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Palladium and platinum sorption using chitosan-based hydrogels

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Abstract Two chitosan hydrogels (prepared by NaOH neutralization and by polyphosphate ionotropic gelation) have been tested in the dry state for Pd(II) and Pt(IV) sorption at pH 2. Similar sorption isotherms with maximum sorption capacities close to 190 $\mathrm{mg\,Pd\,g^{-1}}$ and 235 $\mathrm{mg\,Pt\,g^{-1}}$ were achieved. The sorption mechanism involves electrostatic attraction of the chloro-anionic species onto protonated amine groups; the drastic decrease of sorption capacity with the addition of chloride ions supports this hypothesis. SEM-EDAX analysis suggests that sorption proceeds, in kinetic terms, through a shrinking core mechanism. Metal ions can diffuse throughout all the sorbent volume. The main differences between the sorbents are revealed by kinetics. The hydrogels prepared by ionotropic gelation in polyphosphate (C-PPh) allows reaching equilibrium much faster than the hydrogels prepared by the neutralization process (C-NaOH). While for C-PPh sorbent the chemical reaction rate seems to control sorption profiles, in the case of C-NaOH a combination of mechanisms including intraparticle diffusion resistance controls uptake kinetics. Metal desorption from loaded sorbents is possible using thiourea alone or in association with HCl solutions. The recycling of the sorbents is possible but for a limited number of cycles.

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1 Introduction

Chitosan has been widely studied for the sorption of metal ions (Guibal 2004). The presence of amine groups gives to the biopolymer in acidic media a cationic behavior that makes it unique among polysaccharides. These amine groups are responsible for its excellent sorption properties. Metal binding may occur on the free electronic doublet of chitosan by complexation, chelation mechanisms. Other reactive groups (for example –OH groups) may be involved in the stabilization of metal-amine bonds; however, it is commonly accepted that amine groups are responsible of the binding of metal cations in near neutral solutions. Indeed, in acidic media the competition of protons causes the protonation of amine groups, which are no more active for cation binding. The cationic behavior also accounts for the binding of metal anions (Guibal et al. 1999b), and anionic dyes (Gibbs et al. 2003; Wong et al. 2008): the electrostatic attraction or the ion exchange mechanism allow binding anionic compounds on protonated amine groups.

The protonation of amine groups is also responsible for chitosan dissolving in dilute acidic solutions (with the exception of sulfuric acid) (Roberts 1992). Chitosan dissolution limits the possibility of using this polymer for the treatment of acidic solutions, except when using a cross-linking treatment that strengthens the stability of the polymer in acidic media. A number of chemical reagents may be used for chitosan cross-linking; one of the most frequently used is glutaraldehyde. The aldehyde groups on each side of the cross-linking agent react with amine groups of different polymer chains through a Schiff's base reaction (imine formation) (Roberts 1992): the supplementary linkages allow maintaining the polymer stable in acidic solutions.

Chitosan dissolution is also an important property that was used for the preparation of a number of different physical conditionings. Indeed, polymer solubilization is a necessary step that allows further preparing chitosan hydrogels in the form of spherical particles (Lee et al. 2001), films, membranes (Vieira et al. 2007), fibers and even hollow fibers (Peirano et al. 2008; Vincent and Guibal 2000). The process generally consists in extruding the viscous solution of chitosan into a coagulation or neutralization bath (NaOH, tripolyphosphate). The shape of the hydrogel is controlled by several factors related to the mode of extrusion, the viscosity of the solution, the flow rate, the coagulating bath, among others.

These hydrogels have been used for the recovery of metal ions: (a) metal cations by complexation in near-neutral solutions (Lee et al. 2001), (b) anionic complexes by electrostatic attraction in acidic media (Guibal et al. 1999a). These hydrogels have been designed to make possible the use of chitosan in column systems; indeed, when packed in column chitosan flakes cause column blockage at large scale. Spherical hydrogel particles revealed to be better suited for column design. The main drawback related to hydrogels is the huge amount of water they contain (i.e., generally higher than 95%), and the low volumetric density of sorption sites (Ruiz et al. 2002a, 2002b). This problem can be ruled out by a drying treatment, but at the expense of a decrease in diffusion properties of these materials (Ruiz et al. 2002a). The preparation of hydrogels contribute to reduce the crystallinity of the polymer (polymer dissolution), and to increase the porosity (swelling of the polymer structure). Uncontrolled drying (for example, oven drying or drying at room temperature under air flow) is generally irreversible and the re-hydration does not allow the complete restoring of the diffusion properties of original materials (Ruiz et al. 2002a): this can be measured by the comparison of the diameter or the volume of the bead at each stage of the process. Alternative processes have been tested for efficient drying of chitosan hydrogels: freeze-drying and more recently drying under supercritical CO_2 conditions. Freeze-drying allows partially restoring diffusion properties but this is generally not sufficient and the increase in the specific surface area is relatively limited (except when the hydrogels was submitted to cross-linking). Drying under supercritical CO_2 conditions enables a better management of the capillary forces during the drying process and the modification of porous structure remains reversible (Valentin et al. 2003, 2007). Another process was used for drying chitosan gel beads (Ruiz et al. 2002a): the hydrogels were immersed into a saturated sucrose solution for in-deep diffusion prior to drying. During the drying step, the presence of sucrose in the porous network of the polymer limits the collapse of the porous structure; after rehydration the beads almost recovered their initial size. These processes are complex or expensive and there is still a need for developing alternative routes for the preparation of chitosan hydrogels with improved diffusion characteristics.

