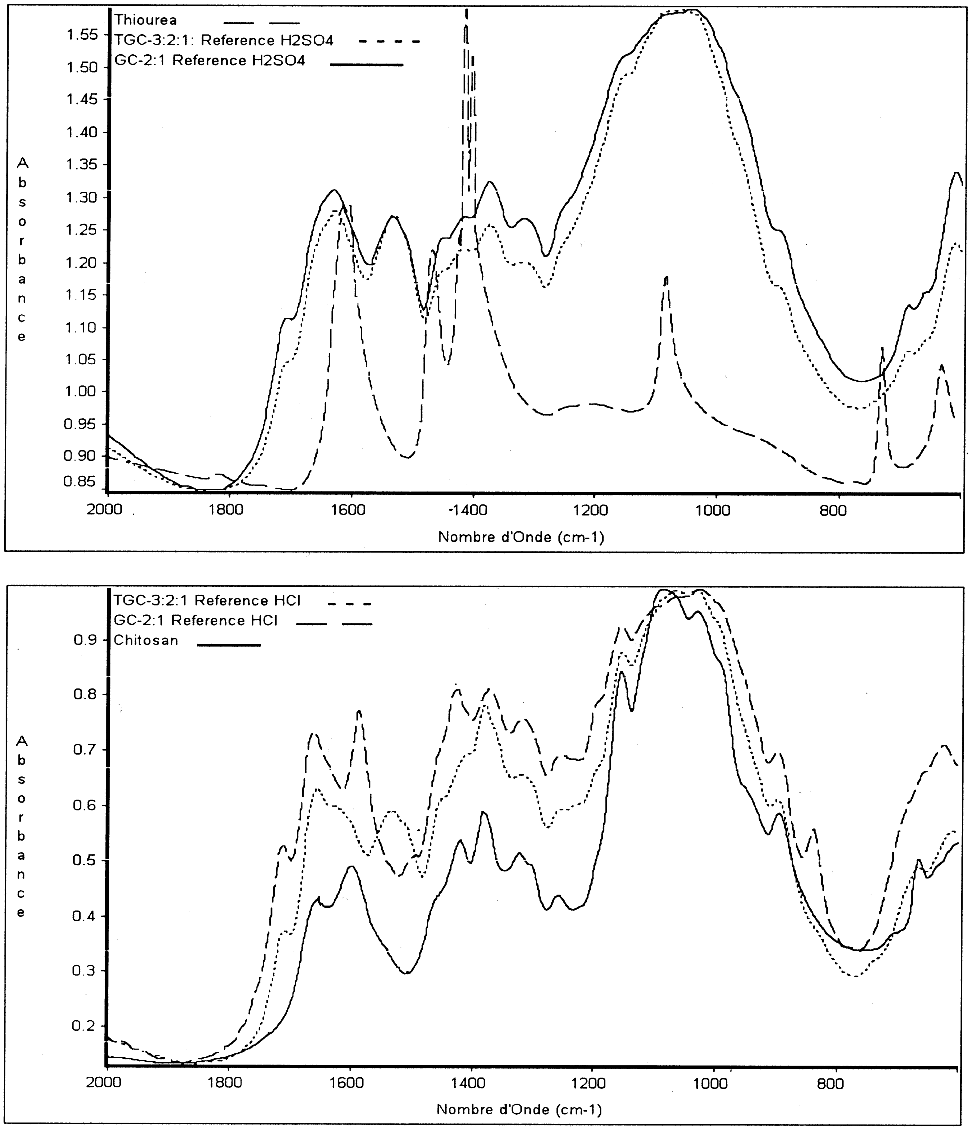

Figure 1. FTIR spectra of chitosan, thiourea, GCC-2:1, and TGC-3:2:1 after contact with either HCl or H_2SO_4. (nombre d'onde = wavenumber).

Similar FTIR analyses were performed on saturated sorbents. Despite the high concentration of platinum sorbed on the biopolymers, no significant differences were detected on the spectra, probably because platinate interactions with the sorbent involve chemical linkages that overlap with the bands of the raw materials.

SEM-EDAX Analyses

Figure 2 shows the distribution of C, O, S, Cl, and Pd (and Pt, respectively) in TGC saturated with Pd (and Pt, respectively) in hydrochloric acid solutions.

