

Palladium and Platinum Sorption on a Thiocarbamoyl-Derivative of Chitosan

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Received 13 July 2009; accepted 12 November 2009

DOI 10.1002/app.31877

Published online 22 February 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Immobilizing thiourea onto chitosan allowed using the polymer for the recovery of platinum groups metals (PGMs) in acidic solutions (up to 1–2M HCl concentrations). At low HCl concentration protonated amine groups may sorb chloroanionic metal species (electrostatic attraction mechanism); however, most of sorption proceeds through chelation on sulfur containing groups (less sensitive to acidic conditions). The bi-site Langmuir equation was used for fitting sorption isotherms. The sorption of PGMs was weakly affected by the composition of the solution (presence of high concentration of anions and base metals). Maximum sorption capacities for Pd(II) and Pt(IV) ranged between 274 and 330 mg g⁻¹ in 0.25M HCl

solutions and decreased to 150–198 mg g⁻¹ in 2M HCl solutions: Pd(II) sorption was systematically higher than Pt(IV) sorption. The pseudo-second rate equation was used for modeling the uptake kinetics. Agitation speed hardly affected uptake kinetics indicating that external diffusion resistance is not the rate controlling step. Desorption yield higher than 85% were obtained using thiourea in 0.1M HCl solution. The adsorbents could be reused for at least three cycles. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3318–3330, 2010

Key words: chitosan; thiocarbamoyl; palladium; platinum; sorption; isotherms; kinetics; desorption

INTRODUCTION

The increasing demand for PGMs (catalytic applications, electronic devices, and high technology field) makes the recovery of precious and strategic metals a key challenge for sustainable growth. The cost and the limited availability of these metals can explain the interest of research community for developing new technologies for their recovery from waste materials (electronic scraps and spent catalysts). Apart of pyrometallurgical processes, hydrometallurgy is frequently used for the recovery of these metals from wastes: grinding, magnetic, and gravimetric separations are preliminary treatments, contributing to the preconcentration of valuable metals, before leaching. In most cases, acidic leaching is used for metal transfer from solid phase to liquid phase. These leachates are generally very acidic containing high concentrations of chloride and nitrate anions, as well as base metals (which were codissolved from wastes). The challenges are (a) the competitive recovery of these metals from low metal concentrations effluents, containing base metals, and (b) the selective separation of these PGMs. Indeed,

the chemistry in solution of metals such as Pt(IV) and Pd(II) is very close; separating these metals to each other requires using a combination of processes (solvent extraction^{1–3}) that remains competitive only for concentrated solutions. Hence, there is still a need for developing new systems for valorizing these PGMs from effluents containing low metal levels. Solvent extraction is specially tailored for the recovery of high metal concentration (containing more than 0.5 g L⁻¹ of target metal), ion exchange or chelating resins are generally more appropriate for the recovery of metals from intermediary concentrations.^{4–6} Impregnated resins and membranes merge the properties of solvent extraction and resin systems.^{7–11} Despite the promising results obtained in these fields, alternative processes may still be of interest for the treatment of dilute effluents (concentration lower than 50 mg L⁻¹). Biosorption is one of the alternative processes cited for the recovery of metal ions from dilute solutions, using the reactive groups present at the surface of algal, bacterial, or fungal biomass.^{12,13} The concept of biosorption was thus extended to the use of materials derived from the treatment of biomass (including agriculture and fishery wastes). Chitosan is a key example of the potential of these materials.¹⁴ The presence of amine groups on the biopolymer explains its interesting properties for the binding of metal cations in near neutral solutions (through complexation on free

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amine groups due to the electronic doublet on nitrogen) and the uptake of metal anions in acidic solutions (through electrostatic attraction/ion exchange mechanism on protonated amine groups). The interest of using chitosan consists in the fact that this is a renewable resource that can be easily modified physically and chemically on both amine and hydroxyl groups. Additionally, it is possible to reinforce the stability of the biopolymer in acidic conditions by crosslinking. Chitosan-based materials have been widely investigated for the sorption of precious metals and PGMs.^{15–21} PGMs in the presence of chloride anions form chloroanionic species that can be bound on protonated amine groups. However, in highly acidic solutions, the dissociation of the acid brings high concentration of counter anions (chloride anion for example) that may compete with anionic metal chloro complexes. The sorption of PGMs on raw chitosan is thus rather limited when pH decreases below pH 2. For this reason, several derivatives of chitosan have been developed immobilizing, for example, pyridil groups^{15,19} or sulfur compounds.^{18,22,23} Thiourea immobilization on amine groups (through bonding via a Schiff's base reaction between aldehyde groups on glutaraldehyde and amine groups, on both thiourea and chitosan) allows the biopolymer to sorb Pd(II) or Pt(IV) on a wider pH range (or HCl concentration range). For example, in the case of sulfur derivatives of chitosan, it was possible adsorbing PGMs at pH below 2.^{17,18} However, the stability of the polymer is strongly reduced at pH below 1. An alternative method has been proposed for the immobilization of sulfur groups on chitosan. This material was tested for Hg(II) sorption.²⁴ This work investigate the potential of this new material for Pt(IV) and Pd(II) sorption.

MATERIALS AND METHODS

Material

Chitosan was purchased from JSC "Sonat" (Moscow, Russia). Degree of acetylation (DA) was determined by ¹H-NMR spectroscopy to be 0.16, whereas the average molecular mass of 2.5×10^5 g mol⁻¹ was established using viscometry.²⁵ All other chemicals for sorbent synthesis were of analytical grade and were used without further purification.

Potassium hexachloroplatinate and palladium chloride salts were supplied by Aldrich Chemie and Acros Organics, respectively.

Sorbent synthesis

The thiocarbamylation of chitosan was performed according the following procedure:

- (a) 20 g (0.12 mol) of chitosan was mixed with 25.6 g (0.34 mol) of ammonium thiocyanate and 12.2 g (0.16 mol) of thiourea.

- (b) the mixture was heated below 130°C for 10 min (formation of a gel-like mass)
- (c) the gel was heated at 130°C for 4 h before being cooled.
- (d) The gel was finally rinsed with water until the reaction of the water phase with ferric ions became negative (complete removal of unreacted SCN⁻), and air-dried.

The synthesis produced 22.8 g of modified material that was called S1. Elemental analysis was performed using an Elemental Analyzer Perkin–Elmer.

The sorbent was crosslinked by contact of thiocarbamoyl derivative with glutaraldehyde.¹⁸ Sixteen grams of thiocarbamoyl chitosan (10.6 mmol amine groups, DS: 0.68) was dispersed in 90 mL of water. The crosslinking solution was prepared by mixing 1.7 g of glutaraldehyde (25% solution, 4.48 mmol) with 30 mL of water. The crosslinking solution was mixed with the thiocarbamoyl chitosan suspension for 24 h at 24°C. The solid was thus filtered, rinsed, and dried at 50°C. This sample is called SC1.

Sorption and desorption experiments

Sorption isotherms were obtained by contact of a given amount of sorbent (i.e., 20 mg) with 25 mL of solution containing increasing concentrations of metal (in the range 0–300 or 0–400 mg L⁻¹ for Pt(IV) and Pd(II), respectively) at target HCl concentration (i.e., 0.25M, 1M, or 2M). Samples were collected after 4 days of agitation and filtered before being analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES JY 2000, Jobin Yvon, Longjumeau, France). The mass balance equation was used for the calculation of sorption capacity (metal concentration in the sorbent). The same experimental protocol was used for the determination of sorption performance at equilibrium when investigating the impact of HCl concentration, the influence of the presence of competitor ions (metal salts or anions, which were directly added to metal solution as solid-state salts).

Kinetics were performed in batch reactor. The sorbent, at the appropriate sorbent dosage (SD), was added to 400 mL of solution with known initial concentration. Samples were regularly collected, filtered, and analyzed for plotting the relative metal concentration (residual concentration divided by the initial concentration) versus time. Experimental conditions (SD, metal concentration, sorbent type, and agitation speed) were varied, and the values of the parameters will be systematically reported in the caption of the figures.

Metal desorption from loaded sorbents has been studied in two steps: (a) the mass balance equation was used to evaluate the amount of metal adsorbed

TABLE I
Element Analysis (%) of Thiocarbamoyl Chitosan S1

Sample		C	H	N	S
S1	Anal.	37.79	6.32	9.63	8.47
	Calc.	37.52	6.28	9.78	8.86

on the polymer at given HCl concentration (20 mg sorbent/15 mL of solution at 100 mg L⁻¹ metal concentration); and (b) the loaded sorbent (after being rinsed with water) was mixed with the eluent solutions (SD: 0.25–1.25 g L⁻¹; contact time 2 h). The eluate was filtered and analyzed using ICP-AES. The comparison of the amounts of metal successively adsorbed and desorbed was used for the calculation of desorption efficiency. Additionally, sorption–desorption cycles were repeated five times using S1 and SC1, for palladium and platinum. For this purpose, 40 mg of sorbent, 50 mL of solution with 160 mg metal L⁻¹ were used for adsorption, and for desorption, 25 mL of eluent 0.1M thiourea in acidic media (0.1M HCl).

