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***N*-(2-(2-Pyridyl)ethyl)chitosan (PEC) for Pd(II) and Pt(IV) sorption from HCl solutions**

L. A. Santos Sopena · M. Ruiz · A. V. Pestov ·
A. M. Sastre · Y. Yatluk · E. Guibal

Abstract Chitosan was modified by grafting 2-pyridyl-ethyl moieties on the biopolymer backbone for the synthesis of a Platinum Group Metal (PGM) sorbent. The sorbent was tested for Pd(II) and Pt(IV) sorption from HCl solutions. Stable for HCl concentrations below 0.5 M, the sorbent reached sorption capacities as high as 3.2 and 2.6 mmol metal g⁻¹ for Pd(II) and Pt(IV), respectively. Metal sorption mainly proceeds by electrostatic attraction in acidic solutions, though a contribution of complexation mechanism cannot be totally rejected. The resistance to intraparticle diffusion is the main controlling

mechanism for uptake kinetics. While agitation speed has a limited effect on kinetics, metal concentration and sorbent dosage have a greater effect on the kinetic profiles. The intraparticle diffusivity varies between 3×10^{-11} and 4.5×10^{-10} m² min⁻¹. Thiourea (combined with HCl solution) is used for Pd(II) and Pt(IV) desorption. The resin could be desorbed and recycled for a minimum of five cycles maintaining high efficiencies of sorption and desorption.

Keywords Chitosan · Pyridyl groups · Palladium · Platinum · Sorption · HCl concentration · Isotherms · Uptake kinetics · Resistance to intraparticle diffusion · Metal desorption · Resin recycling

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Introduction

The extraction and the recovery of precious group metals (PGMs) is becoming a challenge for industry since metals such as palladium or platinum are: (a) widely used (for catalytic applications, and for electronic devices), (b) poorly abundant (the limited resource in a limited number of countries makes these metals very strategic), and (c) very expensive (above 540 and 1700 \$/once for Pd and Pt, respectively). The raw resource being limited, the recovery of the PGMs from secondary sources is attracting a growing number

of studies from academic and industrial communities. The waste materials such as spent catalysts, electronic devices may contain significant amounts of PGMs that deserve designing recovery processes (Kang and Schoenung 2005). The recovery of PGMs from waste materials is operated by a series of steps including grinding, magnetic separation, acidic leaching (for metal transfer from solid to liquid phase), and then selective precipitation, solvent extraction or sorption on resins (Brooks 1991; Barakat and Mahmoud 2004; Barakat et al. 2006; Boricha et al. 2007; Shams and Goodarzi 2006). Sorption allows concentrating the target metals in the solid phase, which can be finally valorized by desorption, thermal degradation and so on. While solvent extraction is generally designed for the extraction of metal ions from high-medium concentrated solutions (Dominguez et al. 2002; Preston and du Preez 2002; Dakshinamoorthy and Venugopal 2005; Malik and Paiva 2009; Ciezynska et al. 2007) sorption processes are preferred when the concentration is below 100 mg L^{-1} . Sorption may proceed on ion exchange or chelating resins (Jermakowicz-Bartkowiak 2005; Venkatesan et al. 2005; Hubicki and Wołowicz 2009; Birinci et al. 2009; Venkatesan et al. 2007; Parodi et al. 2008; Hubicki et al. 2008; Cortina et al. 1998; Jermakowicz-Bartkowiak and Kolarz 2002; Qu et al. 2006; Memon et al. 2008), or extractant impregnated resins (Saitoh et al. 2007; Vincent et al. 2008a, b). However, recently a number of alternative materials have been investigated for the recovery of PGMs from dilute acid solutions. These new materials issued from renewable resources are part of the new class of biosorbents, including algal, bacterial or fungal biomass (Turner et al. 2007), biopolymers (Laudenslager et al. 2008; Dang et al. 2008; Jaworska et al. 2003; Ruiz et al. 2001, 2002; Guibal et al. 1999a, b; Kondo et al. 1997; Inoue et al. 1993), waste materials from agriculture (Parajuli et al. 2008, 2009), and even modified waste materials such as waste newspaper (Adhikari et al. 2008). These biosorbents are generally binding metal ions through sorption mechanisms comparable to those used for ion exchange and chelating resins, with the major interest of using low cost materials, with, in most cases, more environmentally friendly properties (i.e., renewable, more benign thermal degradation at the end of life cycle) than conventional resins.

Among biopolymers, chitosan has retained a great attention, due to its very high sorption properties for

metal ions. Metal ions can bind to this aminopoly-saccharide through chelation/complexation on amine groups in near neutral solutions (Guibal 2004). However, the unique property of this biopolymer among polysaccharides is related to its cationic behavior in acidic solutions (protonation of amine groups) that can explain its high efficiency for binding metal anions (Guibal 2004). Unfortunately, this protonation of amine groups induces its dissolving in acid solutions (with the remarkable exception of sulfuric acid solutions). It is thus necessary cross-linking the biopolymer using for example glutaraldehyde (Ruiz et al. 2002). The dialdehyde reacts on each side with amino groups. The supplementary linkages between the polymer chains increase the stability of the polymer. Glutaraldehyde cross-linked chitosan has been tested for Pd(II) and Pt(IV) sorption from HCl solutions. These metal ions appear in HCl solutions under the form of chloroanionic species (i.e., PdCl_4^{2-} and PtCl_6^{2-}) that can bind to protonated amine groups. The optimum pH is close to pH 2; indeed, at lower pH the competition of the counter anions of the acid (chloride anions, for example) for binding on protonated amine groups drastically reduces metal sorption capacity. Some chitosan derivatives have been synthesized with the objective of increasing sorption capacity (increase of the density of sorption sites grafting polyethyleneimine for example (Chasary et al. 2005)), enlarging the pH range for potential application (grafting new functional groups, such as sulfur compounds (Guibal et al. 2000)), or aminoacids (Ramesh et al. 2008; Fujiwara et al. 2007). The improvement of sorption properties may also consist in grafting other N-bearing groups with acid-base properties compatible with more acidic media. A good example of these modifications is given by the immobilization of pyridyl moieties on chitosan (Baba and Hirakawa 1992; Baba et al. 1996, 1998; Kagaya et al. 2000; Justi et al. 2004, 2005; Dhakal et al. 2008; Sajomsang 2010). The present study proposes a new route for the synthesis of *N*-(2-(2-pyridyl)ethyl)chitosan (PEC). After characterizing the structure of the chitosan derivative, it is tested for Pd(II) and Pt(IV) sorption from HCl solutions. The study first investigates the effect of HCl concentration on sorption isotherms, before carrying out the influence of several experimental parameters on uptake kinetics. Finally, the biosorbent is tested for a series of sorption/desorption cycles.

Materials and methods

Materials

Chitosan was supplied by JSC “Sonat” (Moscow, Russia). The biopolymer was characterized using ^1H NMR spectroscopy for the evaluation of the degree of acetylation (DA) and by viscosimetry for the determination of average molar mass (MW). The DA was close to 16% and the MW was about $2.5 \times 10^5 \text{ g mol}^{-1}$. 2-Vinylpyridine for the synthesis of PEC was supplied by Sigma–Aldrich (Belgium); it was distilled and stabilized with 0.05% hydroquinone prior to use. Reagents for sorption experiments (i.e., palladium tetrachloroplatinic acid and platinum hexachloroplatinic acid) were supplied by Fluka Ag. (Switzerland), and Aldrich chemie/Acros (Belgium).

