

Platinum and Palladium Sorption on Chitosan Derivatives

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Abstract: Chitosan is a unique aminopolysaccharide due to its cationic properties in acid media. The protonation of the amino groups induces ion exchange properties which 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, SEM-EDAX were used for the chemical characterization of chitosan substitution, 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 a special attention was paid to the influence of competitor anions. The grafting of sulfur compounds increased sorption capacities and reduced the competition of sulfate and chloride anions. While cross-linked materials sorbed platinum and palladium through anion-exchange, the grafting of sulfur moieties has changed the ion exchange resin to a chelating resin.

Key Words: platinum, palladium, chitosan, sorption isotherms, sorption kinetics, sulfur derivatives.

INTRODUCTION

Palladium and platinum are some of the most expensive metals, however, due to 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 aimed at their recovery from spent catalysts (1). Ion exchange processes as well as liquid/liquid extraction techniques have been investigated, and the latest developments in Platinum Group Metals (PGMs) recovery have concerned impregnated resins (2). However, these processes are usually efficient at removing PGMs from medium to high concentration solutions. Research of alternative sorbents remains a priority in this field of hydrometallurgy. These new sorbents might be efficient at removing PGMs in complex and dilute solutions, available at low cost or easy to recycle.

Chitosan is an aminopolysaccharide extracted by a deacetylation procedure from chitin, the most abundant biopolymer in Nature after 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. It is thus necessary to stabilize it chemically for the recovery of metal ions in acidic solutions. Several processes have been developed to reinforce its stability using crosslinking treatments. The crosslinking can be accomplished with different chemicals such as epichlorhydrin or glutaraldehyde. Glutaraldehyde has been used by several groups for cadmium recovery on chitosan beads (7), and for molybdenum and vanadium sorption (8). Glutaraldehyde crosslinking occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of chitosan to form imine functions (3). However, depending on the extent of the crosslinking reaction and the concentration of glutaraldehyde in the crosslinking bath, some unreacted aldehyde groups remain free on the sorbent, in a pendant fashion. Chitosan has been widely experimented with for the sorption of noble metals, 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.

Muzzarelli and Tanfani (12) have prepared and tested the metal sorption properties of dithiocarbamate chitosan, though 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 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. This bi-functional 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 had shown 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 glutaraldehyde-crosslinked chitosan. The production of the thiourea derivative sorbent was studied in order to optimize sorption properties for PGMs recovery 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 experimented with for platinum and palladium recovery in solutions whose pH were controlled by either sulfuric acid or hydrochloric acid. The study has been performed through the optimization of the pH, the determination of sorption isotherms, and the observation of the influence of competitor anions. The influence of diffusion mechanisms has been

investigated through the study of sorption kinetics, 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 percentage ca. 87 %, defined by FTIR spectrometry (8). The mean molecular weight was measured at 125,000 using a size exclusion chromatography (SEC) method coupled with a differential refractometer and a multi-angle laser light scattering photometer (6). Moisture content of sorbent particles, for both crosslinked and uncrosslinked sorbents, was determined to be ca. 10 %; sorbent masses are expressed on a wet basis except where otherwise noted.

Chitosan Modification

Chemical crosslinking of chitosan was performed by reacting chitosan flakes with glutaraldehyde aqueous solutions with differing concentrations for 24 hours. The crosslinked chitosan particles were rinsed extensively with demineralized water. This general procedure was applied to manufacture crosslinked chitosan flakes at four particle sizes: $G1 < 125 \mu\text{m} < G2 < 250 \mu\text{m} < G3 < 500 \mu\text{m} < G4 < 710 \mu\text{m}$.

The thiourea grafting was performed in a two steps procedure: (a) thiourea was reacted with glutaraldehyde for 16 hours, and then (b) the mixture was contacted with chitosan for 72 hours. 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:

GC-a:b -> Glutaraldehyde crosslinked 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) and "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) and were purchased from ChemPur (Germany). For the studies of the influence of chloride/sulfate ions, NaCl and Na_2SO_4 salts were added in the solid form to these solutions. The pH of the solutions 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 put in contact with varying sorbent quantities (5 to 30 mg wet mass) at room temperature ($20\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$). After 3 days of agitation, in a reciprocal shaker, the solutions were filtered through $1.2\text{ }\mu\text{m}$ filtration membranes and the filtrates were analyzed using the SnCl_2/HCl spectrophotometric method (using a SHIMADZU 1601 UV-Visible spectrophotometer, Japan) (15), or alternatively using ICP analysis (JOBIN-YVON JY36, France). Control experiments showed that no sorption occurred on either glassware or filtration systems. The sorption capacity, or metal ion concentration in the sorbent, was obtained using a mass balance equation, and was expressed as mg Metal g^{-1} sorbent, without reference to actual chitosan content in the sorbent which is in turn dependent on the crosslinking ratio and the degree of substitution.

For the study of sorption kinetics, a standard procedure was applied (8). One L 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 mL samples were withdrawn at specified times and filtered through a $1.2\text{ }\mu\text{m}$ filtration membrane and analyzed as previously specified.

For the study of sorption in continuous systems, a column (internal diameter: 7 mm, column depth: 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⁻¹ (corresponding to a superficial velocity of 1.5 m h⁻¹, or 0.9 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 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 10¹¹ Pa) for 5 minutes. 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: 4 parts glue and one part lubricant. After a drying phase, of 24 hours 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 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 are 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 25kV. The K_α bands of carbon, oxygen, chlorine, and sulfur were detected at 0.27 keV, 0.53 keV, 2.62 keV, 2.31 keV respectively, the M_α band of platinum and palladium were detected at 2.07 keV and 2.84 keV respectively.

RESULTS AND DISCUSSION

Characterization of Modified Sorbents

FTIR Analyses

Chitosan is an heteropolymer made up of glucosamine and acetylglucosamine units, and its FTIR spectrum is characterized by several amine, amide 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 $>\text{N-H}$ stretching band of amine is detected at 1580-1605 cm^{-1} , the band is shifted to 1550-1480 cm^{-1} when amine functions are protonated. The amide I band (conjugation of $\rightarrow \text{C-O}$ stretching mode with $-\text{N-H}$ deformation mode) is detected at 1650 cm^{-1} , while at 1550-1590 cm^{-1} appears the amide II band (conjugation of $>\text{N-H}$ deformation mode with $>\text{C=N}$ -deformation mode). The amide III band is identified at ca. 1300 cm^{-1} and represents the conjunction of the $>\text{N-H}$ deformation mode with $>\text{C=O}$ and $>\text{C=N}$ stretching modes). The glutaraldehyde crosslinking 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: at 1730-1710 cm^{-1} , the unreacted C=O carbonyl groups appear at 1730-1710 cm^{-1} , while the imine bond, $-\text{C=N}$, which is representative of the chemical reaction, is identified in the 1690-1640 cm^{-1} region. The glutaraldehyde crosslinking 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 crosslinker. 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} ($>\text{C=S}$ stretching), 1590-1420 cm^{-1} (combination of $>\text{C=S}$ and $\rightarrow \text{C-N}$ stretching vibrations) (17). However these bands are superimposed to that of the raw material and to glutaraldehyde crosslinked

chitosan, and then 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 to that of the raw material makes the chemical modifications difficult to detect. For thiourea derivative, the intensity of the carbonyl band at ca. 1715 cm^{-1} is decreased as a result of the reaction between aldehyde moieties 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 are detected for both TGC and GCC, while after HCl treatment, their band appears only with TGC compounds.