RESULTS AND DISCUSSION

Sorbent characterization

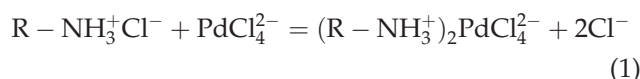
An in-deep characterization of these sorbents was previously given,²⁴ in a study focusing on Hg(II) sorption using the same materials. Although these materials were not fully characterized (including for example the type of distribution of modified units; i.e., blockwise or randomwise distribution) S1 sorbent was analyzed using FTIR spectrometry (identification of –N–H and –S=C–N< groups) and elemental analysis (Table I). These values suggest a possible structure for S1 sorbent; which is presented on Scheme 1. Table I compared analyzed data and calculated values according to the suggested structure: the values are close to each other. The substitution degree was 68%. The titrimetric analysis of sample S1 allowed determining the amounts of amine groups and sulfur groups: 0.42 meq-NH₂/g and 2.64 mmol S/g, respectively.

The sorbents are thus characterized by the coexistence of two types of reactive groups: free amine groups and sulfur compounds (mainly thiourea group). Amine groups are very reactive groups for the complexation of metal cations. However, in very

acidic solutions, the protonation of amine groups generally limits the complexation of cations (due to the competition of protons). This protonation of amine groups only allows the sorption of metal anions through electrostatic attraction mechanism. Sulfur compounds are also very reactive for metal complexation; they are less sensitive to pH than amine groups.²⁶ The modified polymers seem to be stable in acidic solutions: up to a 2M HCl concentration the samples did not appear to be dissolved. However, at long contact time in some cases (especially with S1 sorbent), the observation of kinetic profiles showed a slight increase in metal concentration (possibly due to a partial degradation of the material).

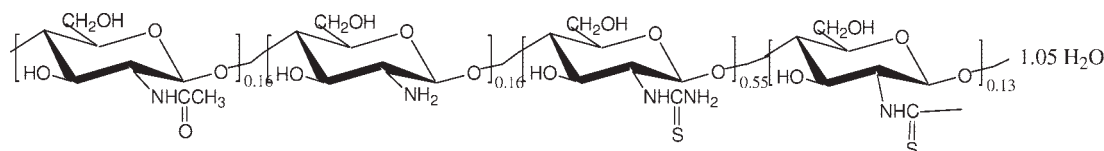
Influence of HCl concentration

Varying HCl concentration may affect metal sorption through the effect of both chloride ions and hydrogen ions. The variation of these concentrations influences the speciation of the metal, which, in turn, can control the affinity of the metal for the binding sites. The thiocarbamoyl derivative of chitosan bears two functional groups that can interact with metal ions: sulfur groups (complexation and possible metal precipitation) and amine groups (electrostatic attraction on protonated amine groups). Hydrogen ion controls the protonation of amine groups, which, in turn, allows anion binding according the equation:



However, an excess of acid leads to the presence of an excess of counteranions (chloride ions) which may compete with metal anions for binding on protonated amine groups.

On the other hand the concentration of hydrogen ions may cause the protonation of thio groups (converted to thiol groups).²⁷ However, the complexation reaction of thio (or thiol) groups (and/or the precipitation of metal ions) will be less influenced by acid concentration. In the present studies, the experiments were performed with only changing HCl concentration. The effects of the concentration of hydrogen and chloride ions were not considered separately. Previous investigations using the



Scheme 1 Structure of S1 sample.

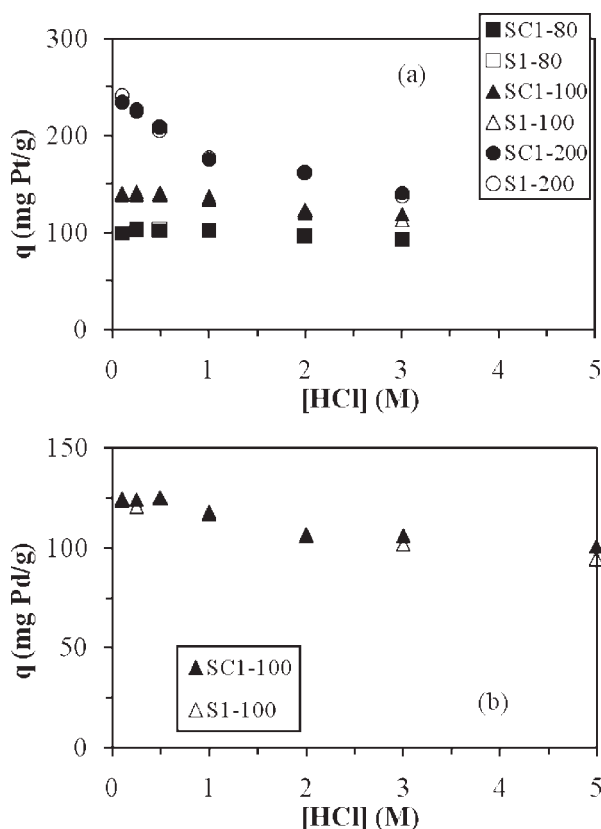


Figure 1 Influence of HCl concentration on Pd(II) and Pt(IV) sorption capacity for both S1 and SC1 sorbents (S1N and SC1N; N: initial metal concentration; SD: 800 mg L⁻¹).

“separate variation” methodology showed a limited impact on Pd(II) and Pt(IV).^{28,29}

The sorption capacities for Pd(II) and Pt(IV) were compared for both S1 and SC1 sorbents in presence of increasing concentrations of HCl (up to 5M) (Fig. 1). Previous investigations have shown that in highly acidic solutions (below pH 2), the competition of chloride ions against chloroanionic species for reacting with protonated amine groups was strong enough to completely inhibit Pd(II) and Pt(IV) sorption on glutaraldehyde crosslinked chitosan.¹⁶ The suspected mechanism for the sorption of PGMs on chitosan is an electrostatic attraction/ion exchange mechanism that is strongly controlled by the presence of competitor anions. For this reason, some sulfur derivatives of chitosan were tested: the immobilization of thiourea (or dithioamide) mediated by glutaraldehyde reaction (aldehyde groups on both side of the crosslinking agent react, via a Schiff’s base reaction, with amino groups of chitosan and thiourea) allowed using the sorbent at pH 1. Indeed, sulfur compounds are very reactive for metal ions over a wide range of pH. However, these materials were not competitive for PGMs recovery at higher HCl concentration (above 0.1M), partly due to their poor stability in acidic solutions. The thiocarbamoyl

derivative of chitosan was less sensitive to HCl concentration than previous sulfur derivatives.

At low metal concentration, the concentration of HCl hardly affected sorption capacity. This is probably due to the excess of sorbent compared with metal content in the solution: the conditions are not favorable for detecting the limiting impact of acid concentration. At high metal concentration, sorption capacity linearly decreased with increasing HCl concentration up to 1M (from 240 mg Pt g⁻¹ to 176 mg Pt g⁻¹), above the sorption capacity tended to decrease but not so extensively (at 5M, the sorption capacity only decreased to 129 mg Pt g⁻¹). Several studies have been carried out using aminoacid (lysine or glycine) derivatives of chitosan for the sorption of Pd(II) and Pt(IV).^{30,31} Optimum sorption was obtained around pH 2 and the sorption capacities significantly decreased with decreasing the pH: below 120 mg g⁻¹ at pH 2. Hubicki’s group investigated several synthetic resins for Pd(II) and Pt(IV) sorption.^{32–34} They also observed a decrease in sorption capacity when the concentration of the acid increased. For example in Pd(II) sorption using synthetic resins, Hubicki et al. found that sorption capacity decreased from 1.1 mmol g⁻¹ to 0.5 mmol g⁻¹, from 1.9 mmol g⁻¹ to 0.8 mmol g⁻¹, and from 0.64 mmol g⁻¹ to 0.45 mmol g⁻¹ when increasing HCl concentration from 0.1 to 3M for resins bearing iminodiacetate groups (Amberlite IRC-718), amidoxime (Duolite ES-346), and aminophosphonic groups (Duolite C-647), respectively.