Synthesis of PEC

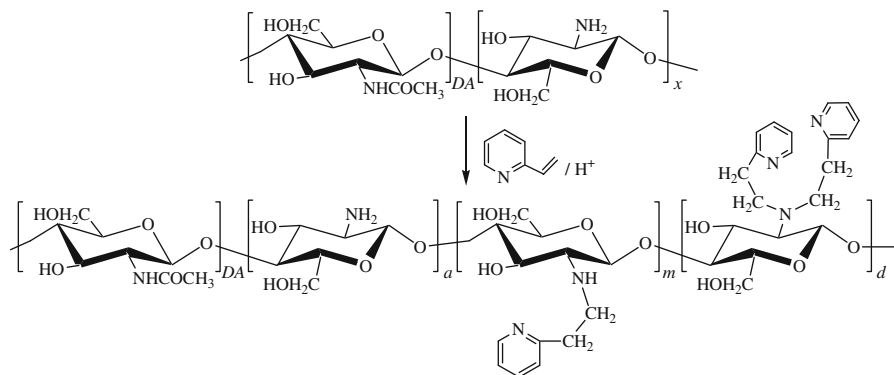
The synthesis of PEC proceeded by reaction of 2-vinylpyridine with chitosan in HCl solution. A gel was prepared by mixing 0.33 g of chitosan (i.e., 2 mmol— NH_2) with 0.42 mL of 2-vinylpyridine (i.e., 4 mmol) in 1.56 mL of a 4.6% w/w HCl solution (i.e., 2 mmol). The gel was heated for 24 h at 70 °C. After cooling, a volume of 7.18 mL of HCl (0.85% w/w solution; i.e., 2 mmol) was added to the reactive suspension. The PEC hydrochloride was precipitated using acetone. Then, the wet solid was washed with isopropanol under reflux for 24 h. Finally, the polymer was dried at 50 °C until reaching a constant mass. The pyridylethylation reaction of chitosan is described on Scheme 1.

The polymer was crosslinked with glutaraldehyde to improve its stability in acidic solutions. Thirteen g of PEC (i.e., 7.62 mmol— NH_2 groups) were dispersed in 50 mL of water before adding 0.13 mL of a 34% w/w HCl solution. The crosslinking bath was prepared by mixing 3.95 g of glutaraldehyde (25% solution; i.e., 10.39 mmol) with 54 mL of water. The suspension (i.e., PEC suspension in HCl solutions completed with the crosslinking agent) was maintained under agitation for 24 h at 24 °C. Finally, the product was filtered, rinsed and dried at 50 °C until reaching a constant mass. Though the synthesis procedure was not formally optimized the present conditions correspond to the best procedure found after several tests (where the temperature and the concentrations of the different reagents were varied) (Pestov et al. 2009).

Sorbent characterization

The sorbent was ground and sieved and the average size of sorbent particles that were used in this study was found to be 0.4 mm. Elemental analysis was performed using an Elemental Analyzer Perkin Elmer (Carlo Erba EA 1108). FT-IR spectra were recorded on a Spectrum One FT-IR spectrometer (Perkin Elmer), equipped with a Smart Orbit Accessory for single-reflection Attenuated Total Reflection (ATR). Fourier Transform facilities were used for subtracting the spectrum of chitosan from the spectrum of PEC to identify more properly the modifications brought by the grafting of new functional groups.

The chemical structures of the materials were determined by ^1H NMR spectroscopy: the samples were dissolved in $\text{D}_2\text{O}/\text{DCl}$ (10 mg mL^{-1}), and



Scheme 1 Reaction of pyridylethylation of chitosan

3-(trimethylsilyl)-1-propanesulfonic acid was used as an external standard. The ^1H NMR spectra were recorded on an Avance DRX400 Bruker NMR spectrometer at the frequency of 400 MHz. The analyses were performed at 70 °C in order to improve signal resolution.

Sorption 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 0–500 mg metal L^{-1}) at target HCl concentration (i.e., 0.1 M, 0.25 M, 0.5 M or 1 M). Samples were collected after 3 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 effect of HCl concentration (with concentrations varying between 0.1 and 2 M).

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, 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 on the polymer at given HCl concentration (20 mg sorbent/25 mL of solution at 70 mg L^{-1} metal concentration); (b) the loaded sorbent (after being rinsed with water) was mixed with the eluent solutions (20 mg sorbent/25 mL of solution; contact time 3 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 PEC. For this purpose 20 mg of sorbent, 25 mL of solution

with 70 mg metal L^{-1} were used for adsorption and for desorption 25 mL of eluent (optimized composition defined by first step of the study, and depending on the metal).

Modeling of experimental results

Sorption equilibria can be described by a number of equations depending on the sorbent and the metal considered. The most frequently used in the field of biosorption are the equations of Langmuir (2-parameters equation), Freundlich (2-parameters equation), Langmuir–Freundlich (3-parameters equation) (Tien 1994). While the Langmuir model is a “mechanistic” equation considering that the equilibrium is reached when the sorption rate equals desorption rates (with appropriate mechanisms attached to the model), the Freundlich equation is an empiric equation. The Langmuir equation assumes that: (a) the sorption occurs as a monolayer on the sorbent surface (the maximum sorption capacity corresponds to the saturation of the monolayer); (b) no interaction may exist between vicinal sorbed molecules, and (c) the sorption energy involved in the binding on the solute is homogeneous over all the sorbent (this also means that the sorbent is homogeneous).

Langmuir equation:

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

with q_m (mg metal g^{-1} , or mmol metal g^{-1}) is the sorption capacity at saturation of the monolayer (maximum sorption capacity) and b is the affinity coefficient (L mg^{-1} metal, or L mmol^{-1} metal). The sorption capacity (or solute concentration in the sorbent), q (mg metal g^{-1} , or mmol metal g^{-1}) is plotted versus the residual metal concentration in the solution, C_{eq} (mg metal L^{-1} , or mmol metal L^{-1}).

Freundlich equation:

$$q = k_F C_{\text{eq}}^{1/n} \quad (2)$$

with k_F ($\text{L}^{1/n} \text{g}^{-1} \text{mg}^{1-1/n}$ metal, or $\text{L}^{1/n} \text{g}^{-1} \text{mmol}^{1-1/n}$ metal) and n are the Freundlich constants.

Several steps may control sorption kinetics (Tien 1994): (a) mass transfer of the solute through the external film and in the porous network (surface and homogeneous diffusion); (b) reaction kinetics. In most cases, binding is controlled by diffusion

mechanisms rather than the reaction rate. The intraparticle diffusion coefficient (D_e , effective diffusivity, $m^2 \text{ min}^{-1}$) was determined using Crank's equation, assuming the solid to be initially free of metal, and the kinetics to be controlled by intraparticle diffusion resistance (Crank 1975):

$$\frac{q(t)}{q_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp\left(\frac{-D_e q_n^2 t}{r^2}\right)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (3)$$

$q(t)$ and q_{eq} are the concentrations of the metal in the resin at time t and at equilibrium, respectively.

And q_n non-zero roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (4)$$

$$\text{with } \frac{q_{eq}}{VC_0} = \frac{1}{1 + \alpha} \quad (5)$$

The MathematicaTM software was used for the determination of the intraparticle diffusion coefficient, D_e , and for the simulation of experimental data (represented by the solid lines on the figures).

Results and discussion

Characterization of the sorbent

The grafting of 2-vinylpyridine on chitosan backbone can only occur on amine groups of chitosan. The polymer has a fraction of nitrogen sites bound with acetyl moieties (according the DA). Since the substitution of 2-pyridylethyl moieties may be incomplete a fraction of amine groups will remain under the free form. Based on these hypotheses it is possible to suggest that the PEC (before glutaraldehyde crosslinking) will have the general structure shown on Fig. 1.