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 platinite interactions with the sorbent involves chemical linkages which overlap with the bands of the raw materials.

SEM-EDAX Analyses

Figure 2 shows the distribution of C, O, S, Cl and Pd (respectively Pt) in TGC saturated with Pd (respectively Pt) in hydrochloric acid solutions. The figure shows that sulfur is distributed homogeneously through the sorbent: the intensity of the band is only slightly higher at the centre 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 density slightly lower at the centre of the particle. The correlation between these elements (Pd and S, Pt and S) may be attributed to the sorption of chloro-metal species. Though a gradient exist in the distribution of metal between the periphery and the centre of the particle, the difference is not so marked as it is with other metal ions (5): the diffusion which 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 hydrolysed species. In these cases, the large ionic size of the metal ions controls, owing steric

hindrance mechanisms, the accessibility to internal sites and then both kinetic and equilibrium performances. In the case of mononuclear platinate and palladate species, these limitations are not active at controlling sorption efficiency.

pH Optimization

Figures 3 and 4 present the influence of pH on sorption equilibria for platinum and palladium respectively. For platinum, the maximum sorption is obtained at pH ca. 2-2.5 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, data lie on a straight line with a slope which tends to +2, while above pH 2-2.5, data lie on a straight line with a slope which tends to -1 (19). In sulfuric acid solutions, the lack of chloride anions (only brought in the solution by the platinum salt dissolving), and the presence of competitor anions is expected to decrease sorption properties: experimental data (not shown) have demonstrated that sorption capacities were decreased at least 3 times at pH 2 in sulfuric acid solutions in comparison to hydrochloric acid solutions.

Thiourea complexation with metal ions in solution is almost independent of the pH, so a lower sensitivity to pH is expected (20). Indeed, Pesanvento 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. They indicate that they are characterized by their intrinsic complexation constants, which are related to the complexation constants in solutions with ligands having structure similar to that of the active groups in the resin. In the case of TGC, the sorbent may be characterized as a mixed ion exchange and chelating resin. Consequently, the chelating part of the polymer is less sensitive to 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 behaviour 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 that obtained in hydrochloric acid solutions. Moreover it seems that the sorption capacity is less sensitive to solution pH. For palladium,

experiments were performed in similar conditions and results may be compared. Sorption capacity increases with the pH till pH 2-2.5 and above this limit pH, palladium sorption capacity decreases again with a steeper slope as it occurred with platinum. Hydrochloric acid solutions are characterized by higher sorption capacity (about 1.5-2 fold) than that in sulfuric acid solutions. Thiourea grafting increases sorption capacity by 15 % in comparison with GCC sorbent in HCl solutions, while in sulfuric acid solutions, the chemical modification is followed by a 15-20 % decrease in comparison with crosslinked chitosan.

It appears that increasing the substitution ratio (as given by the increased amount of glutaraldehyde and thiourea) involves a decrease in the sorption capacity for both GCC and TGC compounds, especially at pH 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 whole range of pH. 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 performances.

At low pH, 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, the decrease in sorption properties was 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 favourable to sorption, chelation and ion exchange. The influence of the pH, and 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 being not adsorbable (ionic charge). Figure 5 presents some examples of palladium speciation with selected experimental conditions according the constants cited by Baes and Mesmer (22) and using HYDRAQL computer programme for metal ion equilibrium in solutions (23)

The unfavourable effect of sulfuric acid on metal ion sorption on chitosan has been previously cited 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 complex with sulfate and the HgCl_2 form is not ionized by sulfate ions; (b) sulfate ions saturate protonated amine groups. On the opposite 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. Similar explanation was 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: amine complexation of copper leads to the formation of a non-adsorbable species ($\text{Cu}(\text{NH}_3)_4^{2+}$).

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 which pH was adjusted with sulfuric acid, and Na_2SO_4 for solution which 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 conclusions given in the preceding section: chelation reaction involved in platinum sorption on TGC allows the influence of sulfate to be reduced.

On the opposite hand, in H_2SO_4 solutions, adding chloride to the solution improves sorption performances, below a chloride addition of 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 which is negligible (close to the sorption level reached in sulfuric acid solution free of additional chloride ions).

These results confirm that platinum sorption is sensible to the speciation of metal ions in solution: the presence of chloride involves the formation of adsorbable platinum complexes and allows the unfavourable 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 then 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.

For platinum sorption, in HCl solutions, both TGC and GCC sorbents exhibit comparable sorption levels: 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. The differences are much more marked in the case of sulfuric acid solutions. Surprisingly, the maximum sorption capacity tends to 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.

For palladium, the influence of the acid used for pH control has been studied on GCC sorbent. The sorption isotherms exhibit shapes similar to that obtained with TGC on platinum sorption. The maximum sorption capacity is comparable 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). It shows that for platinum sorption, in hydrochloric acid solutions, the Langmuir equation fits experimental data better than the Freundlich model, while in sulfuric acid solutions, sorption isotherms are little more accurately described by the Freundlich model. For palladium, in the case of GCC sorbent, for both sulfuric and hydrochloric acid solutions, the Freundlich gives a better correlation of experimental data than 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 these physical hypotheses being verified, the results would indicate that in hydrochloric acid solutions, for both sorbents, platinum sorption is energetically homogeneous. This result is surprising for TGC sorbent for which platinum is expected to occur via two different mechanisms: ion exchange and chelation. On the opposite hand, in sulfuric acid, sorption does not occur with the same mechanism or with different energies: 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.

Influence of Particle Size on Sorption Isotherms

Uranyl sorption is controlled by the size of chitosan particle, similar trend is observed on molybdate sorption using glutaraldehyde crosslinked chitosan, while for raw chitosan flakes sorption capacities are independent of the particle size. 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:

diffusion of large molecules being sterically controlled by the ratio between the solute size and the pore size of the sorbent (26). In the case of crosslinked chitosan particles, palladium and platinum sorption are not influenced by this experimental parameter (Figure 9), may be due to the low ionic size of their mononuclear species. On the opposite hand, for 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 nor external particle surface: it may be explained by (a) the large distribution in each size class and/or (b) the shape of sorbent particles. For calculations, particles are assumed to be spherical, while under an optical microscope, sorbent particles appear as flakes. While for GCC sorbents, sorption occurs in the whole mass of the sorbent, in the case of TGC sorption may occur in the external layer of the sorbent and adsorbed metals do not diffuse completely in the particle. It could explain the small gradient in the distribution of Pd and Pt in TGC as seen in Figure 2. For each system appearing in Figure 9, the sorption isotherms are accurately described by the Langmuir equation (Table 1).