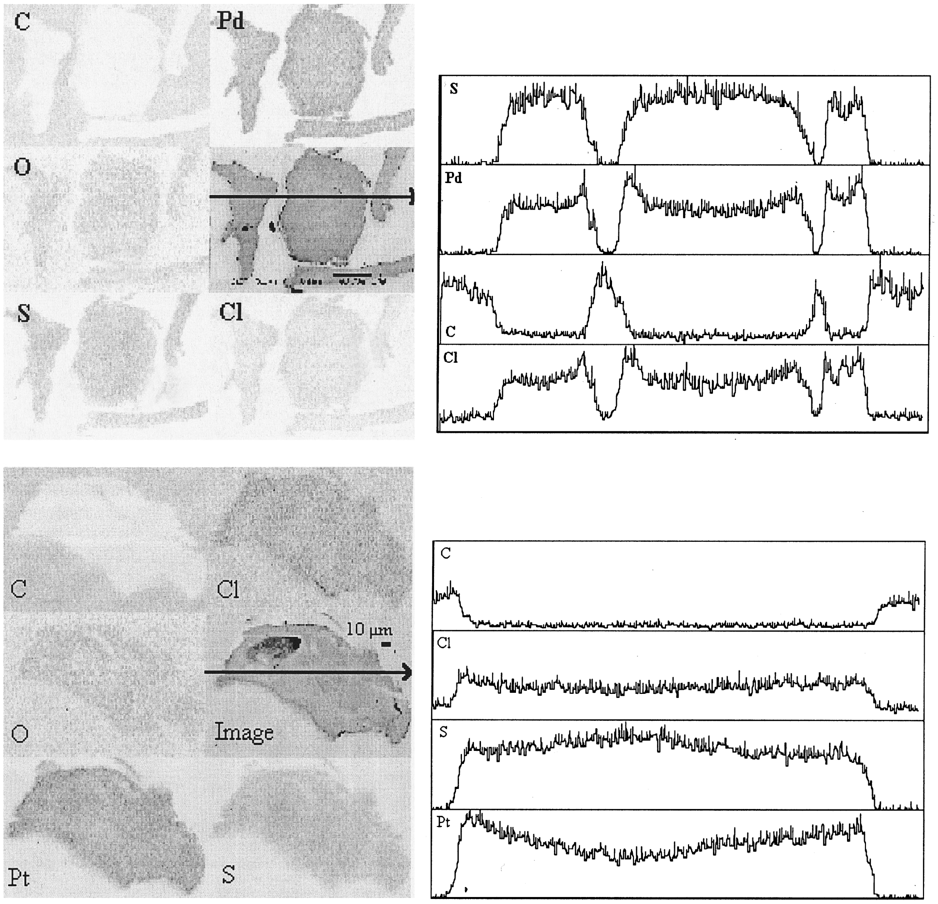

Figure 2. SEM-EDAX analyses of thiourea derivative of chitosan after (a) platinum (TGC-3:2:1) and (b) palladium (TGC-1:1:1) sorption.

This figure indicates that sulfur is distributed homogeneously throughout the sorbent; the intensity of the band is only slightly higher at the center than at the periphery of the particle. The thiourea grafting may be considered as homogeneous over the particle. Both chloride and palladium (or platinum) follow a reverse trend, showing a slightly lower density at the center of the particle. The correlation between these elements (Pd and S, Pt and S) may be attributed to the sorption of chloro-metal species. Even though a gradient exists in the distribution of metal between the periphery and the center of the particle, the difference is not so as marked as that observed for other metal ions (5). The diffusion that was suspected to control uranium sorption in chitosan does not control PGM sorption. Previous work on the sorption of several metal ions on chitosan (5, 18) have correlated uranium and molybdate sorption to the appearance and predominance of polynuclear hydrolyzed species. In these cases, the large ionic size of the metal ions controls, owing to steric hindrance mechanisms, the accessibility to internal sites and, in turn, both kinetic and equilibrium performances. In the case of mononuclear platinate and palladate species, these limitations are not active in controlling sorption efficiency.

Optimization of pH

Figures 3 and 4 show the influence of pH on sorption equilibria for platinum and palladium, respectively. For platinum, the maximum sorption is obtained at pH levels of. ≈ 2.5 with GCC sorbent in HCl solutions. The log-log form of distribution coefficient versus proton concentration gives two linear distributions: below pH 2-2.5, the data lie on a straight line with a slope that approaches +2, while above this pH level, the data lie on a straight line with a slope that ap-

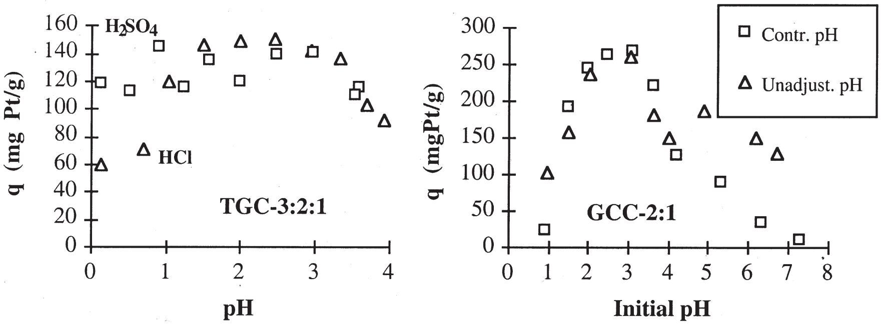

Figure 3. pH optimization for platinum sorption on TGC-3:2:1 (hydrochloric acid (△) and sulfuric acid (□)) and GCC-2:1 (HCl media).

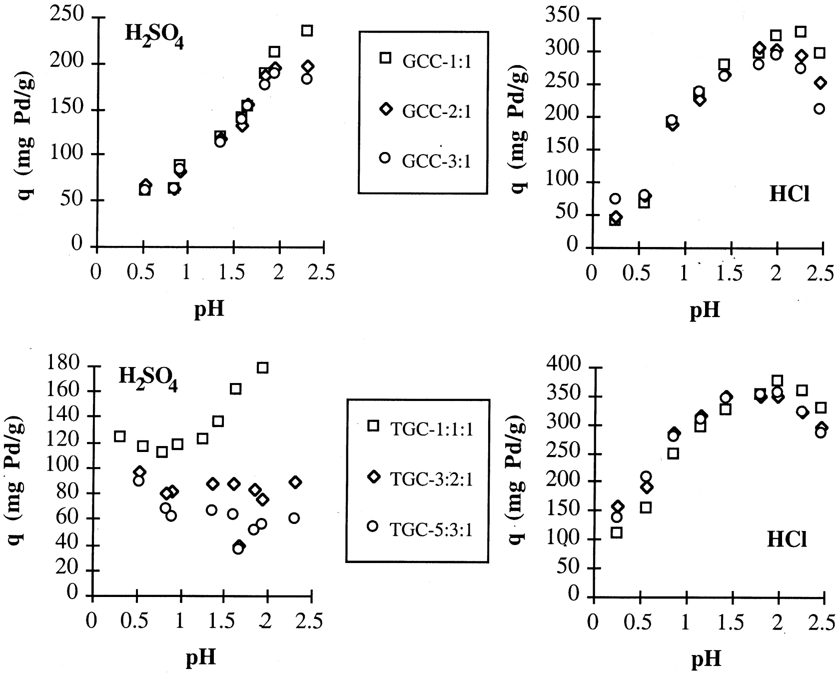

Figure 4. Influence of pH on palladium sorption capacity (pH controlled with sulfuric acid) (C_o: 25 mg L^{-1}; sorbent dosage: 80 mg L^{-1}, acid added (concentration): 0.001-0.0025-0.005-0.01-0.025-0.05-0.1-0.25-0.5 M).

proaches -1 (19). In sulfuric acid solutions, the lack of chloride anions (only brought into the solution by the platinum salt) and the presence of competitor anions are expected to decrease sorption properties. Experimental data (not shown) have demonstrated that sorption capacities were decreased at least three times at pH 2 in sulfuric acid solutions as compared with those measured in hydrochloric acid solutions.