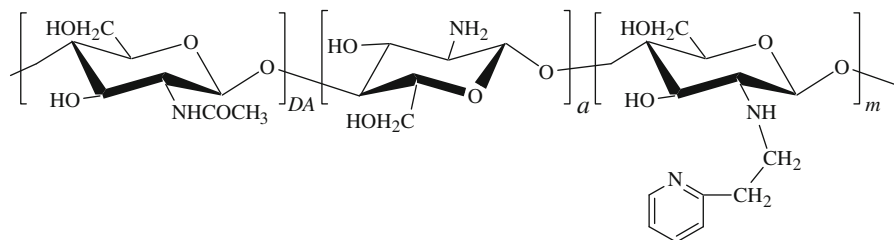


Fig. 1 Schematic representation of PEC derivative

The analysis of ^1H NMR spectra (and more specifically the determination of the areas of the different signals, Fig. 2) served for determining the values of DA, a , and m (see Fig. 1). This first approach gave the following values: $DA = 0.2$, $a = 0.14$ and $m = 0.66$. This means that the substitution degree (DS defined as $DS = m/(a + m)$) was close to 83%. Actually, the process of pyridylethylation is quite difficult to make quantitative. It is common to use long reaction time and higher temperatures for increasing the substitution degree (Reich and Levine 1955). It takes a long reaction time in the case of 2-vinylpyridine addition on chitosan due to considerable steric hindrance effect and the rather weak nucleophilic behavior of the biopolymer (Pestov et al. 2009). Additionally, it is important to state that increasing the temperature may substantially damage the polymer, causing the hydrolysis of the basic chain in acidic medium. Under these conditions the degree of acetylation is not expected to play a significant role in the final substitution degree. Maintaining a non-reacted fraction of amine groups is also important since this free amine groups will be used for the crosslinking of the polymer with glutaraldehyde. The fraction of amine groups that remained free at the end of the synthesis (not reacted with glutaraldehyde) has not been determined.

The elemental analysis gave the following composition: C—54.67%, H—6.95% and N—9.31%. Based on the analysis of ^1H NMR spectra, the expected structure is defined by the general equation: $(\text{C}_8\text{H}_{13}\text{O}_5\text{N})_{0.2}(\text{C}_6\text{H}_{11}\text{O}_4\text{N})_{0.8}(\text{C}_7\text{H}_7\text{N}_2)_{0.66} \cdot 0.20 \text{H}_2\text{O}$. The theoretical composition (based on this structure) would give the elemental composition: C—54.56%, H—6.82% and N—9.58%. These theoretical values are quite close to the results found in the elemental analysis.

The FT-IR analysis shows the bands systematically found on the spectra of chitosan-based materials

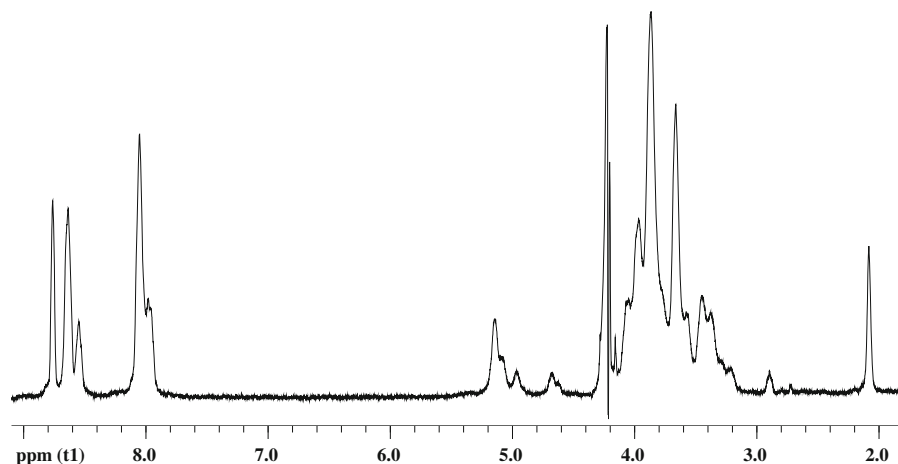


Fig. 2 400 MHz NMR H^1 spectrum (δ , ppm) of PEC solution: 2.07 (CH_3), 3.44–4.21 (CH_2 , $H-2$, 3, 4, 5, 6), 4.66 ($H-1$ of GlcNHAc), 4.95 ($H-1$ of GlcNH $_2$), 5.13 ($H-1$ of GlcNHR), 7.97–8.76 (H of pyridineGlcNR $_2$)

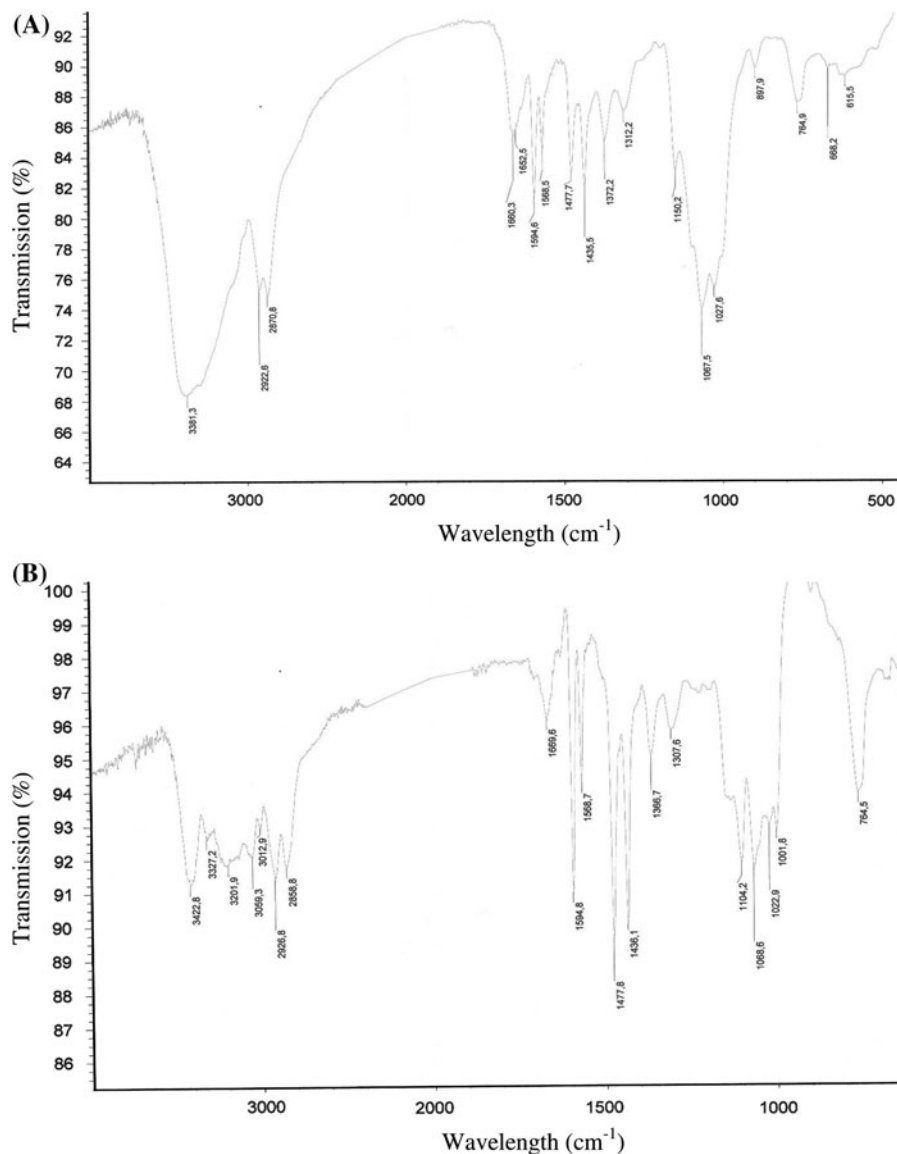
(glucose ring in the range 900–1200 cm^{-1} ; amine and amide bands around 1400–1600 cm^{-1} for example; Fig. 3a). In order to reach a better identification of the functions which were affected by the chemical modification and that even appear (pyridylethyl group, for example) the subtraction of chitosan spectrum from the spectrum of PEC was carried out (Fig. 3b). Apart of the change in the intensity of the typical chitosan bands, which were affected in intensity due to the grafting of new functional groups, new bands appeared around 1594, 1568 cm^{-1} . This band are representative of pyridine ring, for example, *N*-(2-pyridyl)methylchitosan was identified through bands at 1596 and 1571 cm^{-1} (Dhakal et al. 2008).