Though sodium hydroxide was the most frequently used neutralization agent for the elaboration of chitosan hydrogels a number of other agents were also tested, including tripolyphosphate and polyphosphate (Gupta and Jabrail 2007; Hsieh et al. 2008; Mi et al. 1999, 2002; Qi and Xu 2004; Shu and Zhu 2002). The present work compares Pd(II) and Pt(IV) sorption behavior of conventional chitosan hydrogels (neutralization in NaOH bath, C-NaOH) and chitosan ionically cross-linked with sodium polyphosphate (C-PPh). The hydrogels were treated with glutaraldehyde for reinforcing the stability of the polymers and they were used in the dry state. Previous investigations have shown that PGMs (precious group metals, including Pt(IV) and Pd(II)) are preferentially sorbed at pH 2 on glutaraldehyde cross-linked chitosan (Guibal et al. 1999a). In this study all the experiments were performed at this pH. SEM-EDAX analysis was used for the characterization of chitosan hydrogels after metal binding. Sorption properties are compared on the basis of sorption isotherms, uptake kinetics, competition effect of anions, and desorption efficiency.

2 Material and methods

2.1 Materials

Chitosan was supplied by Aber Technologies (Plouvien, France). Molecular weight was previously characterized using light scattering measurement coupled with size exclusion chromatography (Guibal et al. 1998): the MW_w was $125.000\ \mathrm{g\,mol^{-1}}$. The deacetylation percentage (i.e., 87%) was measured by FT-IR analysis.

Potassium hexachloroplatinate and palladium chloride salts were supplied by Aldrich Chemie and Acros Organics, respectively. Stock solutions (i.e., $10\ \mathrm{g\,L^{-1}}$) were prepared by dissolving the salts in concentrated HCl solutions under heating before diluting in demineralized water (final HCl concentration 1.1 M). Sodium polyphosphate (sodium hexametaphosphate) was supplied by Fluka AG (Switzerland).

2.2 Preparation of chitosan hydrogels

Chitosan was dissolved in acetic acid solution: the biomass was first hydrated in water overnight; the acetic acid solution was added in slight excess to the chitosan suspension. The solution was maintained under agitation until complete dissolution. The solution was then filtered and deaerated. The final concentration of chitosan was 2% (w/w). The solution was distributed through a thin nozzle into the neutralization or ionotropic gelation solution. The height of drop and the distribution speed were controlled to adjust the shape of the gel beads as spherical as possible. The conventional hydrogels (C-NaOH) were neutralized in 2 M NaOH solutions. The contact time with the neutralization solution was 16 hours. The beads were then rinsed to remove the excess of reagent. The cross-linking of the hydrogels (C-NaOH) was performed by contact of the beads in the wet form (5 g dry weight) with 1.5 g of glutaraldehyde (solution 50%, w/w) dissolved in 100 mL of demineralized water for 24 hours. Afterwards, the beads were rinsed to remove the excess of glutaraldehyde.

Alternative hydrogels (C-PPh) were prepared by ionotropic gelation into a 1 $\mathrm{g\,L^{-1}}$ solution of sodium polyphosphate containing 1% of glutaraldehyde (50% w/w in water). The beads were maintained for 2 hours in the coagulation solution. The beads were rinsed before being dropped into a saturated NaCl solution. The beads (impregnated with NaCl) were rinsed with methanol before being dried at room temperature overnight. Sodium chloride was removed by contact in two successive baths of demineralized water. Methanol was used for exchanging the solvent (water being replaced with the alcohol) and final drying. The procedure for the synthesis of C-PPh consists both in the ionotropic gelation of chitosan beads and chemical cross-linking (with glutaraldehyde).

The water content of the beads was close to 95% and their drying was performed in two steps: (a) solvent exchange by contact for 10 minutes of the beads with methanol, followed by a new step using a fresh methanol solution for 30-min contact; (b) drying at room temperature.

2.3 SEM-EDAX analysis

The distribution of elements (especially Pd or Pt and phosphorus, as the tracer of polyphosphate) in the beads was investigated by Environmental Scanning Electron Microscopy (ESEM) Quanta.

FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. The system can be used to acquire qualitative or quantitative spot analyses and qualitative or quantitative X-ray elemental maps and line scans. This ESEM allows samples to be analyzed at pressures and humidity which approach normal laboratory conditions and avoids experimental artifact. More specifically, it is possible to analyze the samples at much higher pressure than with conventional SEM. The preparation of the cross-section of the chitosan beads was performed by particle freezing in liquid nitrogen followed by the mechanical breaking of the spherical particles.

2.4 Sorption experiments

Sorption experiments were performed by contact of 80 mL aliquots of aqueous solutions containing variable concentration (10–100 $\mathrm{mg\,L^{-1}}$) of Pt(IV) and Pd(II) with a known amount of dry sorbent (i.e., 20 mg). The pH was controlled to pH 2 using HCl and NaOH solutions. The suspension was maintained in agitation for 3 days at room temperature (i.e., 20 ± 1°C) in a reciprocating shaker (HS 501 Digital, IKA Labortechnik; agitation speed: 200 rpm). The pH was measured at the end of sorption process using a pH 300 (Hanna Instruments) pH-meter. The solution was filtrated and the filtrate was analyzed for Pd(II) and Pt(IV) content using an ICP-AES JY2000 (Jobin-Yvon, Longjumeau, France). The mass balance equation was used for calculating the sorption capacity (q, $\mathrm{mg\,g^{-1}}$ or $\mathrm{mmol\,g^{-1}}$): $q = (C_0 - C_{eq})$ V/m, where C_0 and C_{eq} are the initial and equilibrium metal concentration ($\mathrm{mg\,L^{-1}}$ or $\mathrm{mmol\,L^{-1}}$), respectively; V is the volume of solution (L) and m the mass of sorbent (g).

The influence of salt addition (NaCl) on sorption efficiency was carried out by contact of a given amount of sorbent (i.e., 20 mg) with 80 mL of Pd(II) solution (concentration: 70 $\mathrm{mg\,L^{-1}}$) or Pt(IV) solution (concentration: 80 $\mathrm{mg\,L^{-1}}$) complemented with salt addition (up to 5 $\mathrm{g\,L^{-1}}$ of chloride ions) for 3 days under agitation (at 200 rpm) and at room temperature. Residual concentrations were determined by ICP-AES.

For uptake kinetics 400 mL of solution containing a given concentration of metal (i.e., 10, 30 or 50 $\mathrm{mg\,L^{-1}}$) was maintained under agitation (at 400 rpm) with a fixed sorbent dosage (SD, i.e., 100, 200 or 300 $\mathrm{mg\,L^{-1}}$) at room temperature. Samples were collected at fixed contact times and filtrated before being analyzed by ICP-AES.

2.5 Desorption experiments

A preliminary study investigated several eluents (alkaline, acidic or complexing agents) for their efficiency to desorb Pt(IV) and Pd(II) from loaded sorbents. The preliminary results showed that the best eluents were thiourea (0.25 M) and thiourea in acidic media (0.1 M in 2 M HCl) for Pd(II) and Pt(IV), respectively. The sorbent dosage for both sorption and desorption steps was 200 $\mathrm{mg\,L^{-1}}$; the desorption efficiency was determined comparing the variation of the concentration during the sorption step and the concentration of metal in the eluate. The contact time for the sorption step was 3 days and only 2 hours for the desorption step (resulting from a preliminary optimization step). Five sorption/desorption steps were operated in order to verify the stability of the sorbent for both sorption and desorption operations.