Thiourea complexation with metal ions in solution is almost independent of pH, so a lower sensitivity to pH is expected (20). Indeed, Pesavento and Biesuz (21) used the Gibbs-Donnan model for ion-exchange resins to describe and predict the sorption equilibria of metal ions on chelating resins. The results indicate that they are characterized by their intrinsic complexation constants, which are related to the complexation constants in solutions with ligands having structures similar to those of the active groups in the resin. In the case of TGC, the sorbent may be characterized as a dual ion-exchange and chelating resin. Consequently, the chelating part of the polymer is less sensitive to a competition effect than GCC, while the ion-exchange part of the polymer is influenced by the presence of competitor anions. These hypotheses may explain the intermediary behavior and sensitivity of the sorbent to the composition of the solution.

Thiourea grafting improves sorption properties in sulfuric acid media: sorption capacities are comparable to those obtained in hydrochloric acid solutions. Moreover, it seems that the sorption capacity is less sensitive to solution pH. For palladium, experiments were performed under similar conditions and results may be compared. The sorption capacity increases with pH until a level of 2-2.5 is reached; above this limit, the palladium sorption capacity decreases again with a steeper slope as it did with platinum. Hydrochloric acid solutions are characterized by a higher sorption capacity (about 1.5- to 2-fold) than that in sulfuric acid solutions. Thiourea grafting increases sorption capacity by 15% in comparison with GCC sorbent in HCl solutions, while the chemical modification in sulfuric acid solutions, is followed by a 15-20% decrease in comparison with cross-linked chitosan.

Increasing the substitution ratio (as given by the increased amount of glutaraldehyde and thiourea) decreases the sorption capacity for both GCC and TGC compounds, especially at a pH level above 2. In the case of TGC sorbents and sulfuric acid solutions, increasing the amount of glutaraldehyde and thiourea induces a significant decrease in the sorption capacity in the entire pH range. This surprising result is difficult to interpret and could be attributed to a loss in the stability of thiourea grafting. Assuming this hypothesis, the release of thiourea in the solution involves the complexation of palladium by thiourea and then the metal anions are less adsorbable: the competition between soluble ligands and immobilized ligands induces a decrease in sorption performance.

At low pH levels, the large excess of chloride involves a strong competition between chloride anions and hexachloroplatinate (tetrachloropalladate) anions for sorption on protonated amine groups. At higher pH levels, the decrease in sorption properties is attributed to a low protonation of the sorbent and to a low concentration of adsorbable species. At low chloride concentration, the equilibrium distribution of platinate (palladate) species may be less favorable to sorption, chelation, and ion exchange. The influence of the pH, as well as that of the acid used for pH control, is much more marked for palladium than for platinum. This result may be correlated to the differences in the aqueous chemistry of these metals. While platinum readily forms the most adsorbable hexachloroplatinate species, palladium speciation is much more sensitive to the pH, the concentration of metal, and the concentration of chloride (22). A large number of chloro-palladate species appears in solution as a function of these experimental parameters; some of these species are not adsorbable (ionic charge). Figure 5 presents some examples of palladium speciation with selected experimental conditions according to the constants cited by Baes and Mesmer (22), using the HYDRAQL computer program for metal ion equilibrium in solutions (23).