Influence of HCl and chloride concentration on sorption capacity

Varying the concentration of HCl in the solution may have a dual interaction effect on sorption performance due to the influence of both the acidity and the chloride ions. Chloride ions may have a competitor effect against metal anions for binding on protonated amine groups (Guibal et al. 1999a); however, the presence of chloride anions (at appropriate concentration) may also enhance metal sorption when they contribute to the formation of adsorbable species (Guibal et al. 2000). Indeed, the speciation of metal ions in solution depends on the pH, metal concentration (in some cases more specifically when the metal forms polynuclear species) and the presence of ligands. In the case of precious metals, the presence

of chloride ions induces the formation of anionic species (mainly $PdCl_4^{2-}$ and $PtCl_6^{2-}$) that can bind to protonated amine groups in acidic solutions. In the case of Pt(IV) sorption, Guibal et al. (2000) compared metal sorption in hydrochloric and sulfuric acid solutions (completed with the addition of sulfate and chloride ions, respectively) with two chitosan derivatives: glutaraldehyde crosslinked chitosan (GCC) and a thiourea derivative of chitosan (TGC). In sulfuric acid solutions the concentration of chloride ions is not sufficient (coming only from the dissociation of Pt salt) to promote the formation of chloroanionic species. The addition of small amounts of chloride anions leads to the formation of chloroplatinate species that can bind to protonated amine groups (while above a limit concentration, chloride anions enter in competition with chloroplatinate anions for binding on protonated amine groups). For these reasons, the sorption profiles were compared on Fig. 4 for HCl solutions increasing acid concentration from 0.1 to 5 M and for 0.1 M HCl solutions completed with the addition of chloride ions (at total chloride concentration varying between 0.1 and 5 M). The four curves almost superimposed indicating that the two parameters HCl concentration and chloride concentration roughly play comparable role for Pd(II) and Pt(IV) sorption. Increasing chloride ion concentration (regardless of acid concentration) drastically reduced metal sorption. The protonation of the sorbent is probably the key parameter for metal binding while the presence of excessive concentrations of chloride ions induces a

Fig. 3 FT-IR spectra of PEC (a) and FT-IR analysis of PEC with subtraction of the spectrum of chitosan (b)



strong competition for the availability of the protonated groups (free amine functions, secondary amine groups and pyridine groups). Pd(II) is more sensitive than Pt(IV) to metal speciation effects: Pd(II) is suspected to form more species in solution than Pt(IV) when changing pH, metal and chloride concentrations. The comparable sorption profiles confirm that the competition effect of chloride ions is more important than speciation effects on the control of sorption performance.

The sorption of PGMs on chitosan derivatives has been widely described. On glutaraldehyde cross-linked chitosan the sorption of chloro-anions on

protonated amine groups was attributed to an ion-exchange mechanism (electrostatic attraction of metal anions by protonated biopolymer). This mechanism is strongly influenced by the pH for the sorption step, and it would be expected that the desorption could proceed through pH increase (till reaching free-base form). However, the desorption is non quantitative and it is generally necessary using a strong complexing agent for fully desorbing the metals from loaded sorbent. This result suggests that metal binding proceeds through complexation reaction. However, the strong influence of competitor anions on the sorption of PGMs chloro-anions

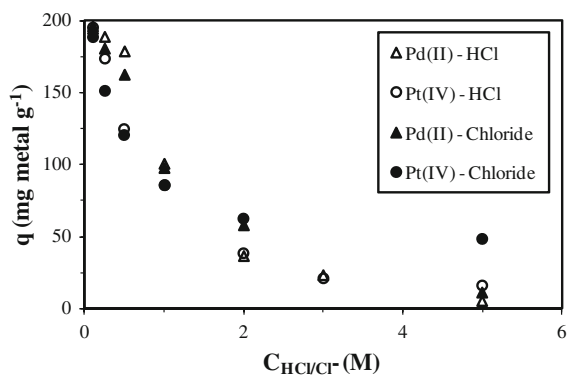
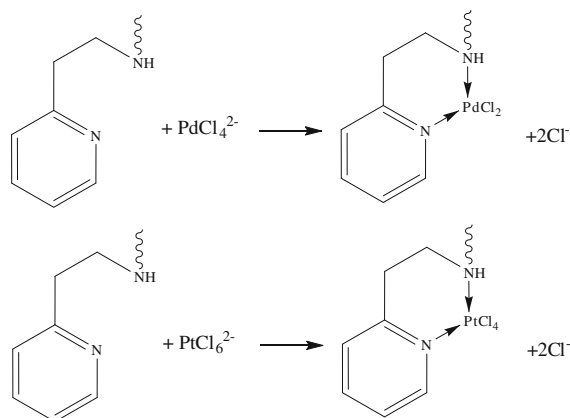


Fig. 4 Influence of the concentration of HCl (*open symbols*) and chloride ions (in 0.1 M HCl solution, *closed symbols*) on Pd(II) and Pt(IV) sorption on PEC (SD: 0.8 g L⁻¹; C₀: 150 mg metal L⁻¹)

supports the hypothesis of an ion exchange mechanism. In the case of pyridine derivatives of chitosan, two possible mechanisms were identified depending on the metal (Inoue and Baba 2007). For copper, Inoue and Baba report the formation of five-membered chelates. In HCl solutions they observe that the sorbent has a high selectivity for Au(III), Pd(II), Pt(IV) and Fe(III) over Cu(II), Ni(II), Cu(II) and Cd(II). This means that the sorbent has a great affinity for metal ions that form chloro-complexes in HCl solutions over those that do not form strong chloro-complexes. Based on the effect of chloride and hydrogen ions on Pd(II) sorption, Inoue and Baba conclude that the binding occurs through an anion exchange mechanism with the formation of an ion pair between tetrachloro complex and protonated form of the pyridine derivative of chitosan. So, the mechanism involved in Pd(II) and Pt(IV) sorption remains debatable though the anion exchange mechanism can be considered a predominant step in the process, but the contribution of chelation mechanism based on the Scheme 2 cannot be totally rejected.