Influence of the Acid on Pt Sorption Kinetics

Figure 10 presents sorption kinetics at pH 2, for platinum sorption 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 H₂SO₄ solutions for thiourea derivative (but with a double sorbent dosage). On the opposite hand, in sulfuric acid solutions, sorption is strongly decreased for GCC compound, but the time required to reach equilibrium is shorter in these experimental conditions.

Sorption curves perfectly overlap for TGC and GCC sorbents in HCl. In H₂SO₄ solutions, TGC exhibits a kinetic curve quite similar to the other curves in the first initial section of the curve and slightly diverges to the other in the second section. The initial section of the curve is usually controlled by external diffusion, while the second section is mainly governed by intraparticle diffusion. Diffusion is not affected by the

type of sorbent, the grafting of thiourea groups does not change external diffusion nor intraparticle diffusion, though complementary linkages may be formed between polymer chains: the low size of platinum can explain this result. With sulfuric acid solutions, it is necessary to introduce a sorbent concentration twice that used for HCl solutions to obtain comparable decay curve. Sulfuric acid solutions slightly increases the time required to reach equilibrium with 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 (7,27). Figures 11 and 12 shows the sorption kinetics for different particle sizes with GCC (TGC respectively) in either HCl or H₂SO₄ solutions.

With GCC-2:1, in hydrochloric acid solutions (Figure 11), for both platinum and palladium, sorption kinetics are comparable for the four size fractions. Though a small decrease in the time required to reach equilibrium is observed with decreasing the size of the sorbent, the differences are not so marked as they are with other metal anions such as molybdate and vanadate (8). The differences in the sorption of these metal anions may be related to the differences in their chemistry and the ability, or inability, to form polynuclear species, as previously stated. With TGC, in hydrochloric acid solutions, palladium sorption kinetics are almost independent of the particle size, even at equilibrium (Figure 12). This result seems in contradiction with previous results obtained in sorption isotherms. However, the palladium sorption isotherms have shown that the differences between the different size fractions are significant mainly at high residual palladium concentration, while in the initial section of the curves, the sorption capacities are comparable. For kinetics, with selected experimental conditions, the sorbent dosage is high enough to remove palladium almost completely: so differences at equilibrium are not very marked. In these conditions, the affinity of the sorbent for

palladium is not a controlling parameters and the similar sorption kinetics for differing particle size, indicates that diffusion is not a limiting parameter.

In sulfuric acid solutions (Figure 11) palladium sorption on GC-2:1 is influenced by the particle size in the initial section of the curve, while the equilibrium concentration is independent of this parameter (Figure 9). The differences may be attributed by part to diffusion resistance (external and intraparticle diffusion) and to the low affinity of crosslinked 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 synthetic solution using GCC-2:1. The breakthrough in fixed-bed systems occurs at ca. 900-950 BV. The concentration in the sorbent reaches 149 mg g^{-1} , at the breakthrough volume, while at the saturation volume (ca. 1550-1600 BV) the sorption capacity tends to 189 mg g^{-1} . This sorption capacity at saturation is comparable to that obtained at equilibrium in batch systems, with comparable concentration and pH. The steep slope of the breakthrough curve confirms that palladium sorption on glutaraldehyde crosslinked chitosan is not strictly controlled by intraparticle diffusion: a lower slope would indicate that the mass transfer zone is large as consequence of a slow accessibility to internal sites (it may result from internal diffusion restrictions).

The faisability of using such system for the treatment of industrial effluents is conditioned by the possibility to desorb metal ions and to recycle the sorbent. Preliminary work using HCl concentrated solutions (2, 5 and 11 M) has shown that mixing 0.5 of exhausted sorbent (containing ca. 200 mg Pd g^{-1}) with 16 mL of elutant for 16 h in agitated systems allows after 2 desorption steps to achieve a desorption yield of 71, 79 and 85 % respectively.

CONCLUSION

Though chitosan is efficient at removing palladium from synthetic and pure acidic solutions, its sorption properties are strongly decreased by the presence of competitor anions. The modification of the ion exchange resin to a chelating resin, resulting from

the grafting of sulfur compounds, improves sorption capacity and reduces the influence of pH and competitor anions.

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

The grafting of sulfur compounds through glutaraldehyde linkage reveals an interesting way to improve sorption properties against platinum group metals. However, the thiourea derivative of chitosan seems to be more interesting for platinum recovery than for palladium sorption: the enhancement of sorption properties is more significant for Pt. The selectivity is also an important criterion to be used for the selection of a sorbent for Pt and Pd recovery, PGMs being frequently present in mixture, or in presence of other metals. The selectivity between palladium and platinum is currently investigated and preliminary results indicate that palladium sorption is less decreased by the presence of platinum than the reverse.

The dynamic sorption of palladium in column systems confirms these preliminary results on synthetic solutions. Though the complete recovery of palladium from exhausted sorbent was not achieved, a concentrated solution (11 M) allows 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 destroying procedure including burning or mineralization of chitosan (in hydrogen peroxide solution followed by an acidic treatment for example).

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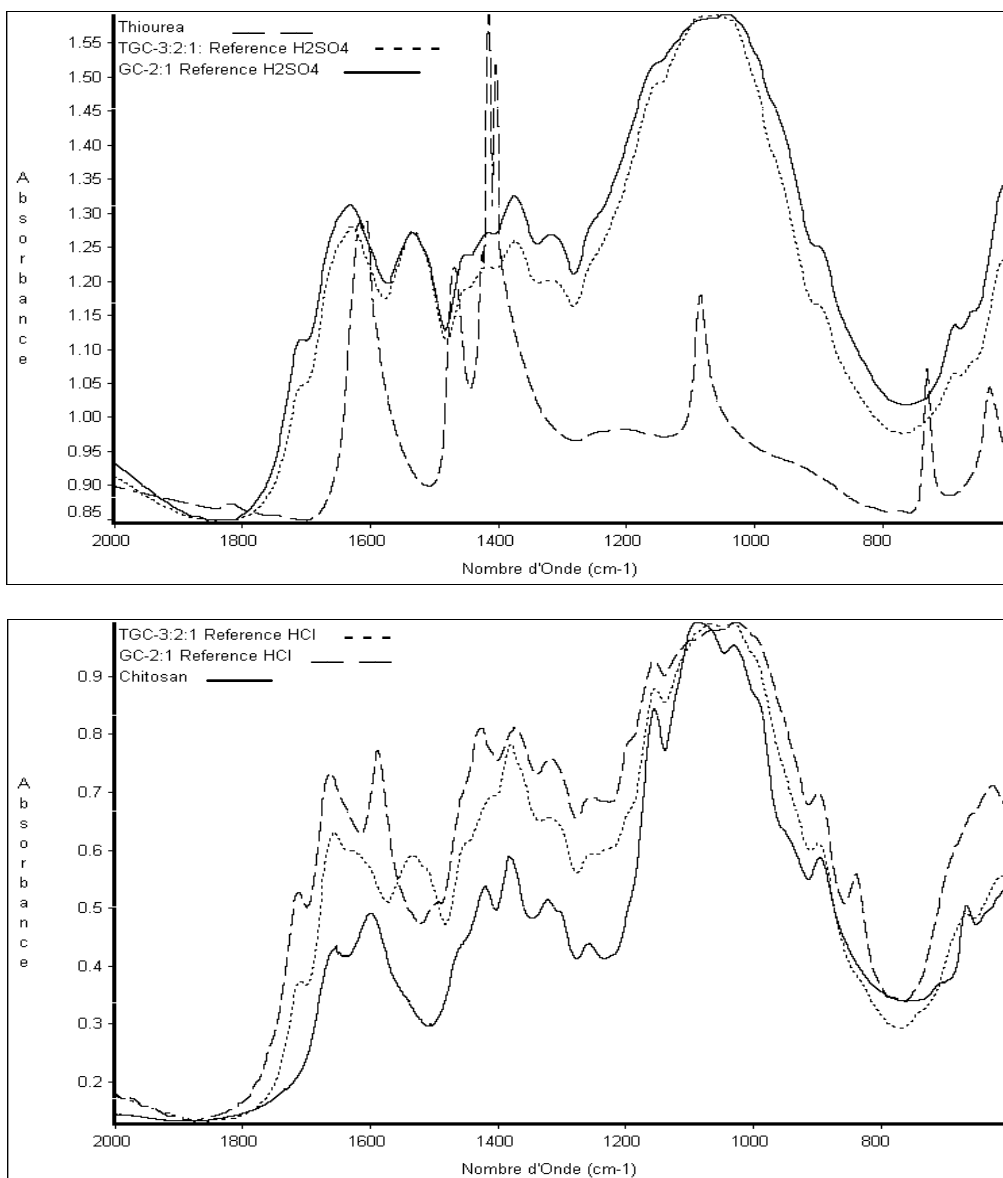