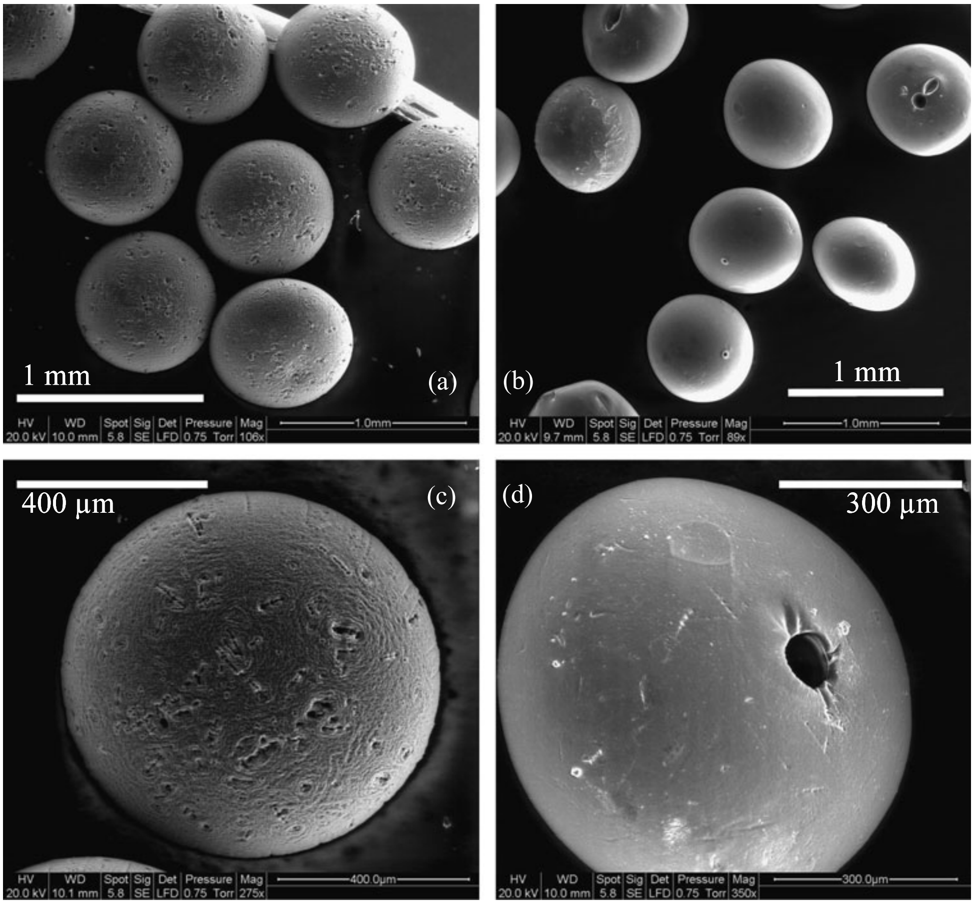


Fig. 1 SEM microphotographs of chitosan hydrogels: C-PPh (**a**) & (**c**), C-NaOH (**b**) & (**d**)

3 Results and discussion

3.1 SEM-EDAX observation of hydrogels

The general aspect of the two lots of chitosan hydrogels is substantially different as shown on Fig. 1. The size of both C-PPh and C-NaOH was in the range 0.7–0.8 mm (0.8 ± 0.05 mm for C-PPh and 0.75 ± 0.05 mm for C-NaOH). The drying of the beads resulted in a slight aspheric aspect. The surface of the C-NaOH beads was characterized by a smooth "skin" with the appearance of a "large" hole, probably due to the fall of the bead in the neutralization bath and the relaxation of the polymer causing this local heterogeneity. In the case of C-PPh, the surface aspect was quite different: the surface shows some indentations ("wavy surface") with micro holes. The C-PPh sorbents are generally more homogeneous in size and aspect than C-NaOH.

The two sorbents were used for Pd(II) and Pt(IV) sorption; similar results were obtained, Figs. 2 and 3 shows the results obtained with Pd(II) binding. SEM-EDAX is used to characterize the distribution of elements along a cross-section of the hydrogel beads. The SEM microphotograph shows that the particle is homogeneous while the SEM-EDAX analysis confirms that all the elements are equally distributed across the section. Phosphorous element, a tracer of the ionic gelation agent, is present even in the center of the particle indicating that the gelation is homogeneous and this could indicate that the material is porous in the whole mass of the material. The ionic cross-linking with hexametaphosphate proceeded by direct interaction of positive charge on chitosan with the anionic groups of polyphosphate (Gupta and Jabrail 2007). These linkages allow stabilizing the polymer, but the cross-linking agent may also play the role of a spacer in the polymer during the drying steps. This probably avoids the collapse of the porous structure. The distribution of Pd is also homogeneous; this means that all the reactive groups present in the particles are accessible and available for metal binding.

In the case of C-NaOH, Fig. 3 shows two series of microphotographs for particles at different stages of saturation. Figure 3(a) shows the aspect of the particle (cross-section and the cartography of elements along the cross-section) in the course of the sorption process (intermediary point) and Fig. 3(b) shows the particle and the distribution of elements at equilibrium and saturation of the sorbent. Figure 3(a) clearly shows that Pd and Cl elements are correlated: Pd(II) is present in the solution (under selected experimental conditions, i.e., in HCl solutions) under the form of