Sorption isotherms

Sorption experiments (for both Pd(II) and Pt(IV)) have been performed using both S1 and SC1 sorbents, investigating the impact of HCl concentration: sorption isotherms have been obtained from 0.25M, 1M, and 2M HCl solutions. All the isotherms have been characterized by a “very favorable” profile: (a) a sharp initial slope and (b) a quasi-plateau (saturation plateau reached at low residual concentration). The sorption capacity (q , mg g⁻¹, or mmol g⁻¹) is correlated to the equilibrium concentration (C_{eq} , mg L⁻¹, or mmol L⁻¹) according the Langmuir equation:

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (2)$$

where q_m (sorption capacity at monolayer coverage, mg g⁻¹, or mmol g⁻¹) and b (affinity coefficient, L mg⁻¹ or L mmol⁻¹) are the parameters of the model.

Figures 2 and 3 show the sorption isotherms for Pd(II) and Pt(IV) using both S1 and SC1 sorbents. The dotted lines show the modeling of experimental data with the Langmuir equation: large dots

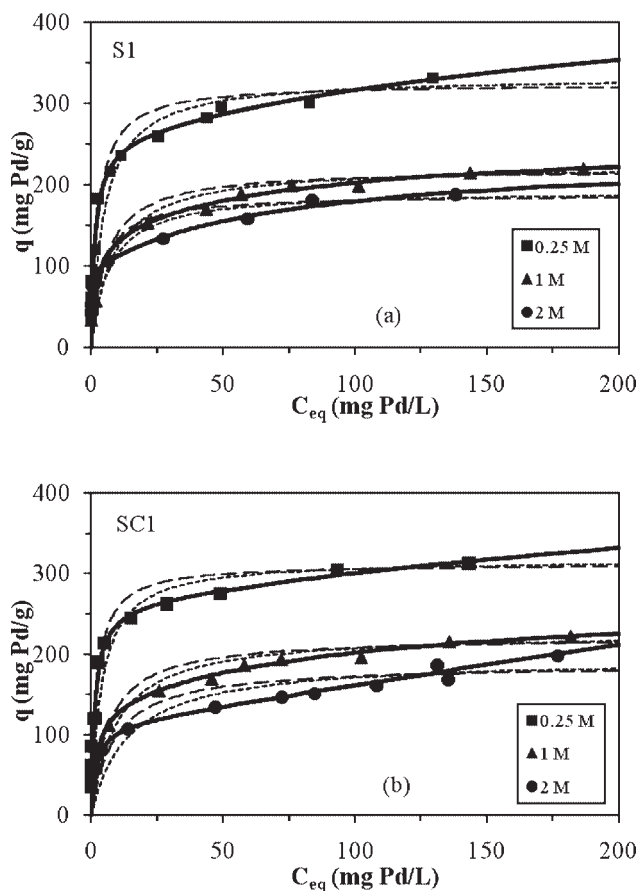


Figure 2 Influence of HCl concentration (0.25, 1, and 2M) on Pd(II) sorption isotherms for sorbents S1 (a) and SC1 (b) (V : 25 mL, sorbent mass: 20 mg).

correspond to the modeling taking into account all experimental data for the calculation of model parameters, whereas small dots represent the modeling taking into account only the points where equilibrium concentration was above 0.5 mg L^{-1} (the impact of analytical discrepancies is too important at concentration below 0.5 mg L^{-1} for an accurate determination of model parameters). The modeled curves did not fit accurately the curved section of the isotherms. They overestimate sorption capacity in the intermediary section of the curve. Escudero et al.³⁵ used a bi-site Langmuir equation for the modeling of hexanol using alginate aerogels. This behavior is typical of systems involving several types of sorption sites with different adsorption energy. The concept of bi-site Langmuir equation was first developed to take into account the heterogeneities of sorbents (presence of different groups with different affinity for target solute). Differences in energy adsorption may also result from changes in the metal species that are adsorbed on the sorbent. This makes the concept of bi-site Langmuir equation extendable to systems involving also the binding of different types of solute (including a sol-

ute present under different forms with different affinities for sorption sites). The speciation of metals is a key phenomenon for the control of sorption properties.^{21,22,33,34,36,37} The speciation may be affected by the pH, the total metal concentration, and the presence of ligands, leading to a change in the predominant species and the affinity of the metal for binding sites.

Assuming that several sites could be involved in the binding (or that several species could be bound with different affinity), the Langmuir equation becomes as follows:

$$q = \frac{q_{m,1}b_1C_{eq}}{1 + b_1C_{eq}} + \frac{q_{m,2}b_2C_{eq}}{1 + b_2C_{eq}} \quad (3)$$

where $(q_{m,1}, b_1)$ and $(q_{m,2}, b_2)$ are the parameters for the two types of sorption sites.

The affinity coefficients (b_1 and b_2) may be significantly different reflecting the differences in strength of the interaction of the solute with these different sorption sites (or different metal species for given sorption sites). The parameters of the Langmuir bi-site model are presented in Table II. The fitted curve

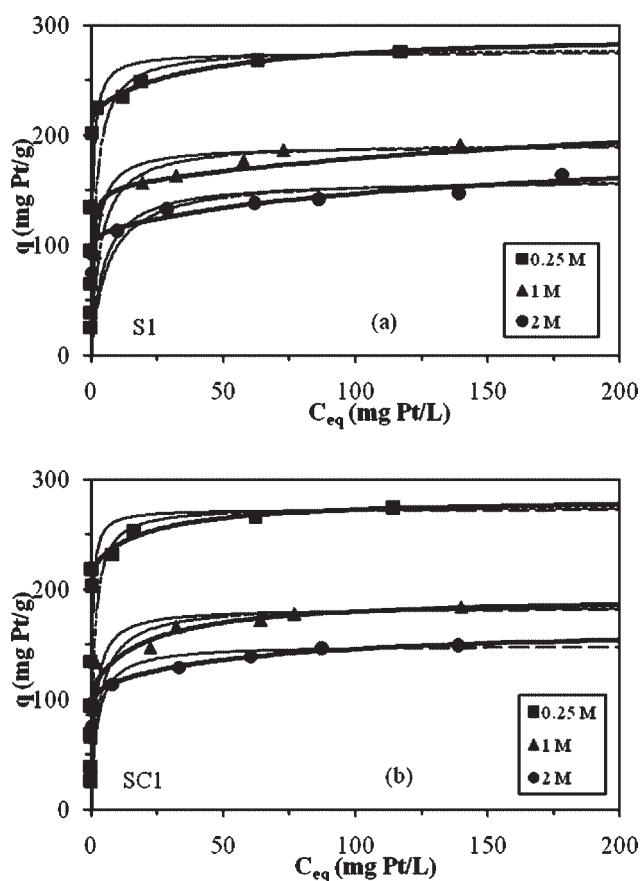


Figure 3 Influence of HCl concentration (0.25, 1, and 2M) on Pt(IV) sorption isotherms for sorbents S1 (a) and SC1 (b) (V : 25 mL, sorbent mass: 20 mg).

TABLE II
Parameters of the Langmuir Model (Bi-Site Model)

[HCl]	Parameter	SC1		S1	
		Pd(II)	Pt(IV)	Pd(II)	Pt(IV)
0.25M	$q_{m,1}$	263.8	220.0	259.0	220.6
	b_1	0.732	52.0	0.658	73.3
	$q_{m,2}$	262.3	63.7	225.8	73.4
	b_2	1.82×10^{-3}	48.7×10^{-3}	3.75×10^{-3}	28.1×10^{-3}
	R^2	0.986	0.961	0.977	0.985
1M	$q_{m,1}$	137.4	110.2	137.3	154.2
	b_1	0.486	28.1	0.509	2.15
	$q_{m,2}$	133.9	84.0	116.1	91.9
	b_2	10.1×10^{-3}	49.7×10^{-3}	14.2×10^{-3}	3.88×10^{-3}
	R^2	0.995	0.880	0.994	0.942
2M	$q_{m,1}$	113.3*	109.2	95.5	111.5
	b_1	0.553*	7.95	6.29	6.93
	$q_{m,2}$	3594*	57.7	142.9	80.7
	b_2	0.142×10^{-3} *	17.8×10^{-3}	14.5×10^{-3}	8.0×10^{-3}
	R^2	0.987	0.995	0.993	0.960

* No physical meaning.