FIG 1. FTIR spectra of chitosan, thiourea, GC-2:1 and TGC-3:2:1 (after contact with either HCl or H₂SO₄) (nombre d'onde : wavenumber).

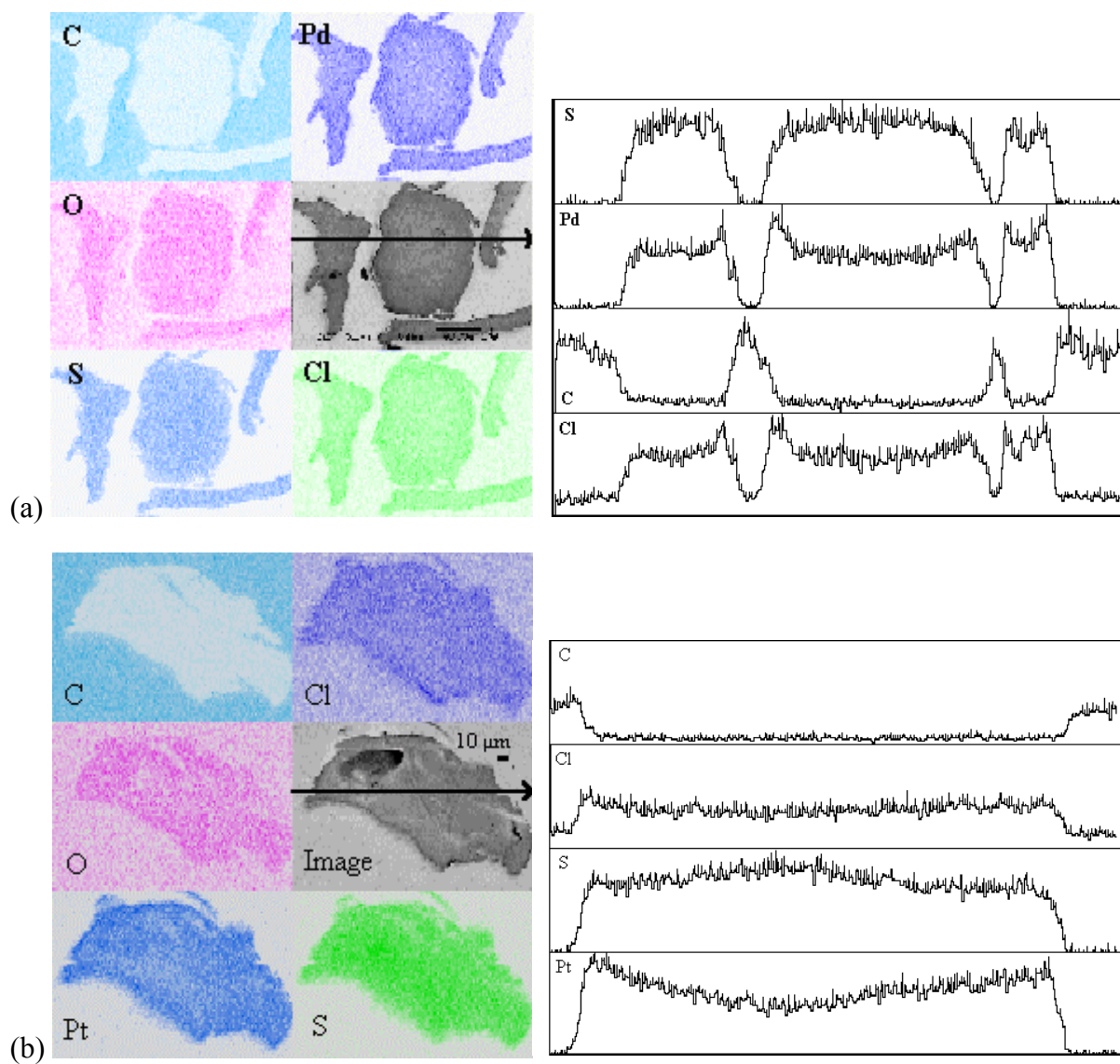


FIG 2. SEM-EDAX analyses of thiourea derivative of chitosan after (a) platinum (TGC-3:2:1) and (b) palladium (TGC-1:1:1) sorption.

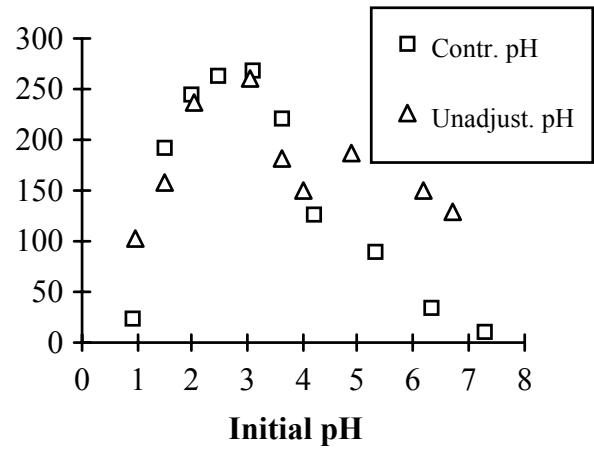
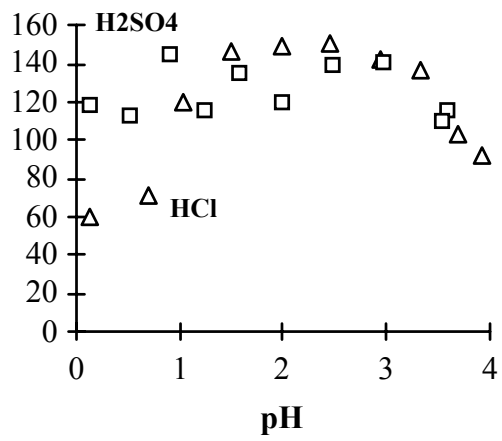


FIG 3. pH optimization for platinum sorption on (a) GCC-2:1 (HCl media) and (b) TGC-3:2:1 (hydrochloric acid (d) and sulfuric acid (a)).