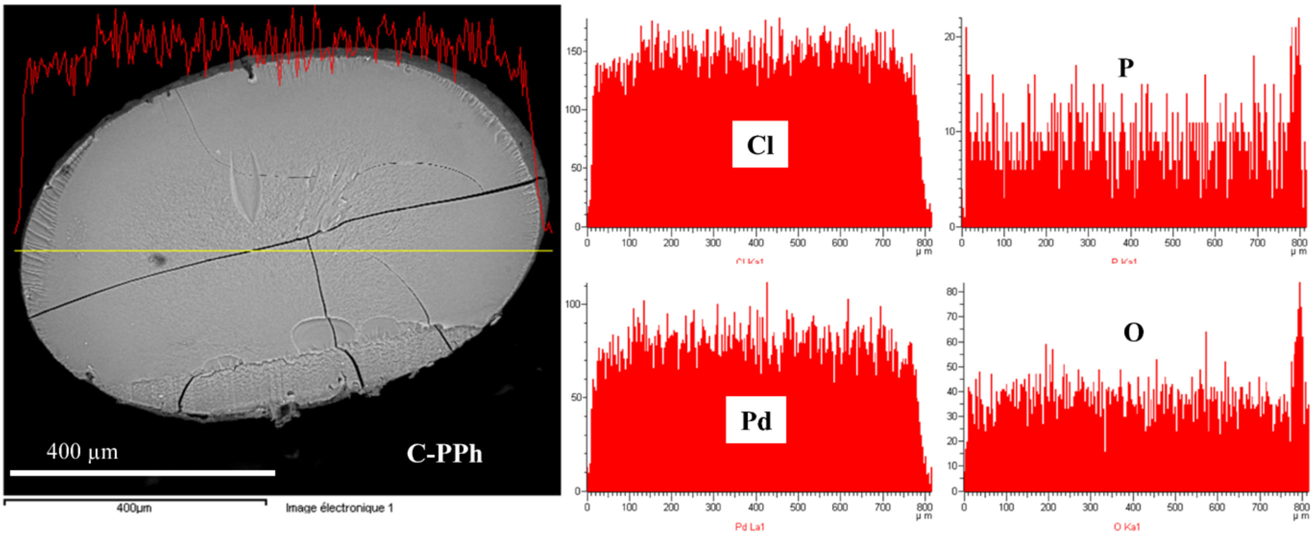


Fig. 2 SEM-EDAX of a cross-section of a C-PPh hydrogel bead saturated with Pd(II)—distribution of Cl, P, Pd and O elements along the cross-section

chloro-anionic species, $PdCl_4^{2-}$ (more than 78%), $PdCl_3^-$ (9–12%) and $PdCl_2$ (4–10%) (Puigdomenech 2002). The sorption probably proceeds through a shrinking core mechanism since the frontier between saturated and metal free region is very thin. The frontier “saturated/free zones” progressively moves to the center of the particle but without formation of a large gradient. The distribution of O elements seems to be “anti-correlated” to those of the other elements, probably due to the decrease in its mass percentage in the bead due to the presence of sorbed species. At saturation of the sorbent (Fig. 3(b)) all the elements are equally distributed in the whole mass of the sorbent. Again, it is possible to conclude that there was no restriction in the access of the metal to the internal sorption sites.

It is thus possible to conclude that the size of the particle will not play a critical role in the control of sorption, at least at equilibrium, as it occurs when polynuclear species of large ionic size (for example uranyl polynuclear species) are sorbed on chitosan flakes (Guibal et al. 1995).

3.2 Sorption isotherms

The sorption isotherms report the distribution of the metals between the liquid and solid phases at equilibrium (Fig. 4). For both Pd(II) and Pt(IV) sorption, C-NaOH sorbent had a slightly better profile than C-PPh. Indeed, the maximum sorption capacity (at saturation of the monolayer) was slightly better for C-NaOH; the initial slope of the isotherm (characteristic of the affinity of the sorbent for the metal) is also slightly better for C-NaOH than for C-PPh. The shape of the isotherm is “favorable”: the formation of a plateau at low residual concentration and the steep slope of the curve in the initial section are two clear signals of the “favorability” of the sorption process. The asymptotic shape allows suggesting that the Langmuir equation will be more appropriate for fitting experimental data than the Freundlich equation (power-type function).

Table 1 Pd(II) and Pt(IV) sorption isotherms for C-PPh and C-NaOH—modeling using the Langmuir equation

	Pd(II)		Pt(IV)	
	C-PPh	C-NaOH	C-PPh	C-NaOH
q_m (mg g^{-1})	192.9	187.8	231.1	238.0
[mmol g^{-1}]	[1.81]	[1.76]	[1.18]	[1.22]
b (L mg^{-1})	0.428	0.841	0.531	1.19
[L mmol^{-1}]	[45.6]	[89.6]	[103.7]	[232.3]
R^2	0.993	0.998	0.995	0.999

Table 1 reports the parameters of the Langmuir equation:

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{1}$$

where q and q_m are the sorption capacity (mg g^{-1} or mmol g^{-1}) in equilibrium with the residual concentration C_{eq} (mg L^{-1} or mmol L^{-1}) and at saturation, respectively; b (L mg^{-1} or L mmol^{-1}) is the affinity coefficient of the sorbent for metal ion.