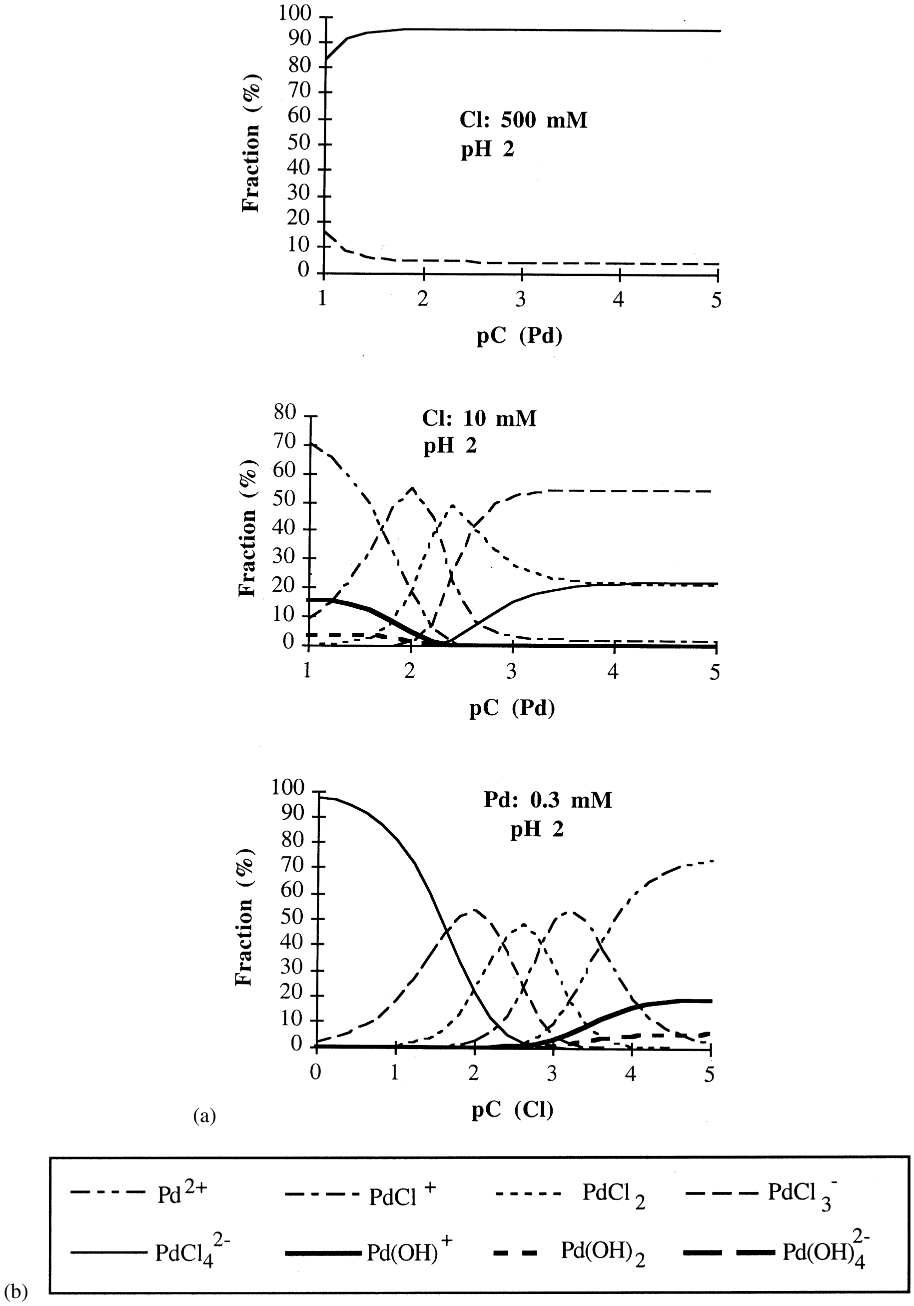

Figure 5. Speciation diagrams for palladium as a function of pH and chloride and palladium concentrations.

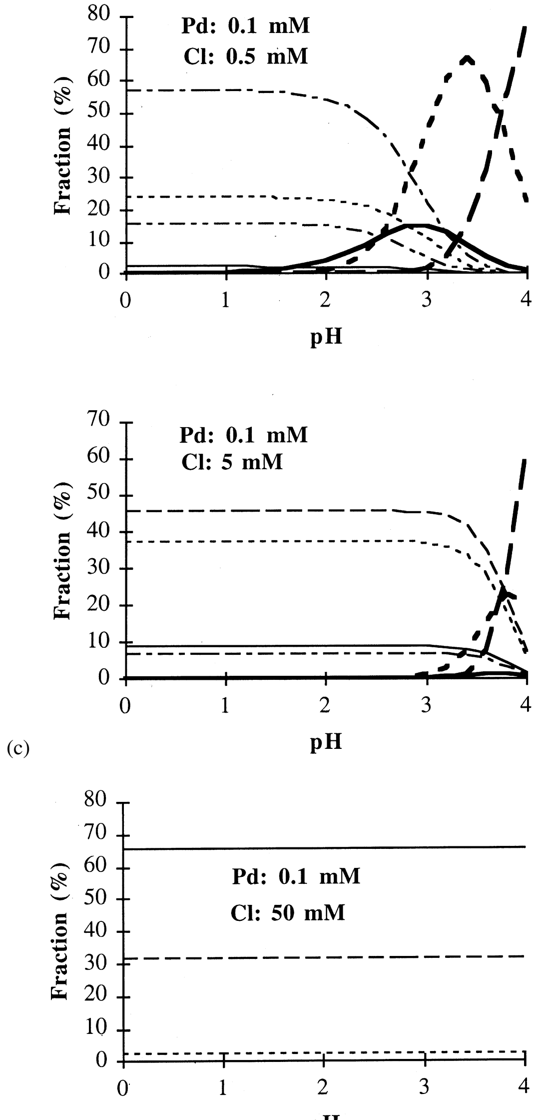

Figure 5. Continued.

The unfavorable effect of sulfuric acid on metal ion sorption on chitosan has been previously discussed by Kawamura et al. (24) for mercury. Two reasons were proposed to explain the decrease in sorption properties in sulfuric acid solutions in comparison with hydrochloric acid solutions: (a) mercury does not form a complex with sulfate, and the $HgCl_2$ form is not ionized by sulfate ions; and (b) sulfate ions saturate protonated amine groups. On the other hand, in hydrochloric acid solutions $HgCl_2$ is ionized in the form $HgCl_3^-$, which is adsorbable on protonated groups. In the case of platinate and palladate sorption, similar mechanisms are expected to occur. The explanation recently given by Baba et al. (25) to interpret the influence of pH on copper sorption in presence of ammonium salt using a new chelating derivative of chitosan was that amine complexation of copper leads to the formation of a non adsorbable species $[Cu(NH_3)_4^{2+}]$.

Influence of Competitor Anions on Platinum Sorption

Figure 6 shows platinum sorption capacity as a function of the competitor anion concentration (NaCl being added to the solution whose pH was adjusted with sulfuric acid, and Na_2SO_4 being added to the solution whose pH was controlled with hydrochloric acid). In HCl solutions, increasing the concentration of sodium sulfate involves a strong decrease in sorption capacity on GCC sorbent, while the variation in sorption capacity with TGC does not exceed 10%. This result confirms the conclusion given in the preceding section namely that chelation reaction involved in platinum sorption on TGC allows the influence of sulfate to be reduced.