(using the bi-site model) is represented by bold lines in Figures 2 and 3. Additionally, the affinity of reactive groups varies with acid concentration. Hence, the protonation of amine groups in very acidic solutions limits metal sorption (competition effect) while sulfur compounds being less sensitive to pH are less influenced by HCl concentration. Additionally, these two reactive groups may have different affinities for the different metal species that coexist in the solution. These differences justify that the sorbent could be described by the bi-site Langmuir model. At low acidity, both amine groups (though to a less extent) and sulfur groups can bind metal chloroanions, whereas at high acidity, only sulfur groups may contribute. This analysis is made complex by the presence of different metal species (in function of HCl and metal concentrations). One would expect that in very acidic conditions, the limited affinity of the amine groups for metal (due to the competition of chloride ions) leads to a superimposition of the bi-site and mono-site Langmuir equation. However, the possibility of different species to coexist and to be bound to reactive groups can introduce heterogeneities that explain the much better fit of experimental data obtained using the bi-site Langmuir equation.

The comparison of sorption isotherms for three different HCl concentrations is consistent with the conclusions reached at the preceding section. The sorption capacity significantly decreased when comparing the curves at 0.25M and 1M HCl concentrations, whereas at 2M HCl concentration, the variation in sorption capacities close to the saturation were much lower.

Maximum sorption capacities were close to 310, 218, and 196 mg Pd g⁻¹, at 0.25M, 1M, and 2M HCl concentrations, respectively. These values corre-

spond, in molar units, to 2.93, 2.1, and 1.85 mmol Pd g⁻¹, respectively. They are close to the density of sulfur compounds (based on elemental analysis), i.e., 2.64 mmol S g⁻¹ (and 0.42 mmol -NH₂ g⁻¹, based on titrimetric analysis). At low HCl concentration, both amine and sulfur compounds may contribute, at least partially, whereas at high HCl concentration, amino groups are probably less involved and only a part of sulfur compounds may contribute. For Pt(IV) sorption similar trends were observed: the maximum sorption capacity (experimental value) at saturation decreased from 275 mg Pt g⁻¹ (in 0.25M HCl) to 183 and 152 mg Pt g⁻¹ at 1M HCl and 2M HCl concentrations, respectively. In molar units, the sorption capacities are much lower (almost halved) compared with Pd(II) sorption: 1.41, 0.94, and 0.77 mmol Pt g⁻¹, respectively. The decrease in sorption capacity is probably related to a better affinity of the sorbent for Pd(II) but also to differences in sorption mechanism (change in the stoichiometric ratio metal/sorption sites). Adhikari et al.³⁸ also observed a much higher sorption capacity for Pd(II) compared with Pt(IV) using a waste paper modified by dimethylamine immobilization (i.e., 2.2 mmol Pd g⁻¹ and 0.9 mmol Pt g⁻¹, in 1M HCl solutions). In the case of imidazol-based resin, Parodi et al.³⁹ also observed a significant decrease of sorption capacity for Pd(II): from 1.7 mmol Pd g⁻¹ to 1.0 mmol Pd g⁻¹ (increasing HCl concentration from 0.1M to 2M), whereas for Pt(IV), the sorption capacity was less affected. The affinity coefficient was strongly reduced when increasing HCl concentration.

Influence of the presence of competitor ions

The recovery of PGMs from industrial solutions is generally made complex by the presence of

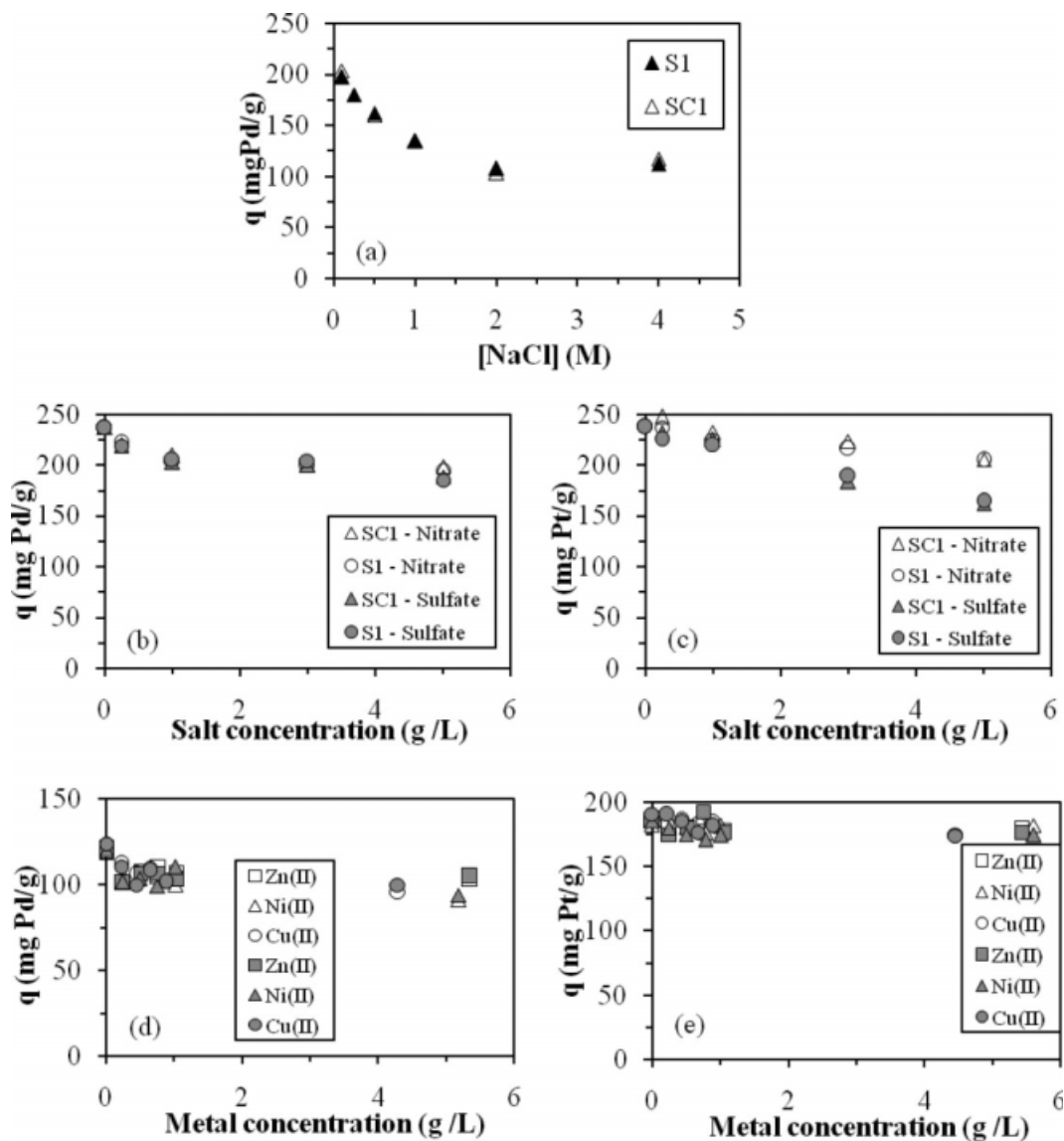


Figure 4 Impact of the composition of the solution (presence of anions and competitor metals) on Pd(II) and Pt(IV) sorption capacity (HCl: 0.1M; SD: 800 mg L⁻¹): (a) effect of NaCl on Pd(II) sorption capacity (C₀: 150 mg L⁻¹); (b) and (c) effect of nitrate and sulfate anions on Pd(II) and Pt(IV) sorption capacity, respectively, (C₀: 200 mg L⁻¹); (d) and (e) effect of Zn(II), Ni(II), and Cu(II) on Pd(II) and Pt(IV) sorption capacity (C₀: 200 mg L⁻¹; open symbols SC1; gray symbols S1).

competitor ions. The leaching of spent catalysts is frequently operated using aqua regia. The concentration of chloride and nitrate anions may be a critical parameter. Figure 4 shows the impact of increasing concentrations of anions (chloride, nitrate, and sulfate) and metal cations (zinc, nickel, and copper, considered representative of base metals) on the sorption capacity. The tests operated on both S1 and SC1 (which gives almost identical results) showed that the presence of chloride ions halved sorption capacities, when increasing chloride concentration up to 2M (above, the decrease tended to stabilize). For nitrate the limiting effect was less marked: sorption capacity only decreased by 15–18% (from 237 mg Pd g⁻¹ to 195 mg Pd g⁻¹ and from 240 mg Pt g⁻¹ to 163 mg Pt g⁻¹).