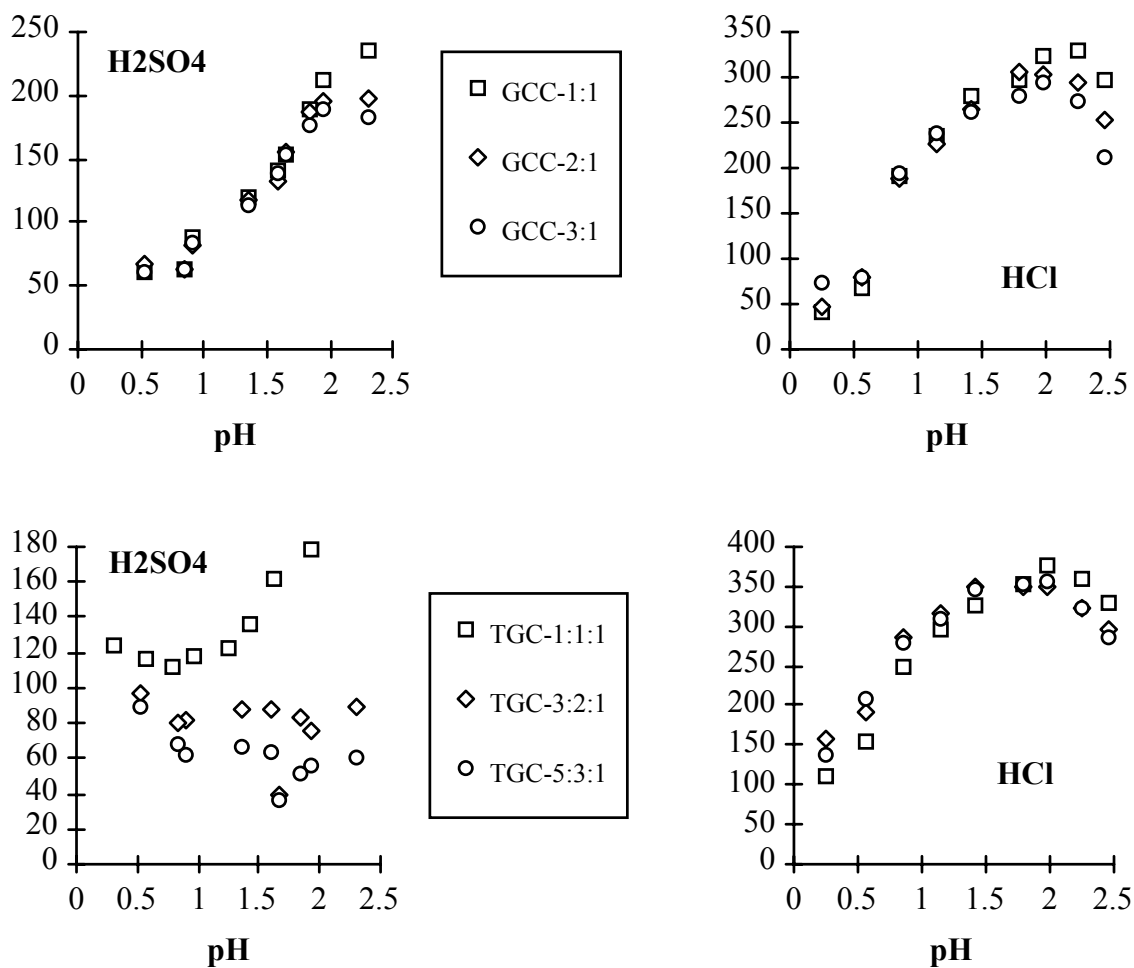
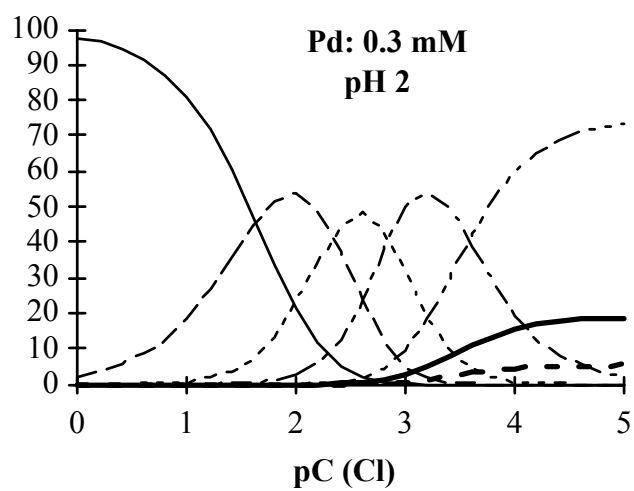
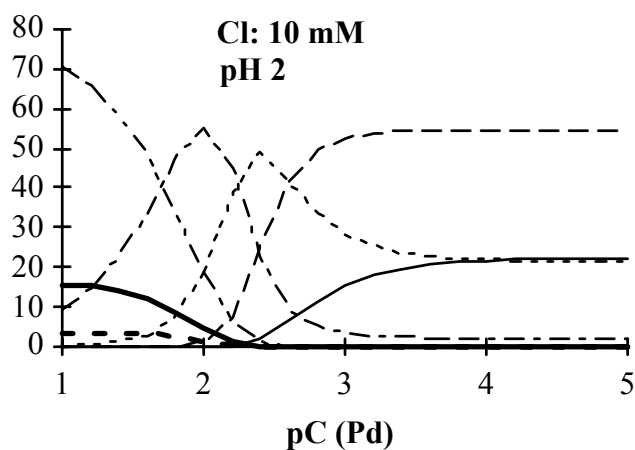
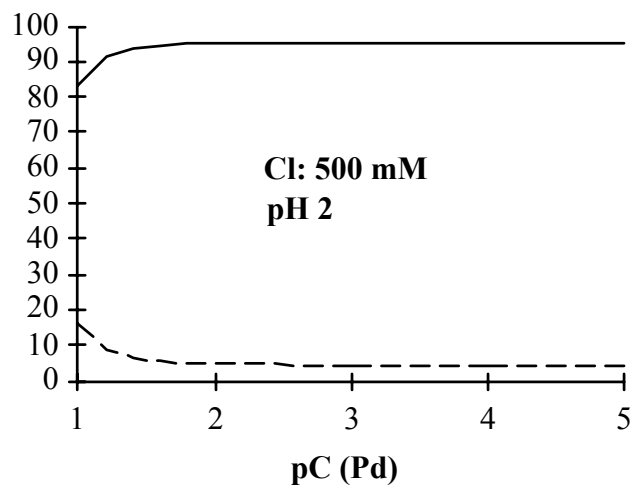
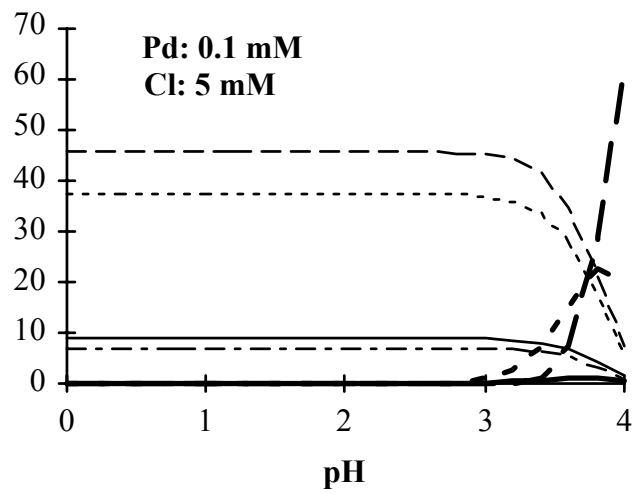
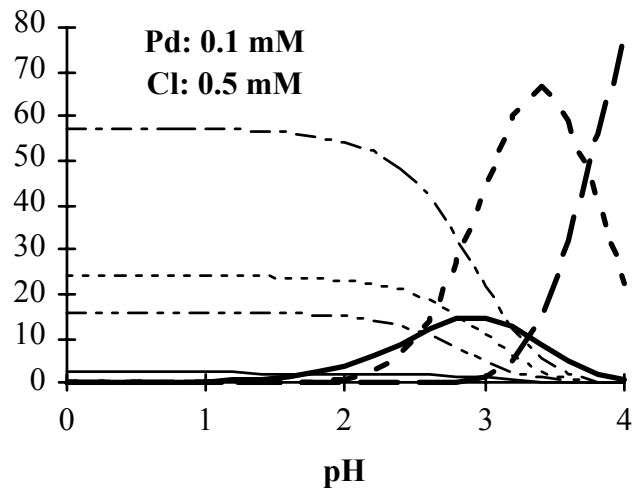
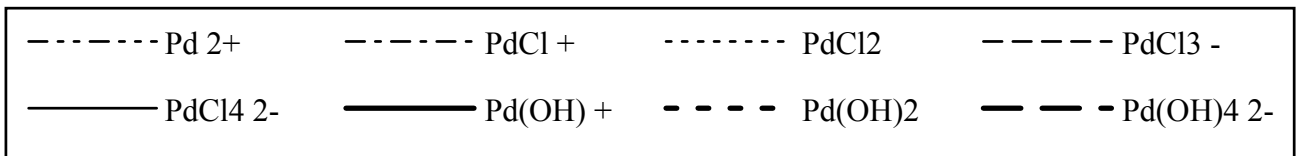