On the other hand, in H_2SO_4 solutions, adding chloride to the solution improves sorption performances, when the chloride addition is below 10 mM. Above this value, the chloride ions act as competitor anions; however, the reduction in sorption capacities is mainly detectable on GCC sorbent, while for TGC, the addition of chloride to a 0.5 M concentration induces a decrease in sorption capacity that is negligible (close to the sorption level reached in sulfuric acid solution free of additional chloride ions).

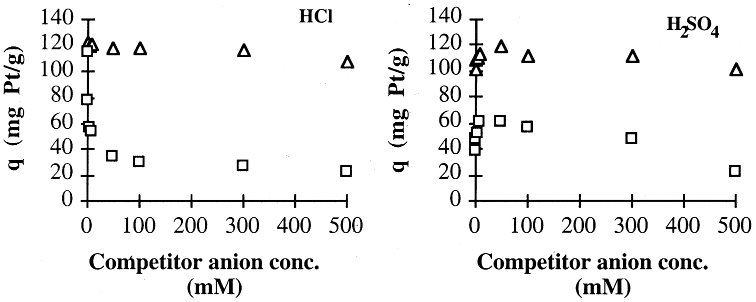

Figure 6. Influence of competitor anions Na_2SO_4 (and NaCl, respectively) on platinum sorption at pH 2 in HCl-controlled and H_2SO_4-controlled pH solution, respectively using TGC-3:2:1 (△) and GC-2:1 (□). Sorbent dosage: 15 mg/200 mL and C_o: 9.4 mg L^{-1}.

These results confirm that platinum sorption is sensitive to the speciation of metal ions in solution. The presence of chloride involves the formation of adsorbable platinum complexes and allows the unfavorable effect of sulfate to be reversed.

Influence of the Acid Used for pH Control on Sorption Isotherms

The study of the influence of the acid media may be completed by the determination of sorption isotherms: the increase in metal concentration can change the speciation of metal ions and, in turn, the reactivity with the sorbent. Figures 7 and 8 show some sorption isotherms obtained at pH 2 with GCC and TGC sorbents in both sulfuric acid and hydrochloric acid solutions.

In HCl solution, TGC and GCC sorbents exhibit comparable levels for platinum sorption The difference in the maximum sorption capacity does not exceed 10% for GCC in comparison with TGC; the affinity coefficient, which is a function of the initial slope of the sorption curve, is only slightly decreased in the case of GCC sorbent. However, the differences are much more marked in the case of sulfuric acid solutions. Surprisingly, the maximum sorption capacity tends to be a value comparable to that obtained in HCl solutions for TGC, while for GCC the sorption is strongly decreased by sulfuric acid. The affinity coefficient is also strongly diminished, especially for GCC sorbent.

The influence of the acid used for pH control has been studied for palladium using GCC sorbent. The sorption isotherms exhibit shapes similar to those obtained with TGC on platinum sorption. The maximum sorption capacity is com-

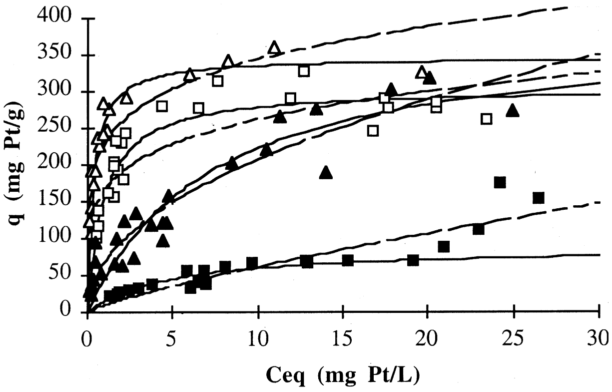

Figure 7. Influence of the acid used for pH control (open symbols, HCl; closed symbols, H_2SO_4) at pH 2 on platinum sorption isotherms using either TGC-3:2:1 (△) or GCC-2:1 (□). Solid lines: Langmuir modeling; dashed lines: Freundlich modeling.

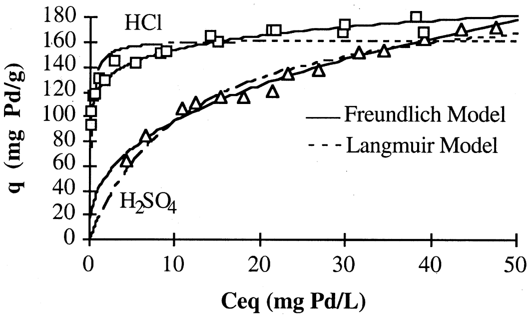

Figure 8. Palladium sorption isotherms on GCC-2:1 at pH 2 ; influence of the acid used for pH control.

parable for both acid solutions, while the affinity coefficient is significantly reduced in sulfuric acid solutions.

The modeling of sorption isotherms was performed with the usual Langmuir and Freundlich equations (Table 1). The results show that for platinum sorption, in hydrochloric acid solutions, the Langmuir equation fits the experimental data better than the Freundlich model, while in sulfuric acid solutions, sorption isotherms are slightly more accurately described by the Freundlich model. For palladium, in the case of GCC sorbent, for both sulfuric and hydrochloric acid solutions, the Freundlich model gives a better correlation of experimental data than does the Langmuir equation. The Langmuir equation assumes a monolayer sorption, with no lateral interactions between sorbed molecules, and a homogeneous distribution of sorption sites and sorption energies, while the empirical Freundlich isotherm supposes the monolayer sorption to be heterogeneous (in sorption energies and sites distribution) and possible lateral interactions between sorbed molecules. Assuming that these physical hypotheses are verified, the results would indicate that in hydrochloric acid solutions, platinum sorption is energetically homogeneous for both GCC and TGC. This result is surprising for TGC sorbent, for which platinum is expected to occur via two different mechanisms - ion exchange and chelation. On the other hand, in sulfuric acid, sorption does not occur with the same mechanism or with different energies; thus the heterogeneities could result from the interferences of sulfate anions with platinum or with sorption sites. For palladium, with GCC, the heterogeneities in sorption energies (indicated by the best fit of experimental data by the Freundlich equation) may result from the changing distribution of chloro-palladate species.