In the case of sulfate anions, differences were observed regarding Pd(II) and Pt(IV) sorption: for Pd(II) the limiting impact of sulfate anions was comparable to the impact of nitrate anions (from 237 mg Pd g⁻¹ to 188 mg Pd g⁻¹), whereas with Pt(IV) above 1M sulfate concentration, the decrease in sorption capacity was more marked (from 240 mg Pt g⁻¹ to 163 mg Pt g⁻¹). In general, the influence of anions may be explained by three major reasons: (a) competitor effect of anions for interacting with protonated amine groups, (b) impact of anions on metal speciation, which, in turn, may affect the affinity of metal species for sorption sites, and (c) increase in ionic strength of the solution. Here, the decrease in sorption properties is

probably attributable to the effect of anions on ionic strength and on the competition for reaction with protonated amine groups. Indeed, nitrate and sulfate do not form complexes with Pd(II) and Pt(IV). The sorption of both Pd(II) and Pt(IV) on imidazol-based resin was significantly reduced with increasing the concentration of chloride anions.³⁹ Similar reduction in sorption capacity was cited for Au(III), Pt(IV), and Pd(II) sorption on chitosan modified by glycine immobilization:³¹ a 30% decrease in the sorption capacity was observed when increasing NaCl concentration to 0.1M. This is a greater impact for this aminoacid derivative of chitosan than the thiocarboamoyl derivative.

The presence of base metals hardly affected metal sorption as shown on Figure 4(c,d). In the case of Pt(IV) sorption, the presence of base metals (such as Zn(II), Ni(II), and Cu(II)) decreased sorption capacity by less than 10%; in the case of Pd(II), the competitor effect was more marked. The variation in sorption capacity reached 13% for Zn(II), and up to 23% for Cu(II) and Ni(II). However, this effect is relatively weak taking into account the concentration of competitor ions (5 g L⁻¹ versus 100 mg L⁻¹ for PGM concentration). The decrease in sorption capacity may proceed through the reaction of metal cations with sulfur containing groups, but may also be due to the effect of chloride ions (resulting from the dissociation of metal salt). Similar trends were obtained in the sorption of Au(III), Pd(II), and Pt(IV) using cyclam-functionalized resin:⁴⁰ the competitor effect was controlled by both HCl concentration and the concentration of competitor metals. However, sorption capacity remained very high (400 mg metal g⁻¹) even in the presence of a large excess of base metal (20-fold excess).

These results confirm that the sorbent maintains high sorption capacity (100 mg g⁻¹ and higher) even in the presence of high concentrations of competitor metals and anions. This is very important for the potential of this process for the treatment of industrial effluents.

Uptake kinetics

Uptake kinetics is an important criterion for the design of a sorption system. It may be controlled by external film diffusion, intraparticle diffusion, and reaction rate. The sorption kinetics was modeled using the pseudo-first-order rate equation, the pseudo-second-order rate equation and the simplified intraparticle diffusion equation (sorption capacity plotted versus the square root of contact time). The testing of these models showed that the pseudo-second-order rate equation was systematically more appropriate for modeling the kinetic profiles.

$$\frac{dq(t)}{dt} = k_2(q_{eq} - q(t))^2 \quad (4a)$$

After integration:

$$q(t) = \frac{q_{eq}^2 k_2 t}{1 + q_{eq} k_2 t} \quad (4b)$$

After linearization:

$$\frac{t}{q(t)} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (4c)$$

where q_{eq} (mg g⁻¹) is the sorption capacity at equilibrium (calculated value from experimental data), k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant.³⁴

Influence of agitation speed

The agitation speed did not significantly affect the kinetic profiles as shown on Figure 5. The pseudo-second-rate equation fitted reasonably experimental data under selected experimental conditions (SD:

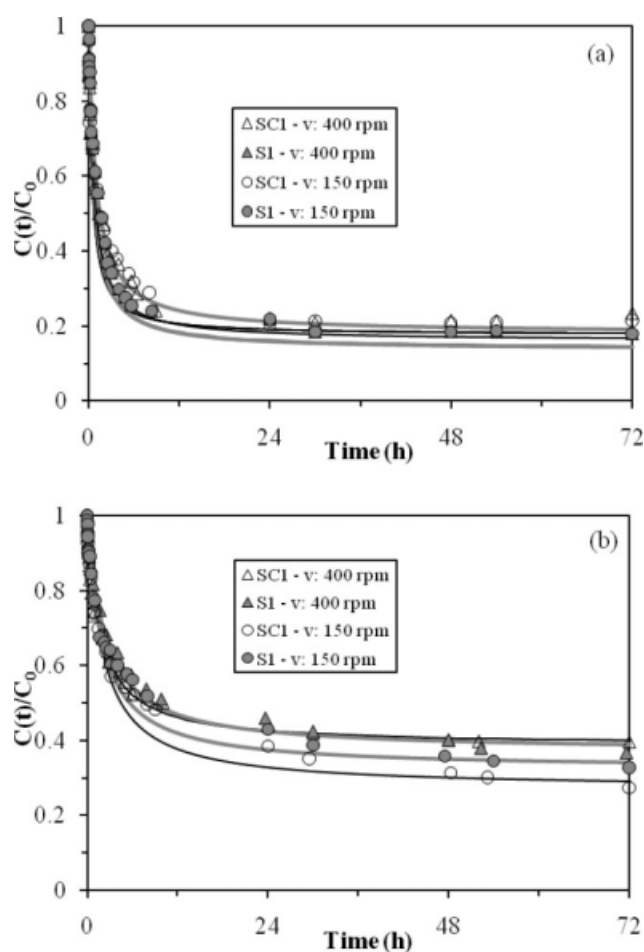


Figure 5 Influence of agitation speed on Pd(II) (a) and Pt(IV) (b) uptake kinetics using SC1 (open symbols) and S1 (closed gray symbols) sorbents (SD: 250 mg L⁻¹; (a) C₀: 30 mg L⁻¹ and (b) C₀: 50 mg L⁻¹).

TABLE III
Uptake Kinetics—Modeling of Pd(II) Sorption Using the Pseudo-Second-Order Rate Equation

SD (mg/L)	v (rpm)	Metal (mg/L)	Sorbent	$q_{\text{eq,exp}}$ (mg g ⁻¹)	$q_{\text{eq,calc}}$ (mg g ⁻¹)	$k_2 \times 10^2$ (mg g ⁻¹ h ⁻¹)	R^2
100	400	30	SC1	121.1	88.5	2.24	0.981
175	400	30	SC1	121.7	112.4	3.60	0.998
250	400	30	SC1	107.8	107.5	1.70	1.000
100	400	30	S1	125.6	116.3	2.39	0.996
175	400	30	S1	116.0	114.9	1.15	0.999
250	400	30	S1	108.1	108.7	1.30	1.000
250	400	30	SC1	113.2	112.4	1.93	1.000
250	150	30	SC1	105.4	106.4	1.43	1.000
250	400	30	S1	112.9	113.6	1.14	1.000
250	150	30	S1	109.4	109.9	0.95	1.000
250	400	8	SC1	31.6	31.7	8.2	1.000
250	400	8	S1	32.5	32.6	7.0	1.000

250 mg L⁻¹). The comparison of S1 and SC1 sorbents shows that the crosslinking treatment hardly impacted the uptake kinetics. The limited impact of agitation speed is also demonstrated by the parameters of the pseudo-second-rate equation reported in Tables III and IV: for Pd(II) the kinetic coefficient varied between 0.95×10^{-2} and 1.93×10^{-2} mg g⁻¹ h⁻¹, whereas for Pt(IV) the coefficient only varied in the range 0.36 – 0.50 mg g⁻¹ h⁻¹ × 10^{-2} . This poor effect of agitation speed makes possible neglecting the contribution of external diffusion resistance on the control of uptake kinetics.