FIG 4. Influence of pH on palladium sorption capacity (pH controlled with sulfuric acid) (C_0 : 25 mg L⁻¹; Sorbent Dosage: 80 mg L⁻¹, acid added (concentration): 0.001-0.0025-0.005-0.01-0.025-0.05-0.1-0.25-0.5 M).





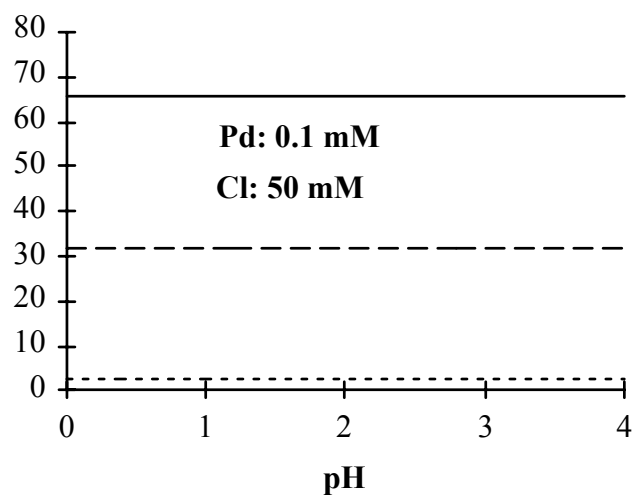


FIG. 5 Speciation diagrammes for Pd as a function of pH, chloride and palladium concentrations.

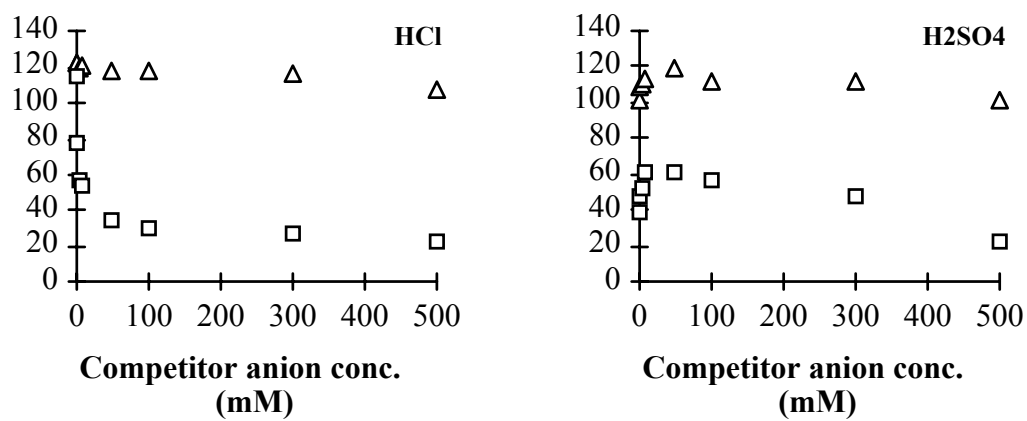


FIG 6. Influence of competitor anion Na_2SO_4 (respectively NaCl) on platinum sorption at pH 2 in HCl-controlled pH solutions (respectively H_2SO_4 -controlled pH solutions)

using TGC-3:2:1 (d), and GC-2:1 (a) (sorbent dosage: 15 mg / 200 mL and C_0 : 9.4 mg L⁻¹)

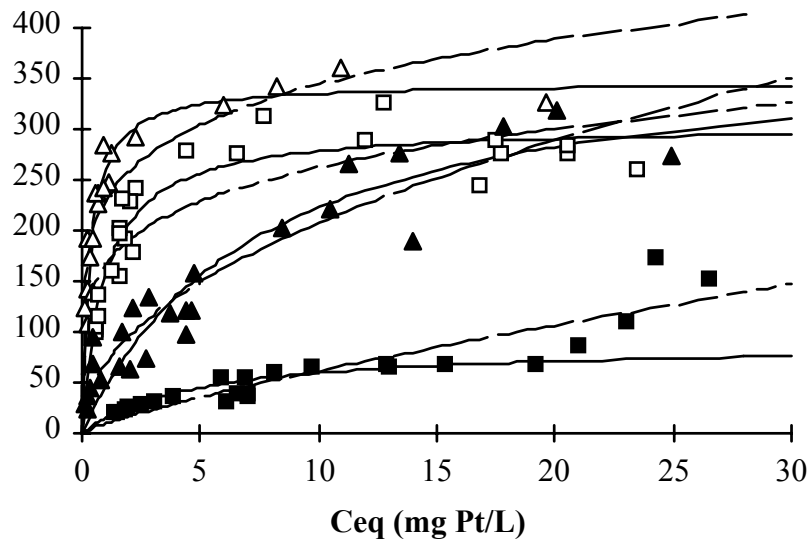


FIG 7. Influence of the acid used for pH control (open symbols: HCl, closed symbols: H₂SO₄) at pH 2 on platinum sorption isotherms using either TGC-3:2:1 (d) or GC-2:1 (a) (solid lines: Langmuir modeling, dashed lines: Freundlich modeling).