Table 1. Coefficients of the Langmuir and the Freundlich Models for Platinum and Palladium Sorption Isotherms $^{(a)}$

				Langmuir model			Freundlich model		
Sorbent	Part. size	Acid	Metal	q_m	b	MSR	k	n	MSR
TGC-3:2:1	G2	HCl	Pt	346.2	3.0	23.7	229.2	5.68	35.0
GCC-2:1	G2	HCl	Pt	304.1	1.08	23.7	166.7	5.08	36.4
TGC-3:2:1	G2	H_2SO_4	Pt	386.9	0.135	31.9	69.0	2.09	28.1
GCC-2:1	G2	H_2SO_4	Pt	288.1	0.208	28.4	9.87	1.26	16.7
GCC-2:1	G2	HCl	Pd	162.6	5.59	11.0	122.7	9.76	4.2
GCC-2:1	G2	H_2SO_4	Pd	204.8	0.09	7.5	40.5	2.64	4.3
GCC-2:1	G1	HCl	Pt	250.4	1.05	20.5	132.4	5.19	19.1
GCC-2:1	G3	HCl	Pt	272.7	1.17	26.0	NS	NS	NS
GCC-2:1	G4	HCl	Pt	279.5	1.21	22.6	148.4	5.10	30.5
GCC-2:1	G1	HCl	Pd	181.3	1.86	13.7	117.1	6.98	5.18
GCC-2:1	G2	HCl	Pd	162.6	5.59	11.0	122.1	9.76	4.17
GCC-2:1	G3	HCl	Pd	196.9	0.70	9.1	105.9	5.55	6.96
GCC-2:1	G4	HCl	Pd	179.7	1.66	13.0	115.0	6.90	4.81
TGC-1:1:1	G1	HCl	Pd	291.9	3.94	36.4	177.5	6.41	48.1
TGC-1:1:1	G2	HCl	Pd	277.5	2.77	28.0	168.9	6.31	39.6
TGC-1:1:1	G3	HCl	Pd	214.5	1.04	17.5	114.2	5.59	29.7
TGC-1:1:1	G4	HCl	Pd	186.0	2.77	13.9	111.5	6.10	15.7

q_m: maximum sorption capacity at monolayer coverage (mg g^{-1}); b: Langmuir coefficient (L mg^{-1}); k and n: Freundlich constants ($mg^{1-1/n}$ $g^{-1}L^{1/n}$ and dimensionless, respectively); MSR: mean square deviation obtained from $\left[\frac{1}{n}\sum_{i=1}^{n}[(X_{\mathrm{exp.},i} - X_{calc.,i})^2]\right]^{1/2}$

Influence of Particle Size on Sorption Isotherms

Uranyl sorption was controlled by the size of the chitosan particle (5). A similar trend was observed for molybdate sorption using glutaraldehyde cross-linked chitosan (8), while sorption capacities for raw chitosan flakes were independent of the particle size (26). The expanding of the polymer network, resulting from gel formation, enhances molybdate sorption on chitosan gel beads and makes sorption capacities independent of sorbent size. Diffusion restrictions are considered to be the main reason for such limitations; the diffusion of large molecules is sterically controlled by the ratio between the solute size and the pore size of the sorbent (27). In the case of cross-linked chitosan particles, the sorption of palladium or platinum is not influenced by this experimental parameter (Figure 9); it may be due to the low ionic size of their mononuclear species. On the other hand, for the thiourea derivative, the particle size influences sorption capacities, especially on the equilibrium plateau, while the affinity coefficient (initial slope of isotherm curves) is almost unchanged. The decrease in sorption capacity with particle size is not proportional to particle size or external particle surface:. This may be explained by (a) the large distribution in each size class and/or (b) the shape of sorbent particles. For calculations, the particles are assumed to be spherical, while under an optical microscope, the sorbent particles appear as flakes. While for GCC sorbents, sorption occurs throughout the entire mass of the sorbent material, sorption in the case of TGC may occur in the external layer of the sorbent and adsorbed metals do not diffuse completely throughout the particle. It could explain the small gradient in the distribution of palladium and platinum in TGC, as seen in Fig. 2. For each system appearing in Fig. 9, the sorption isotherms are accurately described by the Langmuir equation (Table 1).

Influence of the Acid on Platinum Sorption Kinetics

Figure 10 presents kinetics for platinum sorption at pH 2 on both GCC and TGC sorbents. As expected, the equilibrium concentration is almost identical for TGC and GCC in HCl solutions and comparable to that obtained in H_2SO_4 solu-