Influence of HCl concentration on sorption isotherms

In order to confirm these trends complete sorption isotherms have been carried out for both Pd(II) and Pt(IV) at HCl concentrations of 0.1, 0.25, 1 and 2 M (Fig. 5). The sorption isotherms show remarkable differences with changing the concentration of HCl and the metal. At low HCl concentration (i.e., 0.1 and



Scheme 2 Possible mechanisms of chelation involved in Pd(II) and Pt(IV) binding on PEC

0.25 M) the sorption isotherm for Pd(II) is almost irreversible: the sorption capacity drastically increased (almost vertical trend) and reached the saturation plateau at low residual metal concentration. For Pt(IV) despite a favorable trend the initial slopes are lower than those found with Pd(II). At

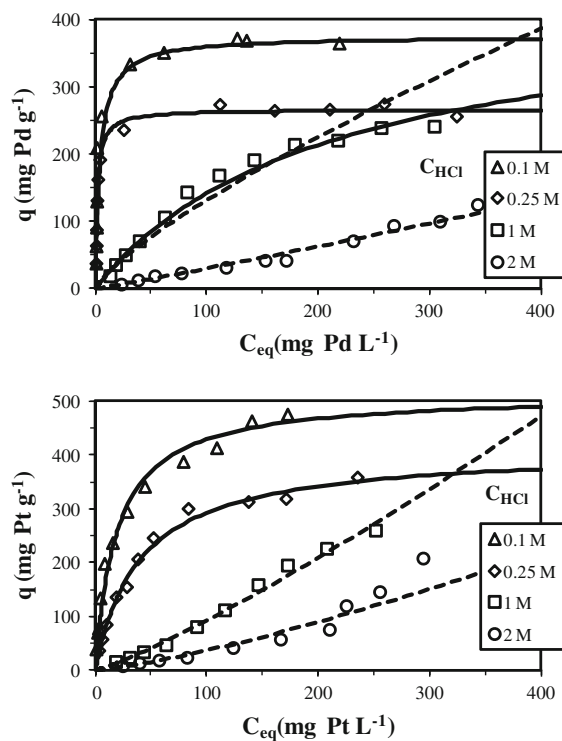


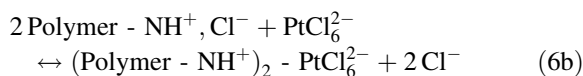
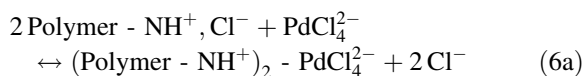
Fig. 5 Influence of HCl concentration on Pd(II) and Pt(IV) sorption isotherms on PEC (*solid lines* Langmuir modeling; *dashed lines* Freundlich modeling)

higher HCl concentration (i.e., 1 and 2 M), the isotherms were defavorable (inversion of the concavity of the plot). The sorption capacities progressively increased with a much slower slope and the saturation plateau is not observed. These trends are confirmed by the modeling of the sorption isotherms (Tables 1 and 2). While for Pd(II) and Pt(IV) sorption, the Langmuir equation (solid lines) fitted well experimental data (correlation coefficient higher than 0.99) for HCl concentrations 0.1 and 0.25 M, at higher HCl concentration the Freundlich equation (discontinuous lines) gave better fits of experimental curves. At high HCl concentration, the strong competition of chloride ions induced less favorable sorption mechanism. The comparison of sorption isotherms also shows that PEC has a marked preference for Pd(II) against Pt(IV). Indeed, at both 0.1 and 0.25 M HCl concentrations, the maximum sorption capacity was higher for Pd(II) (i.e., 3.5 and 2.5 mmol Pd g⁻¹) than for Pt(IV) (i.e., 2.6 and 2.1 mmol Pt g⁻¹). This is also confirmed by the affinity coefficients (b) that were significantly greater (from 5 to 25 times) for Pd(II) compared to Pt(IV). At higher HCl concentration (i.e., 1 and 2 M) the sorption capacity reached appreciable levels only for very high residual metal concentrations, the initial slope of the curves was also considerably decreased making the sorbent difficult to use for the competitive recovery of PGMs at high HCl concentration. Similar trends were observed with chitosan crosslinked with glutaraldehyde: at pH below 2, sorption capacity drastically decreased. The grafting of pyridyl groups allows increasing the sorption capacity at higher acidity; however, the beneficial effect is limited for HCl concentrations greater than 0.25 M. Sulfur derivatives (based on the grafting of thiourea or rubeanic acid) also brought appreciable increase in the sorption performance for Pd(II), Pt(IV) and Au(III) binding by chitosan-based materials (Guibal et al. 2000). However, for reaching high sorption levels in very acidic solutions (above 1 M HCl concentrations) it is necessary using other systems: an example is given by the encapsulation of ionic liquids (alkyl phosphonium salts) into biopolymer capsules (Guibal et al. 2009; Vincent et al. 2008a, b), or on conventional macroporous resins (Gallardo et al. 2008). The elemental analysis has shown that the PEC (prior to glutaraldehyde crosslinking) contains up to 9.3% of nitrogen. This corresponds to 6.6 mmol

Table 1 Modeling of Pd(II) and Pt(IV) sorption isotherms using PEC—Langmuir equation

Metal	C _{HCl} (M)	q _m (mg g ⁻¹)	q _m (mmol g ⁻¹)	b (L mg ⁻¹)	R ²
Pd(II)	0.1	375.6	3.53	0.229	0.999
	0.25	266.5	2.50	0.565	0.998
	1	438.9	4.12	0.005	0.908
	2	NS	NS	NS	–
Pt(IV)	0.1	514.0	2.63	0.050	0.995
	0.25	411.8	2.11	0.024	0.995
	1	NS	NS	NS	–
	2	NS	NS	NS	–

nitrogen per g of sorbent, including free amine groups that could be involved in the crosslinking reaction, acetylamide groups, secondary amine potentially less reactive and pyridine nitrogen. The crosslinking treatment can induce significant variations of the elemental distribution and the relationship between sorption capacity and nitrogen content is difficult to establish. The strong effect of chloride ions confirms that the sorption involves an electrostatic attraction/ion exchange mechanism according:



Several studies have shown that the mechanism of metal sorption on pyridylmethyl chitosan (PMC) depended on the ionic character of the metal: the sorption of metal cations proceeds by chelation while metal ions were bound by an electrostatic attraction mechanism (Baba et al. 1998; Dhakal et al. 2008). This was confirmed by the positive effect of a pH increase on metal cation sorption while the sorption of metal anions (tetrachloroaurate and tetrachloropalladate anions) was enhanced when increasing the acidity of the solution.

Sorption of Pd(II) and Pt(IV) in binary component solutions

The sorption of Pd(II) and Pt(IV) from mono-component solutions has shown that PEC has a

Table 2 Modeling of Pd(II) and Pt(IV) sorption isotherms using PEC—Freundlich equation

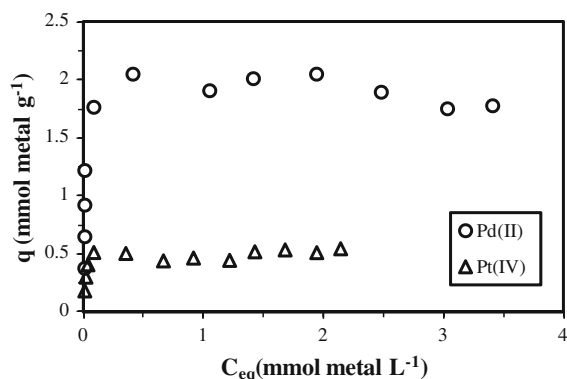
Metal	C _{HCl} (M)	k _F (g L ^{1/n} mg ^{1-1/n})	k _F (g L ^{1/n} mmol ^{1-1/n})	n	R ²
Pd(II)	0.1	85.4	3.60	3.11	0.717
	0.25	85.5	2.35	4.34	0.720
	1	3.57	1.29	1.28	0.958
	2	0.21	0.30	0.93	0.980
Pt(IV)	0.1	45.8	3.19	2.02	0.924
	0.25	21.7	2.10	1.80	0.944
	1	0.40	1.04	0.85	0.993
	2	0.096	0.444	0.775	0.964

greater affinity for Pd(II) over Pt(IV); it is interesting to check if this preferential affinity is verified in metal mixtures. Figure 6 shows the sorption isotherm for Pd(II)/Pt(IV) binary solutions (molar ratio Pd(II)/Pt(IV) close to 2, in 0.1 M HCl solution). The two curves show a very favorable sorption trend: this means that the presence of the competitor metal did not drastically affect the sorption of the other metal. At equilibrium, the distribution of the molar ratio Pd(II)/Pt(IV) on the sorbent varied between 0.8 and 5.5 with a large majority of values above 3. This confirms that PEC has a preference for Pd(II) over Pt(IV) in 0.1 M HCl solutions, though this preference is not sufficient for separating the two metals from binary solutions. The extended Langmuir equation can be used for describing sorption in binary solutions according to Eq. 7a, 7b.