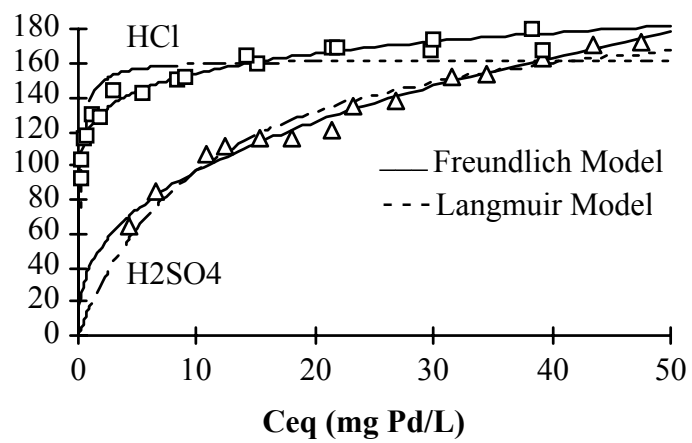


FIG 8. Palladium sorption isotherms on GCC-2-1 at pH 2 - Influence of the acid used for pH control.

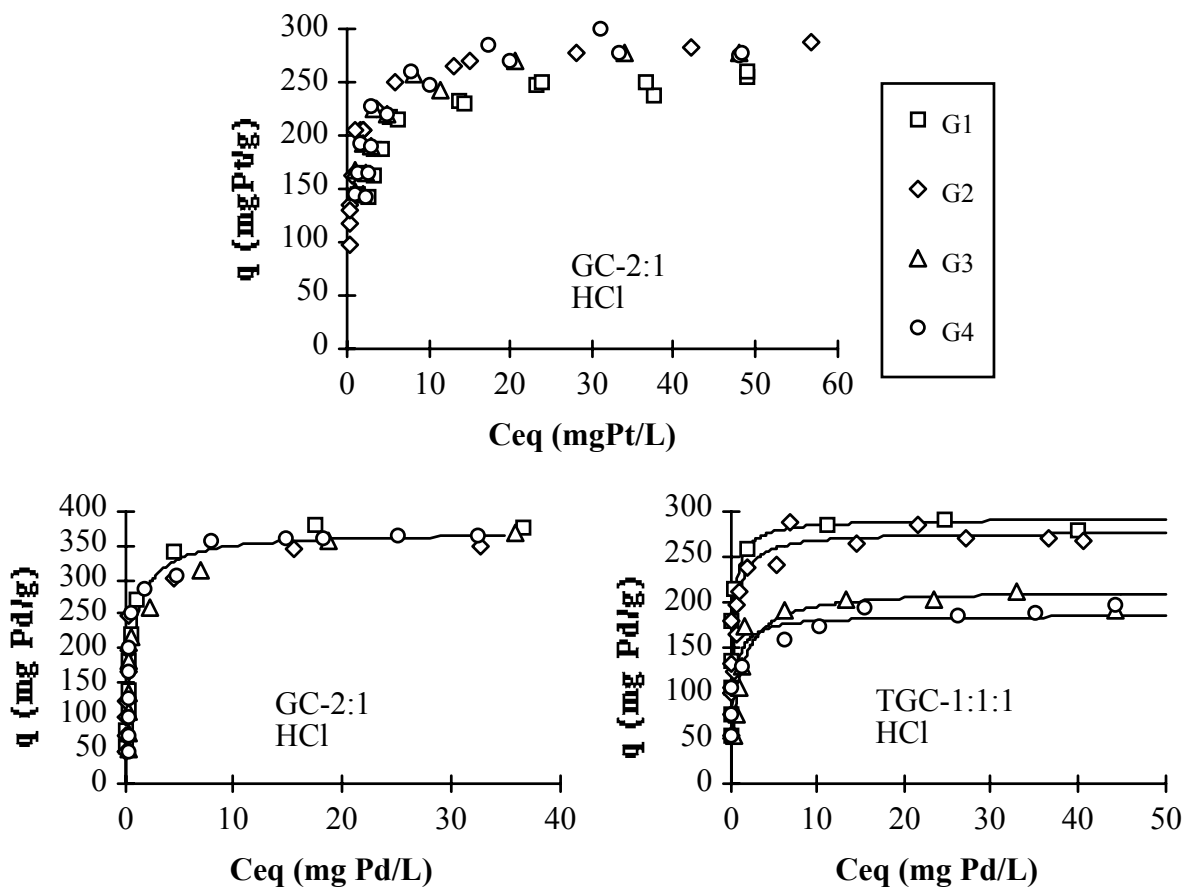


FIG 9. Influence of particle size on platinum sorption in HCl solutions

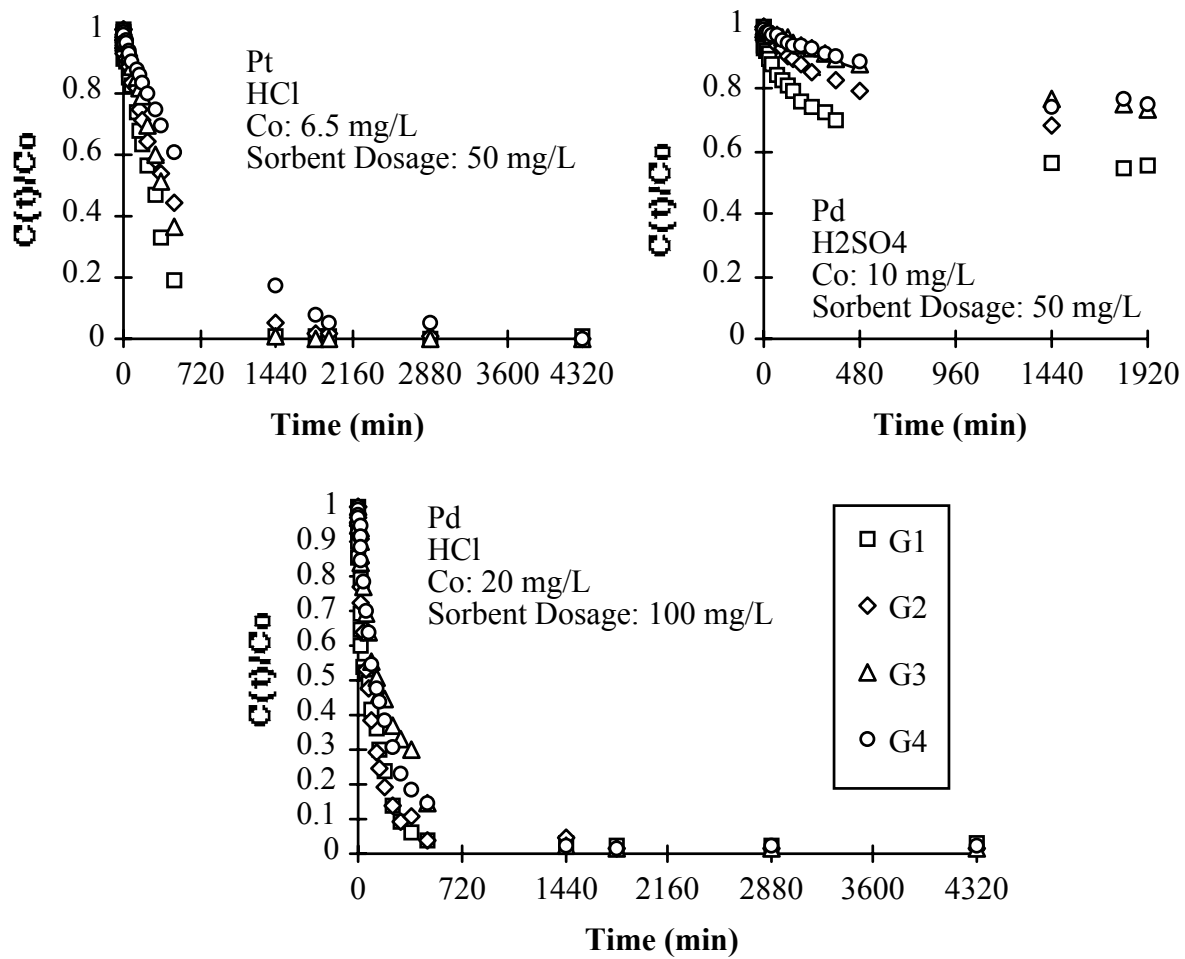


FIG 10. Influence of particle size on Pt/Pd sorption kinetics on GC-2:1 at pH 2.

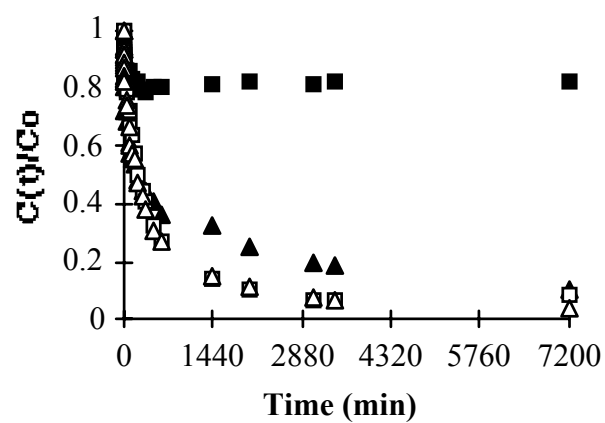


FIG 11. Platinum sorption kinetics using TGC-3:2:1 (d/D) and GC-2:1 (a/A) (C_0 : 10 mg L^{-1} , sorbent dosage: 50 mg L^{-1} , for HCl-controlled pH solution (open symbols), and 100 mg L^{-1} for H_2SO_4 -controlled pH solutions (closed symbols), at pH 2)

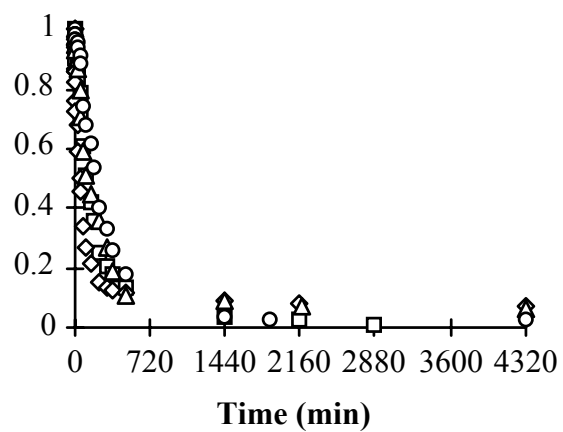