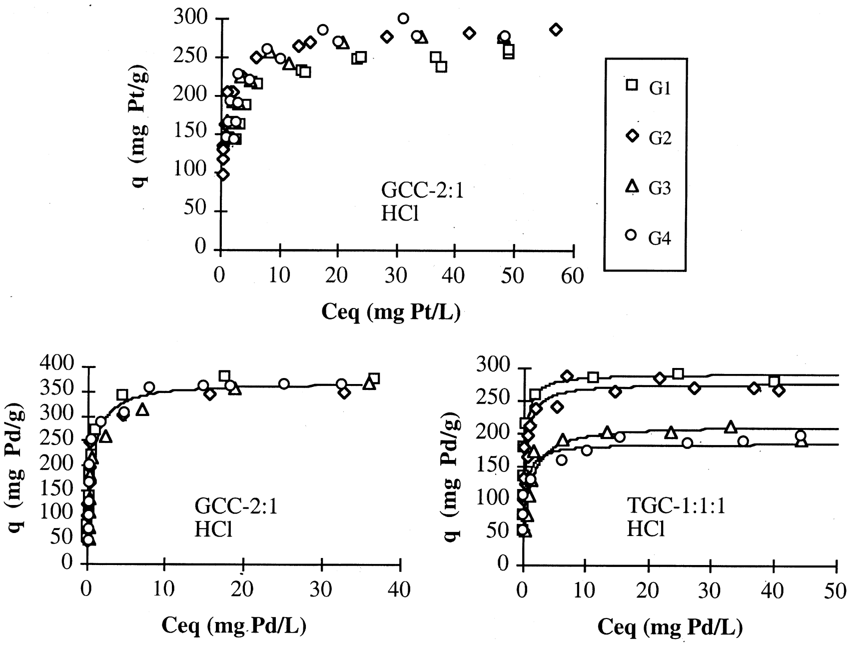

Figure 9. Influence of particle size on platinum sorption in HCl solutions.

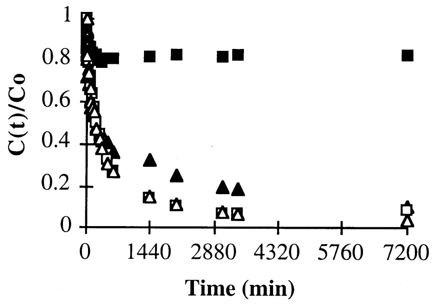

Figure 10. Platinum sorption kinetics at pH 2 using TGC-3:2:1 (△/▲) and GC-2:1 (□/■) (C_o: 10 mg L^{-1}, sorbent dosage: 50 mg L^{-1}, for HCl-controlled pH solution (open symbols); sorbent dosage: 100 mg L^{-1} for H_2SO_4-controlled pH solutions (closed symbols)).

tions for the thiourea derivative (except that twice the amount of sorbent is used). On the other hand, in sulfuric acid solutions, sorption is strongly decreased for the GCC compound, but the time required to reach equilibrium is shorter under these experimental conditions.

The sorption curves overlap perfectly for TGC and GCC sorbents in HCl. However, in H_2SO_4 solution, TGC exhibits a kinetic curve quite similar to the other curves initially but slightly diverges at longer times (greater than 1 day). The initial section of the curve is usually controlled by external diffusion, while the second section is governed primarily by intraparticle diffusion. Diffusion is not affected by the type of sorbent. The grafting of thiourea groups does not change external diffusion or intraparticle diffusion, although complementary linkages may be formed between polymer chains; the low ionic size of platinum can explain this weak effect. With sulfuric acid solutions, it is necessary to introduce a sorbent concentration twice that used for HCl solutions in order to obtain a comparable decay curve. Sulfuric acid solutions slightly increase the time required to reach equilibrium with the thiourea derivative. However, the mass transfer rate seems to be mainly influenced by the low affinity of the sorbent for metal ions in this unfavorable solution.

Influence of Particle Size on Sorption Kinetics

Despite the weak effect of particle size on sorption equilibria, it may influence mass transfer (7, 28). Figures 11 and 12 shows the sorption kinetics for different particle sizes with GCC and TGC, respectively, in either HCl or H_2SO_4 solution.

With GCC-2:1, in hydrochloric acid solution (Fig. 11), for both platinum and palladium, the sorption kinetics are comparable for the four size fractions. Even though a small decrease in the time required to reach equilibrium is observed

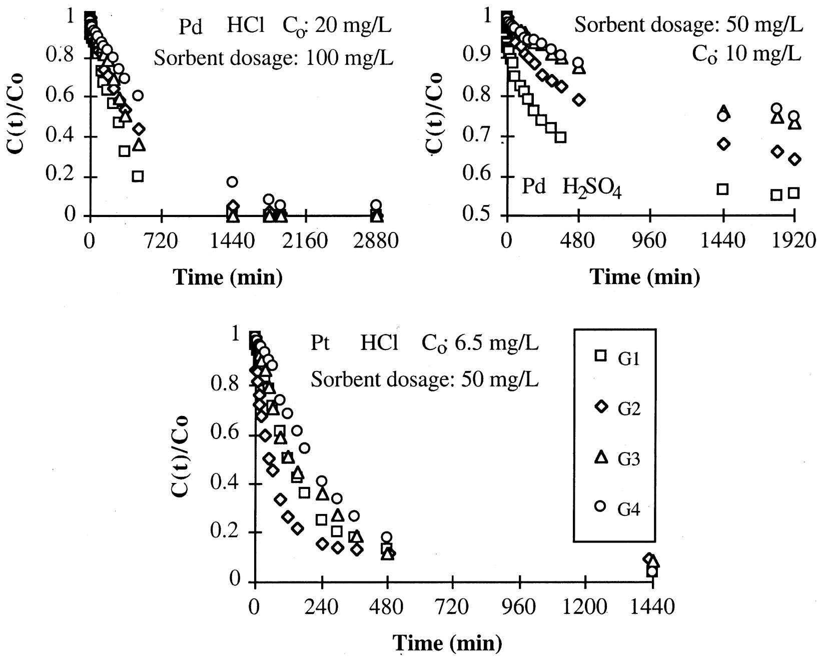

Figure 11. Influence of particle size on platinum/palladium sorption kinetics on GCC-2:1 at pH 2.

as the size of the sorbent decreases, the differences are not as marked as they are with other metal anions such as molybdate and vanadate (8). The differences in the sorption capacities of these metal anions may be related to the differences in their chemistry and their ability (or inability) to form polynuclear species, as pre-