$$q_{Pd} = \frac{q_{m,Pd} b_{Pd} C_{eq,Pd}}{1 + b_{Pd} C_{eq,Pd} + b_{Pt} C_{eq,Pt}} \quad (7a)$$

$$q_{Pt} = \frac{q_{m,Pt} b_{Pt} C_{eq,Pt}}{1 + b_{Pd} C_{eq,Pd} + b_{Pt} C_{eq,Pt}} \quad (7b)$$

with $q_{m,i}$, b_i , are the Langmuir constants for mono component solutions. The plot of simulated curves using the constants shown on Table 1 (See Appendix, Fig. 12) shows that this simplified model is not appropriate for simulating the sorption of Pd(II) and Pt(IV) in binary component solutions. The simulated curve overestimated sorption capacity for Pt(IV) (the overestimation tended to be negligible at high metal concentration) while for Pd(II) the simulated curve underestimated sorption capacity at low metal concentration and overestimated the sorption capacity at high residual metal concentration. This evolution is consistent with the preferred sorption of Pd(II) over

**Fig. 6** Pd(II) and Pt(IV) sorption isotherm using PEC in 0.1 M HCl solutions

Pt(IV). With other chitosan derivatives (PEI-grafted chitosan, sulfur derivative of chitosan), the sorbent had also a slight preference for Pd(II) over Pt(IV), but not enough for allowing the selective separation of these PGMs (Chassary et al. 2005).

Effect of HCl concentration on Pd(II) uptake kinetics

Figure 7 shows the kinetic profiles for Pd(II) sorption on PEC at different HCl concentrations. The figure shows that under selected conditions the equilibrium was reached within a few hours (2–4 h depending on HCl concentration). As expected from previous sections the equilibrium concentration increased with HCl concentration. Another important phenomenon is identified for the uptake kinetics in 1 M HCl solutions: after 6 h of contact the concentration of Pd(II) in the solution increased. The metal previously bound was progressively released. At high HCl

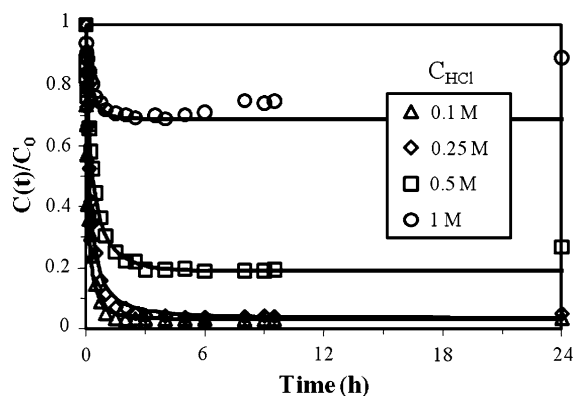


Fig. 7 Influence of HCl concentration on Pd(II) uptake kinetics using PEC (SD: 0.25 g L⁻¹; v: 400 rpm; C₀: 30 mg Pd L⁻¹; *solid lines* modeling with the model of resistance to intraparticle diffusion)

concentration the sorbent is partially degraded leading to the reversibility of metal binding. This phenomenon was also observed but to a lesser extent with other HCl concentrations and for greater contact times (2/3 days). The instability of the sorbent, especially in very acidic solutions, at long contact time may explain the significant decrease in the sorption capacity obtained for 1 and 2 M HCl solutions (Fig. 5) since the contact time was fixed to 3 days.

The solid lines show the modeling of the uptake kinetics with the model of resistance to intraparticle diffusion. This simplified model (the so-called Crank's equation) fitted well experimental data. The Table 3 summarizes the values of the intraparticle diffusivity. The intraparticle diffusion coefficient roughly increased with HCl concentration. The decrease of sorption capacity with this parameter may explain that the equilibrium is reached faster.

Table 3 Pd(II) uptake kinetics—intraparticle diffusivity

HCl (M)	C ₀ (mg L ⁻¹)	SD (g L ⁻¹)	V (rpm)	D _{eff} × 10 ¹¹ (m ² min ⁻¹)	EV
0.1	30	0.25	400	6.48	0.021
0.25	30	0.25	400	3.53	0.012
0.5	30	0.25	400	11.0	0.017
1	30	0.25	400	38.9	0.190
0.1	30	0.1	400	7.99	0.015
0.1	70	0.1	400	38.0	0.088
0.1	100	0.1	400	35.6	0.226
0.1	30	0.025	400	28.5	0.115
0.1	30	0.1	200	9.84	0.024
0.1	30	0.1	600	9.75	0.024

EV estimated variance

Influence of agitation speed on Pd(II) and Pt(IV) uptake kinetics

The agitation speed may affect uptake kinetics through the effects of film diffusion. Indeed, the agitation speed contributes to controlling the thickness of the film surrounding sorbent particles. In the case of ion exchange mechanisms controlled by the resistance to film diffusion the rate varies with agitation speed, while this parameter does not influence ion exchange rate when the sorption kinetics is controlled by the resistance to intraparticle diffusion (Helfferich 1995). Figure 8 compares for both Pd(II) and Pt(IV) the uptake profiles when varying the agitation speed from 200 to 600 rpm. Surprisingly, the agitation speed 200 and 600 rpm superimposed at higher concentration levels than the curve obtained with 400 rpm. It seems that the optimum value for agitation is close to 400 rpm, regardless of metal. For other experiments, the agitation speed was systematically maintained at 400 rpm. Tables 3 and 4 show the intraparticle diffusion coefficient. In the case of Pd(II), the coefficient D_{eff} varied between 8 × 10⁻¹¹ and 9.8 × 10⁻¹¹ m² min⁻¹; this confirms the poor effect of agitation speed and the resistance to film diffusion on the control of uptake kinetics. In the case of Pt(IV), the intraparticle diffusivity varied between 4.7 × 10⁻¹¹ and 1.8 × 10⁻¹⁰ m² min⁻¹. The limited influence of agitation speed confirms that the uptake kinetics are mainly controlled by the resistance to intraparticle diffusion.