Influence of sorbent dosage (SD)

Figure 6 shows the influence of increasing sorbent dosage on Pd(II) and Pt(IV) uptake kinetics. This figure shows that S1 and SC1 sorbents obeyed the same kinetic behavior. The crosslinking treatment

poorly affected uptake kinetics. The pseudo-second-order rate equation fitted well experimental data, especially for Pd(II) sorption and for high sorbent dosage. With Pt(IV) some discrepancies were observed in the curvature zone and with low sorbent dosage. This may explain that the k_2 parameter was significantly greater at low sorbent dosage (i.e., 100 mg L⁻¹) compared with 175–250 mg L⁻¹ sorbent dosages. Tables III and IV report the parameters of the model. The values of the parameters confirm the preliminary observations: the quality of the modeling is improved when increasing sorbent dosage. The comparison of sorption capacity at equilibrium for experimental and calculated values: at SD 175 and 250 mg L⁻¹ the values were very close contrary to SD 100 mg L⁻¹. The kinetic coefficient k_2 was systematically lower for Pt(IV) compared with Pd(II) (for SD: 175–250 mg L⁻¹): in the range 1.15 – 3.6×10^{-2} mg g⁻¹ h⁻¹ for Pd(II) and in the range 0.45 –

TABLE IV
Uptake Kinetics—Modeling of Pt(IV) Sorption Using the Pseudo-Second-Order Rate Equation

SD (mg/L)	v (rpm)	Metal (mg/L)	Sorbent	$q_{\text{eq,exp}}$ (mg g ⁻¹)	$q_{\text{eq,calc}}$ (mg g ⁻¹)	$k_2 \times 10^2$ (mg g ⁻¹ h ⁻¹)	R^2
100	400	30	SC1	120.9	88.5	5.80	0.980
175	400	30	SC1	124.8	125.0	0.55	0.998
250	400	30	SC1	122.6	122.0	0.46	0.997
100	400	30	S1	90.0	73.0	3.13	0.983
175	400	30	S1	115.2	112.4	0.98	0.998
250	400	30	S1	120.9	122.0	0.45	0.999
250	400	50	SC1	115.6	117.7	0.50	0.996
250	150	50	SC1	138.5	138.9	0.36	0.997
250	400	50	S1	116.6	117.6	0.38	0.997
250	150	50	S1	128.9	129.9	0.39	0.998
250	400	7.5	SC1	28.8	29.2	6.19	1.000
250	400	7.5	S1	30.8	31.0	7.35	1.000
250	400	30	SC1	114.3	114.9	0.52	0.998
250	400	30	S1	112.3	112.4	0.58	0.998

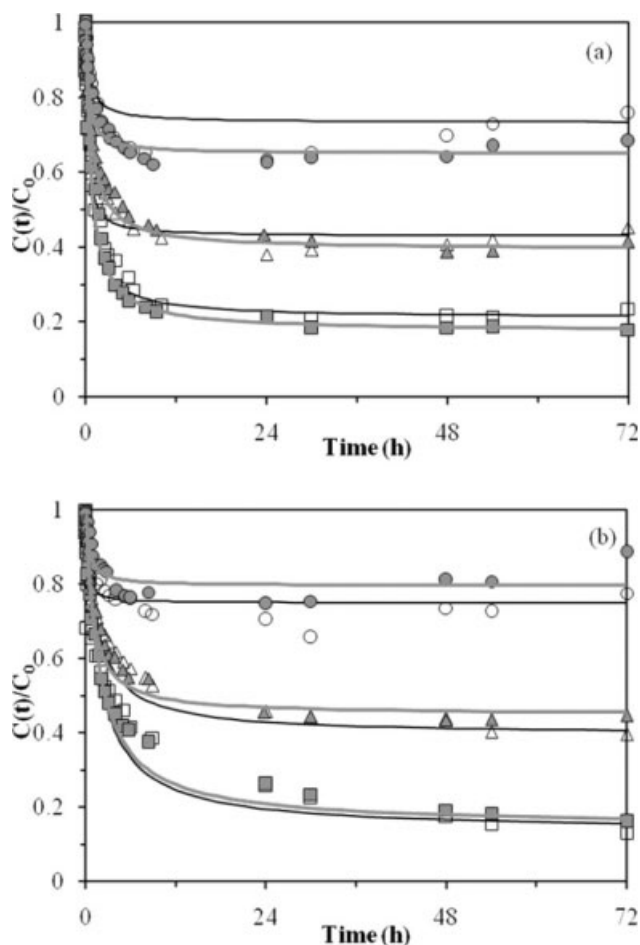


Figure 6 Influence of sorbent dosage (\circ : 100 mg L^{-1} ; Δ : 175 mg L^{-1} ; \square : 250 mg L^{-1}) on Pd(II) (a) and Pt(IV) (b) uptake kinetics using SC1 (open symbols) and S1 (closed gray symbols) sorbents (v : 400 rpm ; C_0 : 30 mg L^{-1}).

$0.98 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$ for Pt(IV). Additionally, the kinetic coefficient tended to slightly decrease when the sorbent dosage increased.

Influence of metal concentration

Figure 7 shows the kinetic curves for Pd(II) and Pt(IV) sorption with different metal concentration. The pseudo-second-order rate equation fitted well experimental data for medium/high metal concentration while at low metal concentration the curvature was not respected. Indeed, the excess of sorbent (compared with metal content) resulted in the complete (more than 95%) removal of the metal within the first 6–8 h. Again, both experimental curves and fitted curves were very close for S1 and SC1 sorbents. The kinetic coefficients significantly decreased when metal concentration increased: around $7 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$ for Pd(II) and Pt(IV) at low metal concentration (i.e., $7.5\text{--}8 \text{ mg L}^{-1}$), it decreased to $0.38\text{--}0.58 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$ for Pt(IV) and to 1.1--

$1.7 \times 10^{-2} \text{ g}^{-1} \text{ h}^{-1}$ for Pd(II). The decrease in sorption capacity is significant between 7.5 and 30 mg Pt L^{-1} but tended to stabilize above 30 mg Pt L^{-1} (Table IV).

The modeling of the data was improved when sorbent dosage was high (around 200 mg L^{-1} for a metal concentration close to 30 mg L^{-1}) and when the experimental conditions corresponded to an excess of metal (compared to sorbent). With favorable conditions (SD: around 200 mg L^{-1} and metal concentration higher than 30 mg L^{-1}), the kinetic coefficient was in the range $0.38\text{--}3.6 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$. The kinetic coefficient was systematically higher for Pd(II) than for Pt(IV). These orders of magnitude are comparable to those obtained on Pd(II) and Pt(IV) sorption using an imidazol-based resin,³⁹ and amino-acid modified chitosan,^{30,31} but slightly lower than the kinetic parameter found for Pd(II) adsorption on Amberlyst resins.³⁴

Desorption study

The reversibility of metal sorption was tested as a key parameter for evaluating the potential of the

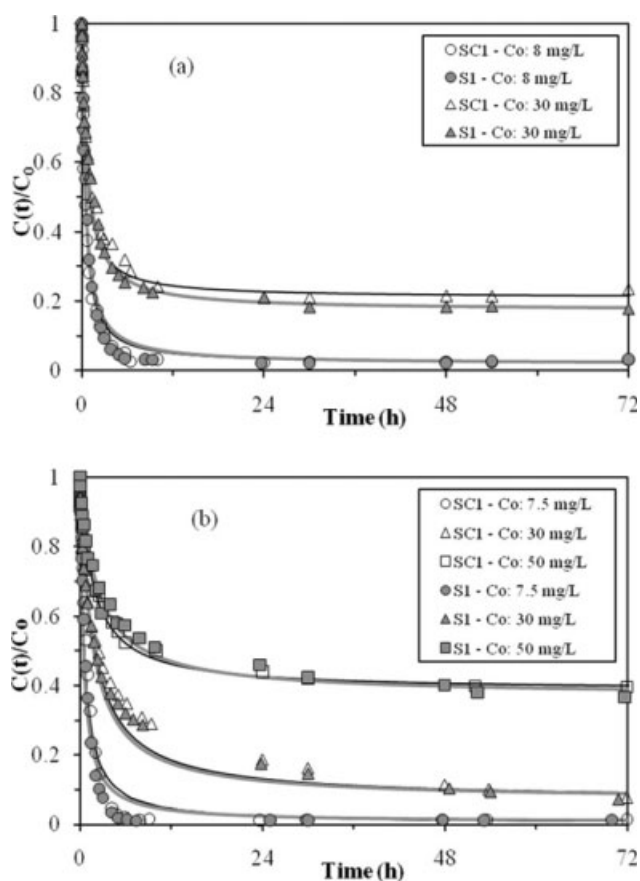


Figure 7 Influence of metal concentration on Pd(II) (a) and Pt(IV) (b) uptake kinetics using SC1 (open symbols) and S1 (closed gray symbols) sorbents (SD: 250 mg L^{-1} ; v : 400 rpm).

TABLE V
Pd(II) Desorption (S1 and SC1 Sorbent)

HCl (M)	Thiourea (M)	L/S ratio (mL/mg)	Desorption yield (%)	
			S1	SC1
0	0.1	1.25	69	70
0.1	0.1	1.25	69	70
0.5	0.1	1.25	62	63
2	0.1	1.25	57	57
2	1	1.25	82	78
0	0.1	0.625	73	67
0.1	0.1	0.625	67	66
0.5	0.1	0.625	62	59
2	0.1	0.625	20	48
2	1	0.625	83	79

sorbent for large scale application. The respective costs of palladium (or platinum) and chitosan do not make necessary polymer recycling: the thermal degradation of the loaded sorbent can be sufficient. This is different for modified chitosan: the chemical modification of the polymer may substantially increase the cost of the sorbent and warrants its recycling.