The modeling of experimental data gives an objective comparison of sorption affinity of the sorbents for Pd(II) and Pt(IV): the sorption capacity at saturation of the monolayer (q_m) was comparable for C-PPh and C-NaOH. The maximum sorption capacity was close to 190 mg g^{-1} (i.e., about 1.8 mmol g^{-1}) and to 235 mg g^{-1} (i.e., 1.2 mmol g^{-1}) for Pd(II) and Pt(IV), respectively. These values are consistent with those of chitosan-based sorbents (Ruiz et al. 2000,

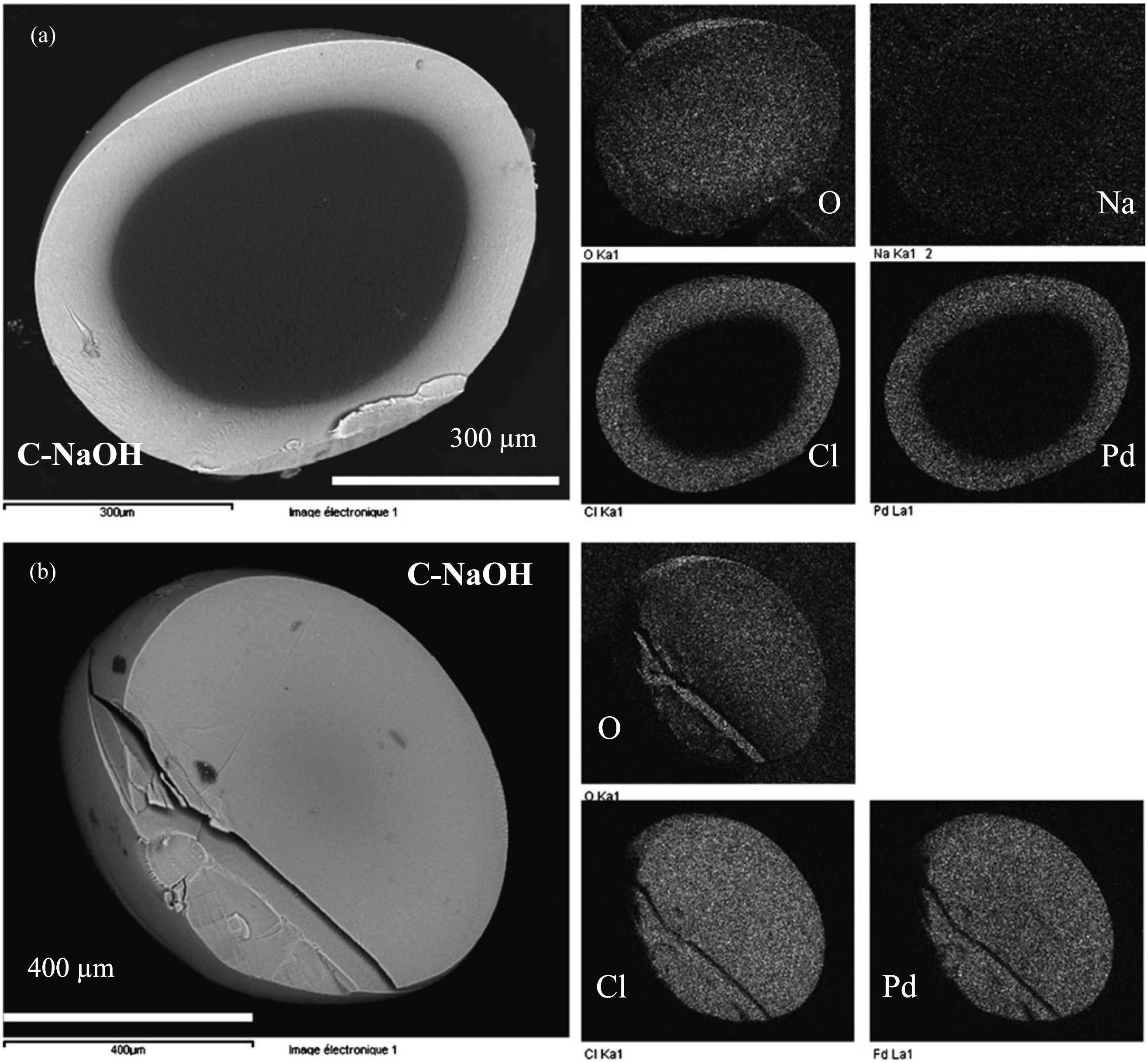


Fig. 3 SEM-EDAX of a cross-section of a C-NaOH hydrogel bead loaded with Pd(II)—distribution of Na, O, Cl and Pd along the cross-section: (**a**) unsaturated particle; (**b**) saturated particle

2001). Values of the same order of magnitude were obtained with synthetic resins (Parodi et al. 2008); however, these materials bearing specific functional groups (imidazole for example) maintain high sorption capacities even in very acidic solutions (up to 1 or 2 M HCl solutions). Recently, a new class of extractant impregnated resins was prepared by immobilization of Cyphos IL-101 (alkylphosphonium chloride ionic liquid) in biopolymer capsules (alginate-based beads) (Vincent et al. 2008a, 2008b). They obtained comparable sorption properties for Pd(II) and Pt(IV) in 0.1 M–2 M HCl.