Influence of metal concentration on Pd(II) and Pt(IV) uptake kinetics

The metal concentration influences the gradient between the solution and the surface of sorbent

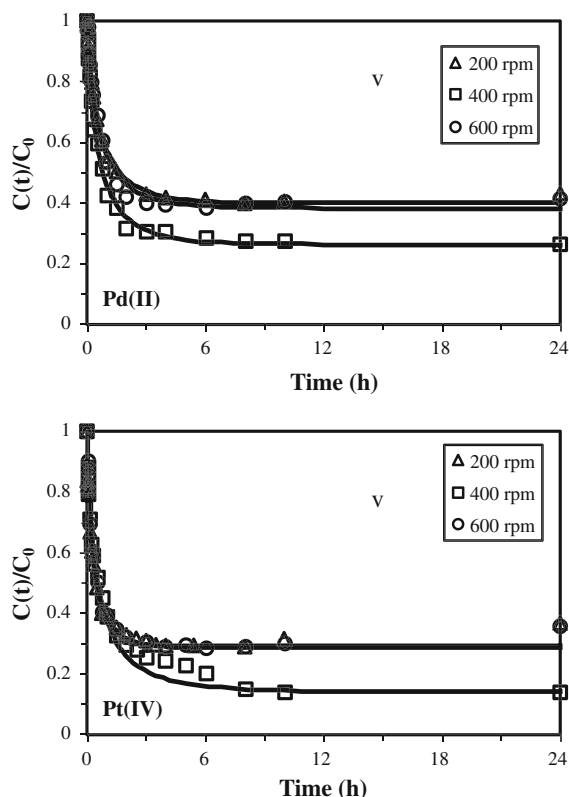


Fig. 8 Influence of agitation speed on Pd(II) and Pt(IV) uptake kinetics using PEC (C_0 : 30 mg L^{-1} ; SD: 0.1 g L^{-1} ; C_{HCl} : 0.1 M ; *solid lines* modeling with the model of resistance to intraparticle diffusion)

particle (resistance to film diffusion) and between the surface of the particle and the sorption sites located in the center of the particle. Helfferich (1995), summarizing the effect of a series of experimental parameters on ion exchange rate, observed that the rate varies with the concentration in the case of a mechanism controlled by the resistance to film diffusion while for mechanisms controlled by the resistance to intraparticle diffusion the rate is independent of the concentration. The resistance to film diffusion plays generally a significant role in the initial stage of the kinetics. Since the initial slope did not appear to be controlled by metal concentration (Fig. 9), this confirms that uptake kinetics were mainly controlled by the resistance to intraparticle diffusion. The intraparticle diffusivity increased with metal concentration (Tables 3 and 4) by a factor close to 4 between 30 and $100 \text{ mg metal L}^{-1}$, regardless of the metal from 8×10^{11} to $38 \times 10^{11} \text{ m}^2 \text{ min}^{-1}$ for Pd(II) and between 10^{10} and $4.4 \times 10^{10} \text{ m}^2 \text{ min}^{-1}$

for Pt(IV). Increasing metal concentration in the solution induces a greater concentration gradient between the solution and the center of the particle. This may contribute to increasing the diffusivity of metal ions in the porous network of the polymer.

Influence of sorbent dosage on Pd(II) and Pt(IV) uptake kinetics

When increasing sorbent dosage the residual metal concentration logically decreased. More interesting is the comparison of initial slopes. The slope of the concentration decay curve tended to increase with increasing sorbent dosage (Fig. 10). Obviously, increasing the amount of sorbent induces an increase of sorbent exchange surface (and sorption reactive groups) available for metal binding. The external surface area is correlated to resistance to film diffusion; increasing sorbent dosage will enhance uptake kinetics. The comparison of intraparticle diffusion coefficients shows a decreasing trend when the sorbent dosage increased. When increasing the amount of sorbent, the sorption capacity at equilibrium decreases; as a consequence, the concentration gradient between the solution and the internal reactive groups (i.e., the driving force for intraparticle diffusion) decreases. The intraparticle diffusion coefficients varied between 6.5×10^{11} and $2.8 \times 10^{10} \text{ m}^2 \text{ min}^{-1}$ for Pd(II) and between 4.7×10^{11} and $2.2 \times 10^{10} \text{ m}^2 \text{ min}^{-1}$ for Pd(IV). This is about four orders of magnitude lower than the values of molecular diffusivities of tetrachloropalladate and hexachloroplatinate anions in water (Marcus 1997).

Metal desorption and sorbent recycling

Several eluents have been tested for Pd(II) and Pt(IV) recovery from loaded sorbents. Most interesting results are summarized in Tables 5 and 6. Additionally, ammonia solutions (at different concentrations; i.e., between 0.5 and 3 M) have been also tested. Ammonia solutions recovered less than 10% of the metal initially sorbed. Thiourea is a ligand that was frequently used for the recovery of precious metals from loaded sorbents and resins. This ligand is generally used in acidic solutions for enhancing metal recovery (Sanchez et al. 2001; Adhikari et al. 2008; Donia et al. 2005). Tables 5 and 6 show the results obtained varying both thiourea and HCl concentration

Table 4 Pt(IV) uptake kinetics—intraparticle diffusivity

HCl (M)	C_0 (mg L ⁻¹)	SD (g L ⁻¹)	V (rpm)	$D_{\text{eff}} \times 10^{11}$ (m ² min ⁻¹)	EV
0.1	30	0.025	400	21.6	0.230
0.1	30	0.1	400	4.69	0.057
0.1	30	0.25	400	10.4	0.016
0.1	70	0.1	400	16.1	0.022
0.1	100	0.1	400	43.9	0.053
0.1	30	0.1	200	17.6	0.046
0.1	30	0.1	600	15.2	0.018

EV estimated variance

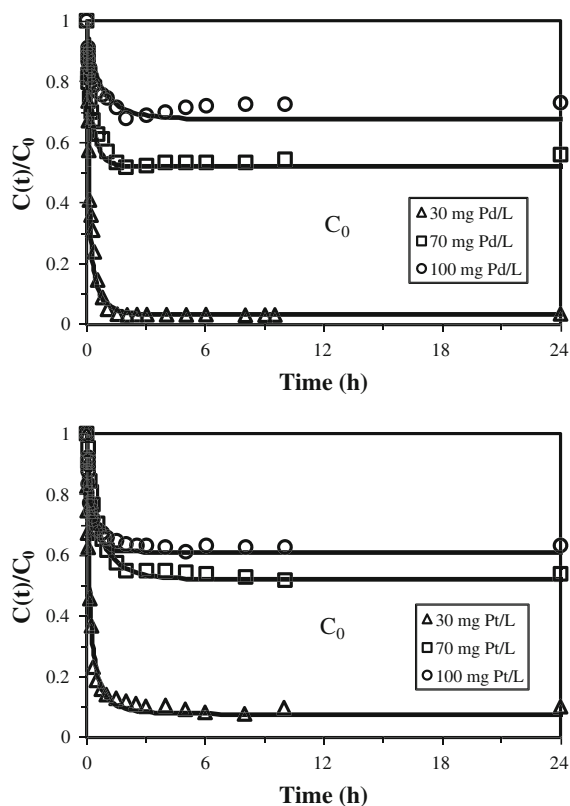


Fig. 9 Influence of metal concentration on Pd(II) and Pt(IV) uptake kinetics using PEC (SD: 0.25 g L⁻¹; v: 400 rpm; C_{HCl} : 0.1 M; *solid lines* modeling with the model of resistance to intraparticle diffusion)

in the eluent. In the case of Pd(II), the desorption of the metal was slightly enhanced by the addition of HCl to the thiourea solution (TU): the desorption yield reached 91% for 0.05 M TU in 0.1 M HCl solution. Increasing TU concentration did not significantly improve desorption efficiency, at least in 0.1 M HCl solutions, while for 0.5 M HCl solutions,