FIG 12. Influence of particle size on palladium sorption kinetics by TGC-1:1:1 at pH 1.3 (HCl solutions) (Sorbent Dosage: 55 mg L⁻¹, C₀: 18.7 mg L⁻¹).

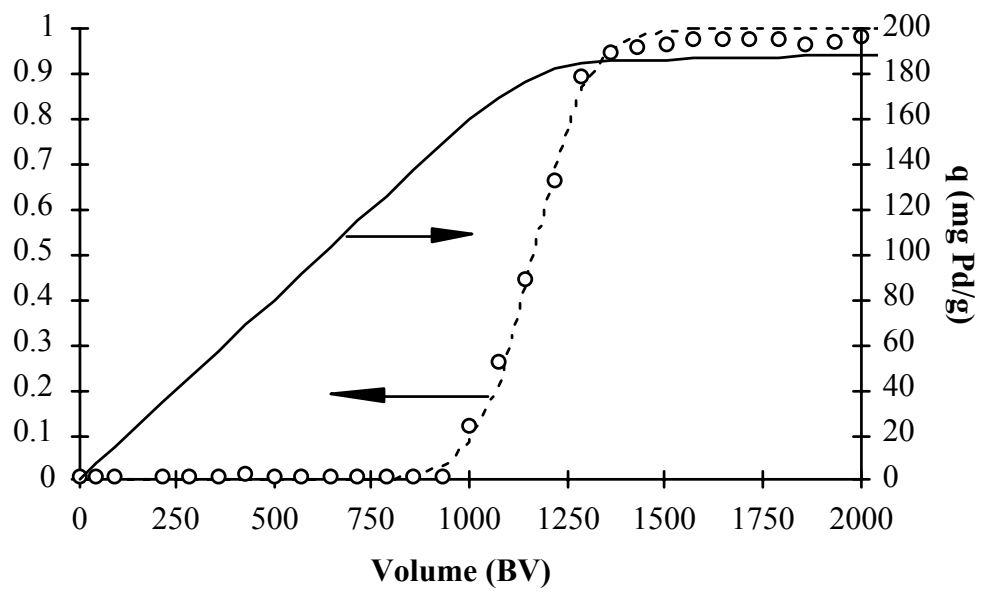


FIG 13. Breakthrough curve for Pd sorption on GC-2:1 at pH 2.

TABLE 1
Coefficients of the Langmuir and the Freundlich models for Pt and Pd sorption
isotherms

Sorbent	Part. Size	Acid	Metal	Langmuir Model			Freundlich Model		
				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 ₂ SO ₄	Pt	386.9	0.135	31.9	69.0	2.09	28.1
GCC-2:1	G2	H ₂ SO 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 ₂ SO 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⁻¹L^{1/n} and dimensionless, respectively)

MSR: mean square deviation obtained from $\left[\frac{\sum_{i=1}^n (X_{\text{exp},i} - X_{\text{calc},i})^2}{n} \right]^{1/2}$

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