Both C-PPh and C-NaOH have a preference for Pd(II) over Pt(IV) on the basis of this study, complement experiments in binary solutions should be carried out to confirm this conclusion. Previous studies using chitosan flakes (and sulfur derivatives of chitosan) have also concluded on the preference of chitosan for Pd(II) over Pt(IV) (Guibal et al. 2001). The comparison of affinity coefficients (i.e., *b*) shows more differences: for both Pd(II) and Pt(IV) the affinity coefficient of C-NaOH was roughly the double of the values reached with C-PPh. Additionally, the values of the affinity coefficient were, for both C-PPh and C-NaOH, almost doubled for Pt(IV) compared to Pd(II). This probably means that at low residual concentration the sorption of Pt(IV) will be better than for Pd(II), especially for C-NaOH. However, all

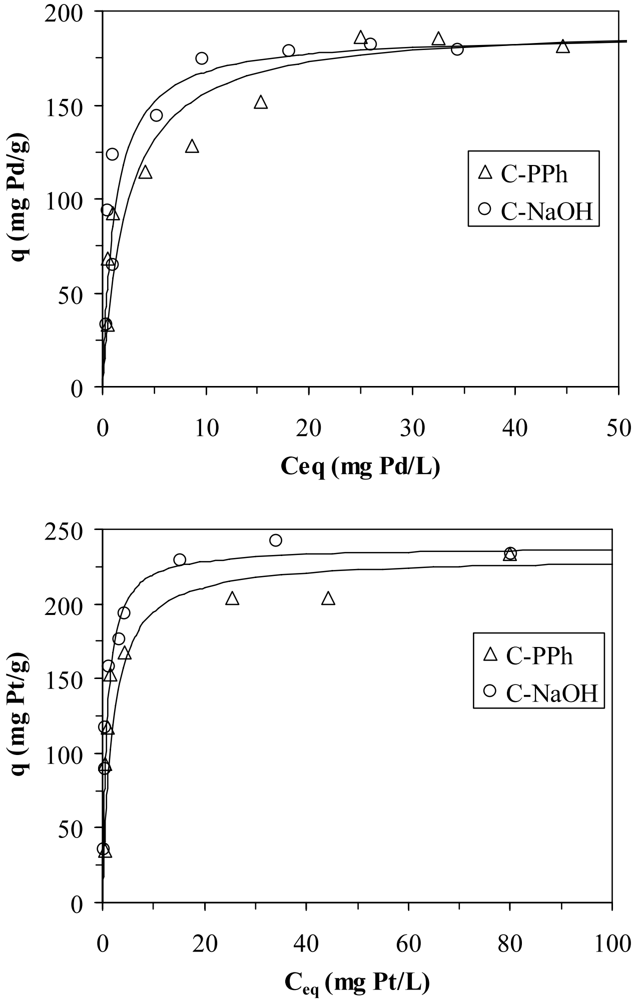


Fig. 4 Comparison of Pd(II) and Pt(IV) sorption isotherms (pH 2)

these differences are not very marked and it is possible to assume that the two sorbents will have very similar sorption properties for both Pd(II) and Pt(IV), at least at equilibrium. Though, the equilibrium performance was slightly better for the conventional sorbent (C-NaOH), the kinetics should be considered for definitive conclusion.

It is important to take into account in the discussion of these results that in the C-PPh sorbent, some amine groups are linked to phosphate groups, which in turn may be less reactive; additionally, the presence of polyphosphate results in a relative decrease in the amount of chitosan really added to the reaction media (the work was performed at constant sorbent mass). The amount of polyphosphate (and consequently of chitosan) present in the sorbent was not determined; however, Fig. 2 showed the presence of P element. Maintaining the same sorption capacity, in these conditions, means that despite the possible decrease in the amount of active polymer the reactive groups remain effective (and perhaps more reactive than in the C-NaOH sorbent).