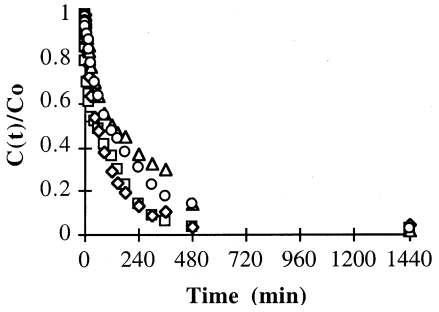

Figure 12. Influence of particle size on palladium sorption kinetics by TGC-1:1:1 at pH 1.3 (HCl solutions). Symbols : see Fig. 11; sorbent dosage: 55 mg L^{-1}; C_o: 18.7 mg L^{-1}).

viously stated. With TGC, in hydrochloric acid solutions, palladium sorption kinetics are almost independent of the particle size, even at equilibrium (Fig. 12). This result seems to be in contradiction with previous results relative to sorption isotherms. However, the palladium sorption isotherms have shown that the differences between the various size fractions are significant primarily at high residual palladium concentrations, while the sorption capacities are comparable in the initial sections of the curves. For kinetics, under selected experimental conditions, the sorbent dosage is sufficiently high to remove palladium almost completely: thus differences at equilibrium are not very marked. Under these conditions, the affinity of the sorbent for palladium is not a controlling parameter and the similar sorption kinetics for differing particle sizes indicates that diffusion is not a limiting parameter.

In sulfuric acid solution (Fig. 11), palladium sorption on GCC-2:1 is influenced by the particle size in the initial section of the curve, while the equilibrium concentration is independent of this parameter (Fig. 9). The differences may be attributed, in part, to diffusion resistance (external and intraparticle diffusion) and to the low affinity of cross-linked chitosan for palladium in sulfuric acid solutions.

Palladium Sorption in Fixed-Bed Column System and Desorption

Figure 13 shows the breakthrough curve obtained at pH 2 with a synthetic solution using GCC-2:1. The breakthrough in fixed-bed systems occurs at ≈ 900-950 BV. The concentration in the sorbent reaches 149 mg g^{-1} at the breakthrough volume, while at the saturation volume (≈ 1550-1600 BV) the sorption capacity

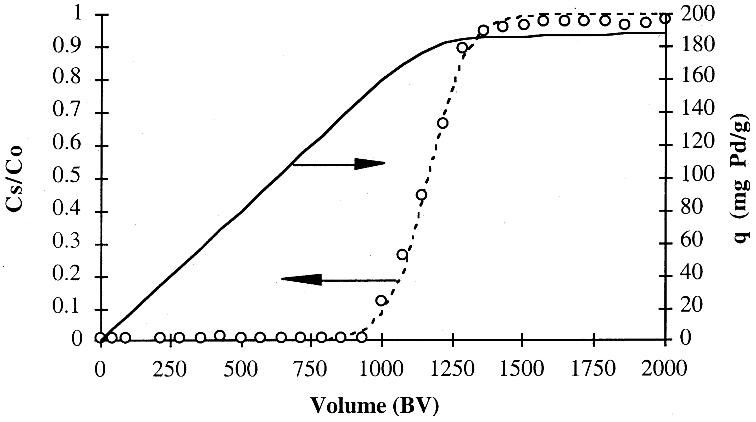

Figure 13. Breakthrough curve for palladium sorption on GCC-2:1 at pH 2.

approaches 189 mg g^{-1}. This sorption capacity at saturation is comparable to that obtained at equilibrium in batch systems, when comparable concentration and pH values are used. The steep slope of the breathrough curve confirms that palladium sorption on chitosan cross-linked with glutaraldehyde is not strictly controlled by intraparticle diffusion. A lower slope would indicate that the mass transfer zone is large as a consequence of a slow accessibility to internal sites (it may result from internal diffusion restrictions).

The feasability of using such a system for the treatment of industrial effluents is constrained by the necessity to desorb metal ions and to recycle the sorbent. Preliminary work using concentrated HCl solutions (2, 5, and 11 M) has shown that mixing 0.5 g of exhausted sorbent (containing $\approx$ 200 mg Pd g^{-1}) with 16 mL of eluent for 16 h in agitated systems allows desorption yields of 71, 79, and 85%, respectively, to be achieved after two desorption steps.

CONCLUSIONS

Although chitosan is efficient at removing palladium from both synthetic and pure acidic solutions, its sorption properties are strongly decreased by the presence of competitor anions. Modification of the ion-exchange resin to a chelating resin, via the grafting of sulfur compounds, improves sorption capacity and reduces the influence of pH and competitor anions.

Sorption kinetics are fast in comparison to those of some other metal anions, but a 2-day period is necessary to reach final equilibrium. More than 90% of the total sorption is achieved within the first 6 h of contact.

The grafting of sulfur compounds through glutaraldehyde linkage reveals an interesting method for improving sorption properties for platinum group metals (PGM). However, the thiourea derivative of chitosan seems to be more useful for platinum recovery than for palladium sorption; the enhancement of sorption properties is more significant for platinum. The selectivity is also an important criterion to be used for the selection of a sorbent for platinum and palladium recovery, PGMs are frequently present in a mixture, or may occur in the presence of other metals. The selectivity between palladium and platinum is currently being investigated and preliminary results indicate that palladium sorption is decreased to a lesser extent by the presence of platinum than is platinum sorption by the presence of palladium.

The dynamic sorption of palladium in column systems confirms these preliminary results obtained by using synthetic solutions. Even though the complete recovery of palladium from exhausted sorbent was not achieved, a concentrated solution (11 M) allowed more than 85% of sorbed palladium to be eluted. It appears difficult to reuse the sorbent for a number of sorption/desorption cycles. Palladium may be also recovered by a destructive procedure, including burning or mineralization of chitosan (in hydrogen peroxide solution followed by an acidic treatment, for example).

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