Several eluents were tested based on previous experiments on Pd(II) and Pt(IV) sorption: acidic solutions (HCl) and complexing agents (thiourea). Tables V and VI summarize the desorption yield for Pd(II) and Pt(IV) (on S1 and/or SC1 sorbents) when varying the concentration of HCl and thiourea, and the liquid/solid (*L/S*) ratio.

When *L/S* ratio increased, the desorption yield increased. However, the variation was not very marked. The improvement in the desorption efficiency is not sufficient to justify increasing the volume of eluent. Indeed, the optimization of desorption should not take into account the recovery of the metal but also the concentration of the metal for its subsequent valorization. If the improvement in the desorption efficiency is not significant increasing the volume of eluent will only contribute to dilute the metal in the eluate. Increasing HCl concentration decreased desorption efficiency, more specifically when the *L/S* ratio was low. Increasing thiourea

TABLE VI
Pt(IV) Desorption (SC1 Sorbent)

HCl (M)	Thiourea (M)	L/S ratio (mL/mg)	Desorption yield (%)
0.1	0.1	1.2	86
0.5	0.1	1.2	77
2	0.1	1.2	54
0.1	0.1	0.75	84
0.5	0.1	0.75	68
2	0.1	0.75	46
0.1	0.1	0.5	77
0.1	0.1	0.25	72

concentration resulted in a significant increase in Pd(II) desorption. Using high thiourea concentration (i.e., above 0.1M), low HCl concentration (about 0.1M) and an appropriate *L/S* ratio (close to 1) allowed optimizing Pd(II) recovery (desorption efficiency close to 90%). Complementary experiments are necessary for achieving a better optimization of experimental conditions in relation with both desorption efficiency, concentration effect and stability of the sorbent (recyclability issues). These results are consistent with those cited in the literature: the combination of acid (HCl or HNO₃) with thiourea was used for the recovery of PGMs from loaded sorbents such as aminoacid derivatives of chitosan,^{30,31} imidazolium-bearing resin,⁴¹ and dimethylamine-modified waste paper³⁸: desorption yield may reach up to 90–95% under optimum conditions.

Figure 8 shows an example of desorption kinetics for Pt(IV). This kinetic profile shows that a contact time of 2 h was sufficient for achieving more than 95% of equilibrium desorption. Under selected experimental conditions, the desorption efficiency varied between 66 and 75% for S1 and SC1, respectively. Desorption steps are frequently faster phenomena than sorption steps.^{42,43} Five sorption/desorption cycles were operated (Fig. 9). The figures show that sorption and desorption efficiencies progressively decreased for both Pd(II) and Pt(IV) (regardless of the sorbent). The effect of sorbent recycling on metal sorption was more marked for Pt(IV) than for Pd(II). The sorption efficiency decreased from 83 to 84 to 54% for Pd(II) and from 81% to 31–34% for Pt(IV) after five cycles. This decrease in sorption efficiency can be attributed to a progressive saturation of the sorbent. Indeed, metal desorption cannot be completely achieved: the maximum desorption was close to 80% at the first cycle

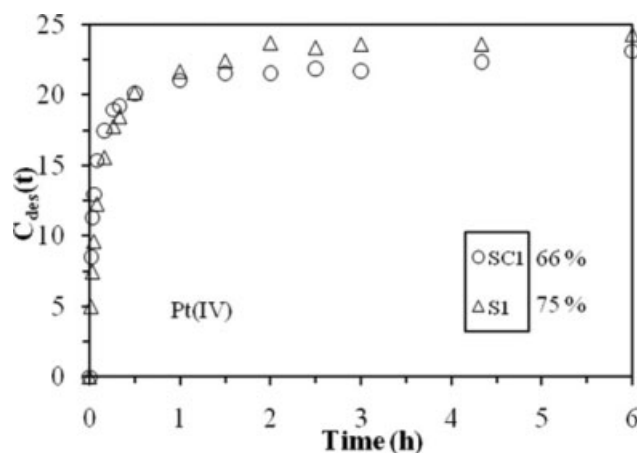


Figure 8 Desorption kinetics for Pt(IV). (Adsorption: [HCl]: 1M; Co: 50 mg L⁻¹; *v*: 150 rpm; Desorption: 0.1M thiourea/0.1M HCl; *v*: 400 rpm; the numbers on caption side shows the desorption yield at equilibrium).

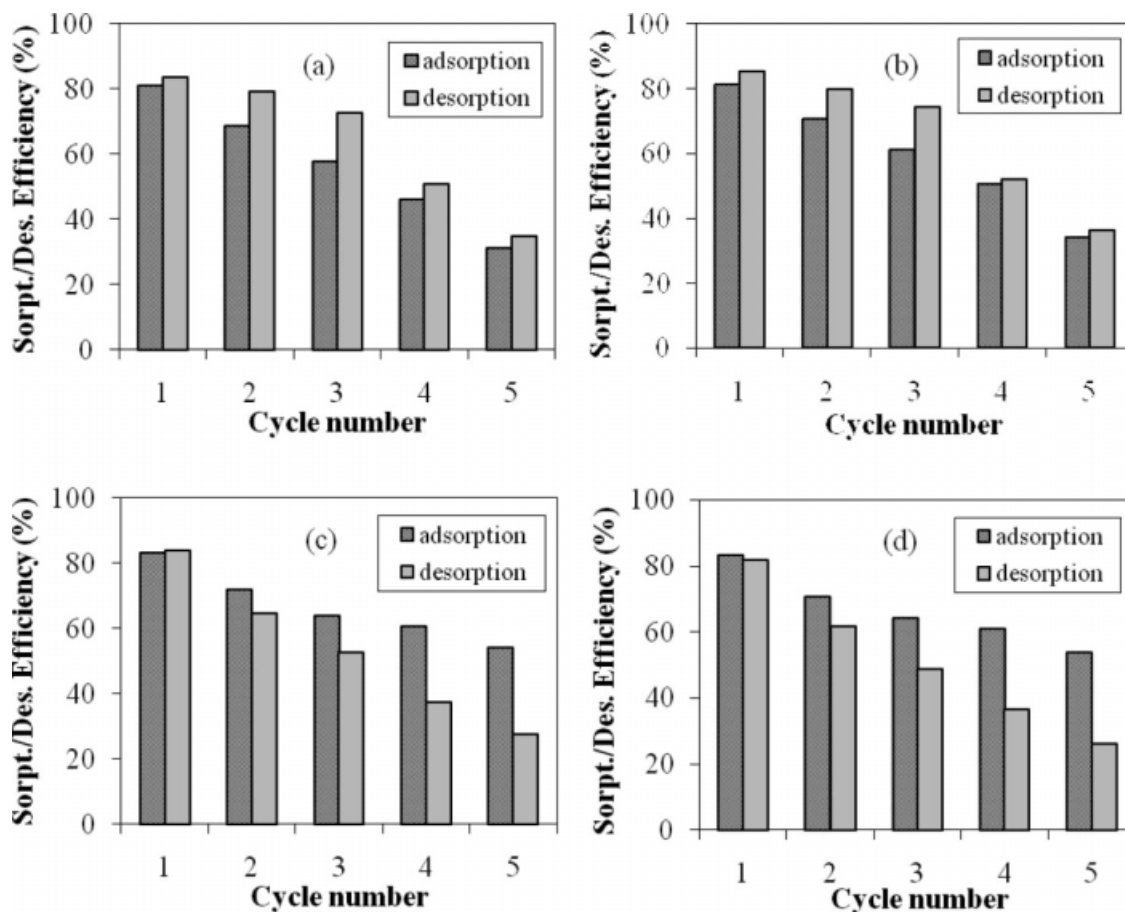


Figure 9 Sorption/desorption cycles: (a) Pt-SC1, (b) Pt-S1, (c) Pd-SC1, and (d) Pd-S1 (mass(ads.): 40 mg; Adsorption: V : 50 mL; contact time: 48 h; v : 200 rpm; [HCl]: 1M; Desorption: V : 25 mL; contact time: 3 h; Eluent: 1M thiourea + 2M HCl).

and decreased even more for next sorption/desorption cycles. The desorption efficiency dropped from about 80% to 27% for Pd(II), and from 82% to 36% for Pt(IV). Using high thiourea concentrations may induce the presence of residual amounts of the ligand absorbed in the sorbent. Its release in the solution at the next sorption step may cause competition effects with sulfur containing groups on the sorbent for metal binding. The changes in the composition of the solution may also cause partial degradation of the sorbent.