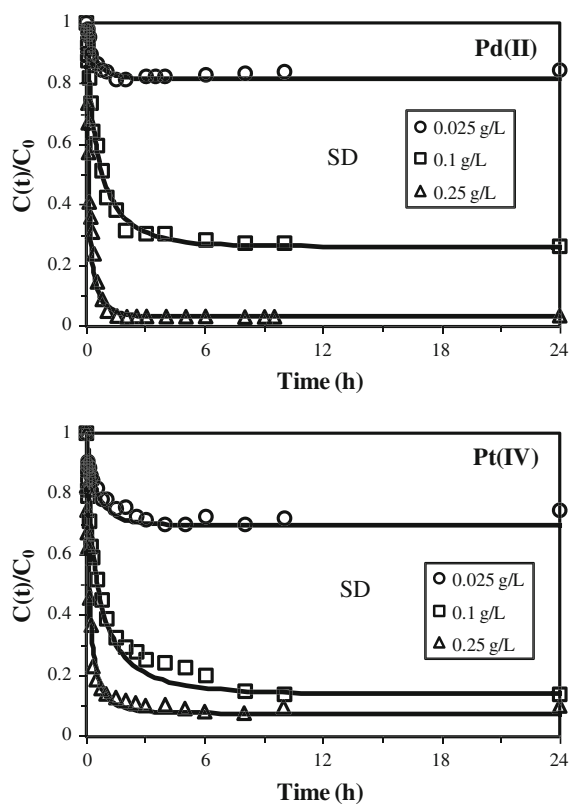


Fig. 10 Influence of sorbent dosage on Pd(II) and Pt(IV) uptake kinetics using PEC (C_0 : 30 mg L⁻¹; v: 400 rpm; C_{HCl} : 0.1 M; *solid lines* modeling with the model of resistance to intraparticle diffusion)

the efficiency slightly increased when the TU concentration reached 0.3 M. Optimum desorption (close to 91%) was obtained for 0.05 M TU + 0.1 M HCl solution (and for 0.3 M TU + 0.5 M HCl solutions). For Pt(IV), the desorption efficiency also exceeded 90% with 0.1 M TU + 0.5 M HCl solutions.

Table 5 Eluent selection for Pd(II) loaded on PEC

Thiourea (M)	C _{HCl} (M)	Desorption efficiency (%)
0.05	–	85
0.05	0.1	91
0.05	0.5	89
0.1	0.5	86
0.2	0.5	72
0.3	0.5	91
1	2	84
0.7	2	63

Pd(II) sorbent loading: 87 mg Pd g⁻¹. The bold entries represent optimum results (selected experimental conditions and maximum desorption efficiencies)

Table 6 Eluent selection for Pt(IV) loaded on PEC

Thiourea (M)	C _{HCl} (M)	Desorption efficiency (%)
0.05	0.5	64
0.1	0.5	92
0.2	0.5	79
0.3	0.5	88
0.05	0.1	61

Pt(IV) sorbent loading: 85 mg Pt g⁻¹. The bold entries represent optimum results (selected experimental conditions and maximum desorption efficiencies)

These solutions were used for testing the recycling of the resins. Figure 11 shows the amount of metal (Pd and Pt) adsorbed and desorbed at each sorption/desorption cycle. This figure shows that the amount of metal sorbed at each stage, regardless of the metal, decreased very slightly with the number of operations for Pt(IV) (from 1.8 to 1.5 mg) and remained roughly constant for Pd(II) (1.6 mg ± 6%). For desorption, Pd(II) recovery was also more stable along the five cycles compared to Pt(IV): the average desorbed amount was 1.3 mg (±6%), while for Pt(IV) it reached 1.2 mg (±9%). The cumulative desorption efficiency for Pd(II) reached 85% against 75% for Pt(IV). These results confirm that the desorption of both Pd(II) and Pt(IV) was not complete, slightly higher for palladium compared to platinum. Despite these decreasing trends the sorbent could be re-used for a minimum of five cycles maintaining high sorption performance.

Thiourea being a strong complexing agent for PGMs, the addition of thiourea in acidic media contributes to displace the metal from the loaded

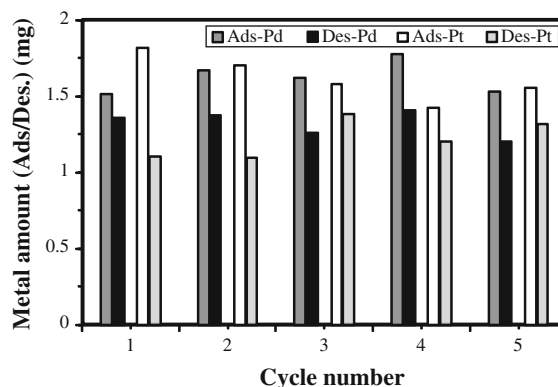


Fig. 11 Sorption/desorption cycles for Pd(II) and Pt(IV) recovery from HCl solutions using PEC (Desorption of Pd(II): 0.1 M thiourea in 0.5 M HCl solution; desorption of Pt(IV): 0.05 M thiourea in 0.1 M HCl solution)

sorbent. In the perspective of sorbent recycling it is important to carefully clean the sorbent after the desorption step to remove any trace of the ligand since it could contribute to a competitive complexation of target metals for the next sorption steps.

Conclusion

The modification of chitosan with grafting pyridyl reactive groups allows extending the range of application of chitosan-based materials for the sorption of precious metals to more acid solutions (compared to glutaraldehyde cross-linked solutions). The main limitation for using these materials for more acidic media is probably due to the progressive degradation of the material at long contact time when the concentration of HCl exceeds 0.5 M. The sorption mechanism involves the interaction of chloroanionic metal species with protonated amine and the pyridyl groups in acidic media.

Sorption capacities as high as 3.5 and 2.6 mmol - metal g⁻¹ were obtained in 0.1 M HCl solutions for Pd(II) and Pt(IV), respectively. The sorption capacity decreases with increasing HCl concentration (probably due to the competition effect of high chloride ion concentration). The sorbent reveals poorly stable in very acidic solutions leading to low sorption capacities when HCl concentration reached 1 M (especially at long contact time). The Langmuir equation fits well experimental data for 0.1 and 0.25 M HCl concentrations, while for higher HCl concentrations the Freundlich equation is more appropriate for

simulating experimental curves. Though the sorbent has a preference for Pd(II) over Pt(IV) (based on maximum sorption capacity and affinity coefficient) the sorption isotherm in binary solutions shows that the separation effect is not sufficient for promoting Pd(II) selective recovery.

Though the combination of several limiting processes can be involved in the control of uptake kinetics, the resistance to intraparticle diffusion seems to play the major role. The limited effect of the agitation speed confirms that the resistance to film diffusion is not the main controlling step in the mass transfer. Among tested experimental parameters, metal concentration and sorbent dosage have the major influence on the kinetic rates. The intraparticle diffusivity varies in the range $3 \times 10^{-11} \text{ m}^2 \text{ min}^{-1}$ – $4.5 \times 10^{-10} \text{ m}^2 \text{ min}^{-1}$.

The best desorption (close to 90%) of Pd(II) and Pt(IV) was obtained using a thiourea/HCl solutions (with respective concentrations depending on the metal). The resin was successfully carried out for five successive sorption/desorption cycles, maintaining high metal recovery levels.

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Appendix

See Fig. 12.

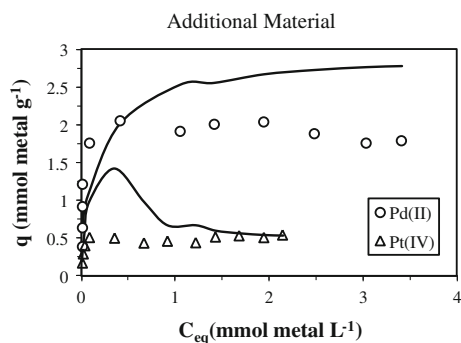


Fig. 12 Simulation of Pd(II) and Pt(IV) sorption isotherms in binary solutions (0.1 M HCl solution) using the extended Langmuir equation (Eq. 7a, 7b) with the parameters of the Langmuir equation for mono-component solutions (Table 1) (simulated curves were calculated with discrete values of experimental concentrations and the trends were extrapolated joining point-to-point)

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