CONCLUSIONS

Thiocarbamoyl chitosan obtained by the immobilization of sulfur containing groups on chitosan backbone allowed recovering Pd(II) and Pt(IV) from HCl solutions. In very acidic solutions (above 2M), the biopolymer suffered a partial degradation (also observed with other sulfur derivatives of chitosan) that leads to a decrease in sorption capacity. How-

ever, even at 1M HCl concentration, sorption capacities as high as 200 mg g^{-1} were obtained for both Pd(II) and Pt(IV). In less drastic conditions (for example, 0.25M HCl), sorption capacities exceeded 300 mg g^{-1} . Although at low HCl concentration protonated amine groups may contribute to metal sorption, the most part of metal uptake proceeds through reaction with sulfur groups: the coexistence of two kinds of reactive groups is confirmed by the modeling of sorption isotherms using the bi-site Langmuir equation. The good fit of experimental data with this model can be also explained by the sorption of different metal species (having different affinities for reactive groups). The strong contribution of sulfur compounds in the sorption of PGMs may also explain the relatively weak effect of competitor anions on sorption performance: the presence of sulfate, nitrate, or chloride anions decreased metal sorption but not so extensively as it was previously observed with raw chitosan. Metal cations weakly impacted metal sorption: under these acidic conditions sulfur containing compounds have probably a

greater affinity for PGMs than for base metals. Thiocarbamoyl chitosan showed higher sorption of Pd(II) compared with Pt(IV), regardless of HCl concentration.

Uptake kinetics were fitted by the pseudo-second-order rate equation (especially when the experimental conditions do not correspond to an excess of sorbent). Agitation speed did not interfere with kinetic profiles contrary to other conventional experimental parameters such as sorbent dosage or metal concentration. However, the variation in the kinetic coefficient was rather limited (between 0.5×10^{-2} and $1 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$ for Pt(IV) and between 1×10^{-2} and $3.6 \times 10^{-2} \text{ mg g}^{-1} \text{ h}^{-1}$ for Pd(II)). The kinetic coefficient was systematically higher for Pd(II) than for Pt(IV).

Sorbed metals can be recovered from loaded sorbents using a combination of HCl and thiourea: a low HCl concentration and an intermediary thiourea concentration are required for reaching a substantial metal desorption. The desorption kinetics was much faster than the sorption process. The sorbents were operated for three sorption/desorption cycles maintaining high levels of metals recovery, after three cycles the decrease in efficiency limits the interest of sorbent recycling.

Authors thank La Région Languedoc Roussillon for the fellowship of A. B. during her stay at Ecole des Mines d'Alès.

References

- Hung, N. T.; Watanabe, M.; Kimura, T. *Solvent Extr Ion Exch* 2007, 25, 407.
- Malik, P.; Paiva, A. P. *Solvent Extr Ion Exch* 2009, 27, 36.
- Terada, Y.; Harada, A.; Saito, K.; Murakami, S.; Muromatsu, A. *Bunseki Kagaku* 2003, 52, 725.
- Akita, S.; Hirano, K.; Ohashi, Y.; Takeuchi, H. *Solvent Extr Ion Exch* 1993, 11, 797.
- Chanda, M.; Rempel, G. L. *React Polym* 1990, 12, 83.
- Iglesias, M.; Anticó, E.; Salvadó, V. *Anal Chim Acta* 1999, 381, 61.
- Rovira, M.; Cortina, J. L.; Arnaldos, J.; Sastre, A. M. *Solvent Extr Ion Exch* 1999, 17, 351.
- Rovira, M.; Hurtado, L.; Cortina, J. L.; Arnaldos, J.; Sastre, A. M. *Solvent Extr Ion Exch* 1998, 16, 545.
- Saitoh, T.; Nakane, F.; Hiraide, M. *React Funct Polym* 2007, 67, 247.
- Sakamoto, D.; Narita, H.; Tanaka, M.; Morisaku, K. *Solvent Extr Res Dev Jpn* 2007, 14, 79.
- Shiomori, K.; Yoshizawa, H.; Fujikubo, K.; Kawano, Y.; Hatate, Y.; Kitamura, Y. *Sep Sci Technol* 2003, 38, 4057.
- de Vargas, I.; Macaskie, L. E.; Guibal, E. *J Chem Technol Biotechnol* 2004, 79, 49.
- Sari, A.; Mendil, D.; Tuzen, M.; Soylak, M. *J Hazard Mater* 2009, 162, 874.
- Guibal, E. *Sep Purif Technol* 2004, 38, 43.
- Baba, Y.; Hirakawa, H. *Chem Lett* 1992, 1905.
- Guibal, E.; Larkin, A.; Vincent, T.; Tobin, J. M. *Ind Eng Chem Res* 1999, 38, 4011.
- Guibal, E.; Vincent, T.; Mendoza, R. N. *J Appl Polym Sci* 2000, 75, 119.
- Guibal, E.; Von Offenbergs Sweeney, N.; Vincent, T.; Tobin, J. M. *React Funct Polym* 2002, 50, 149.
- Inoue, K.; Yamaguchi, T.; Iwasaki, M.; Ohto, K.; Yoshizuka, K. *Sep Sci Technol* 1995, 30, 2477.
- Jaworska, M.; Kula, K.; Chassary, P.; Guibal, E. *Polym Int* 2003, 52, 206.
- Ruiz, M.; Sastre, A. M.; Guibal, E. *React Funct Polym* 2000, 45, 155.
- Guibal, E.; Milot, C.; Roussy, J. *Sep Sci Technol* 2000, 35, 1021.
- Guibal, E.; Ruiz, M.; Vincent, T.; Sastre, A.; Navarro-Mendoza, R. *Sep Sci Technol* 2001, 36, 1017.
- Campos Gavilan, K.; Pestov, A. V.; Maldonado Garcia, H.; Yatluk, Y.; Roussy, J.; Guibal, E. *J Hazard Mater* 2009, 165, 415.
- Gamzazade, A. I.; Slimak, V. M.; Skljár, A. M.; Stykova, E. V.; Pavlova, S. A.; Rogozin, S. V. *Acta Polym* 1985, 36, 420.
- Ringbom, A. *Complexation in Analytical Chemistry*; Wiley: New York, 1963.
- Donia, A. M.; Atia, A. A.; Heniesh, A. M. *Sep Purif Technol* 2008, 60, 46.
- Vincent, T.; Parodi, A.; Guibal, E. *Sep Purif Technol* 2008, 62, 470.
- Vincent, T.; Parodi, A.; Guibal, E. *React Funct Polym* 2008, 68, 1159.
- Fujiwara, K.; Ramesh, A.; Maki, T.; Hasegawa, H.; Ueda, K. *J Hazard Mater* 2007, 146, 39.
- Ramesh, A.; Hasegawa, H.; Sugimoto, W.; Maki, T.; Ueda, K. *Bioresour Technol* 2008, 99, 3801.
- Hubicki, Z.; Leszczynska, M.; Lodyga, B.; Lodyga, A. *Miner Eng* 2006, 19, 1341.
- Hubicki, Z.; Wojcik, G. *Desalination* 2006, 197, 82.
- Hubicki, Z.; Wolowicz, A. *Hydrometallurgy* 2009, 96, 159.
- Escudero, R. R.; Robitzer, M.; Di Renzo, F.; Quignard, F. *Carbohydr Polym* 2009, 75, 52.
- Guzman, J.; Saucedo, I.; Navarro, R.; Revilla, J.; Guibal, E. *Langmuir* 2002, 18, 1567.
- Guzman, J.; Saucedo, I.; Revilla, J.; Navarro, R.; Guibal, E. *Int J Biol Macromol* 2003, 33, 57.
- Adhikari, C. R.; Parajuli, D.; Kawakita, H.; Inoue, K.; Ohto, K.; Harada, H. *Environ Sci Technol* 2008, 42, 5486.
- Parodi, A.; Vincent, T.; Pilsniak, M.; Trochimczuk, A. W.; Guibal, E. *Hydrometallurgy* 2008, 92, 1.
- Jermakowicz-Bartkowiak, D. *React Funct Polym* 2007, 67, 1505.
- Venkatesan, K. A.; Selvan, B. R.; Antony, M. P.; Srinivasan, T. G.; Rao, P. R. V. *Hydrometallurgy* 2007, 86, 221.
- Michard, P.; Guibal, E.; Vincent, T.; LeCloirec, P. *Microporous Mater* 1996, 5, 309.
- Campos, K.; Vincent, T.; Bunio, P.; Trochimczuk, A.; Guibal, E. *Solvent Extr Ion Exch* 2008, 26, 570.