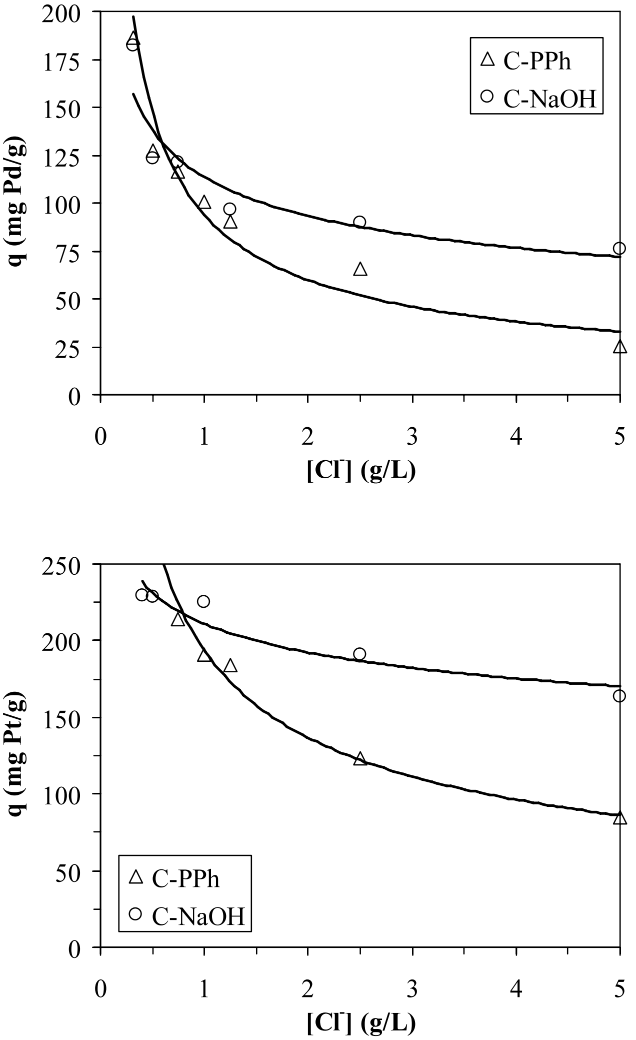


Fig. 5 Influence of chloride ion concentration on Pd(II) and Pt(IV) sorption using C-PPh and C-NaOH (pH 2)

3.3 Influence of chloride concentration

The impact of adding increasing concentrations of chloride anions on Pd(II) and Pt(IV) sorption has been measured under selected conditions (Fig. 5). The chloride ions may have a double effect on sorption: (a) a direct competition of Cl^- for binding on protonated amine groups; (b) an impact on metal speciation. The impact of chloride ions on metal sorption confirms that the sorption should involve a strong contribution of ion exchange/electrostatic attraction mechanism. The figure shows that the presence of chloride ions strongly impacted the sorption capacity of the chitosan hydrogels. This parameter had a much lower impact on Pd(II) and Pt(IV) sorption when using imidazole resins (Parodi et al. 2008), or biopolymer-immobilized ionic-liquid resins (Vincent et al. 2008a, 2008b). However, this effect is significantly more marked for C-PPh than for C-NaOH. Up to a concentration in chloride anions of 1 $g\,L^{-1}$ the sorption capacities remained comparable for C-PPh and C-NaOH; however, above this concentration the limiting effect of chlorides increased much more substantially for C-PPh. At a concentration of chloride ions of 5 $\mathrm{g\,L^{-1}}$ the sorption capacities of C-NaOH were more than two times greater than the values obtained with C-PPh.

It is noteworthy observing that the impact of chloride ions was more marked for Pd(II) than for Pt(IV). This is probably due to differences in metal speciation. Indeed, under experimental conditions selected in the present work Pd(II) predominates under the form of chloro-anionic species and the concentration of chloride poorly changes the predominance of metal species (i.e., $\mathrm{PdCl_4^{2-}}$). In the case of Pt(IV) the chloro-anions species that predominate in highly acidic solutions tend to hydrolyze when pH increases (more specifically at low chloride concentration), forming species such as: $\mathrm{PtCl_5(OH)^{2-}}$, $\mathrm{PtCl_4(H_2O)(OH)^{-}}$ or $\mathrm{PtCl_4(OH)^{2-}}$. This tendency to form chloro-hydroxo complexes may explain the limited impact of chloride ions compared to Pd(II) species.

3.4 Uptake kinetics

Uptake kinetics is a key point in the selection of sorbents. Reminding that the alternative ionotropic gelation system has been proposed for elaborating dried hydrogels with improved diffusion properties, the comparison of kinetic profiles will help in concluding on the enhancement of porous characteristics. Figure 6 shows the kinetic profiles for Pd(II) and Pt(IV) sorption with both C-PPh and C-NaOH. The experimental conditions have been selected in order to make possible the detection of diffusion limitations. Indeed, an excess of sorbent would induce faster kinetics (complete removal of metal) and the sorption could be limited to the external layers of polymer particles. Selecting unfavorable conditions (excess of metal) allows the shrinking core mechanism (as suggested by SEM-EDAX analysis) to take place up to the center of the particle and to allow the impact of diffusion restrictions to be visualized.

As expected from sorption isotherms the equilibrium concentrations were very close. More interesting is the comparison of the time required for reaching the equilibrium. In the case of C-PPh, less than 24 hours were sufficient for reaching the equilibrium while for C-NaOH from 48 to 72 hours were necessary.

A detailed analysis of the initial stage of the kinetics shows that the dry sorbents require a lag-time, which depends on the hydrogel, before sorption begins to be significant. This lag-time is especially important for C-NaOH sorbent (10–20 minutes for C-PPh, 30–60 minutes for C-NaOH). The lag-time is related to the re-hydration and swelling of sorbent particles. This is a supplementary step in the control of mass transfer performance that should be probably taken into account in the modeling of uptake kinetics. However, in the present study, the swelling was not integrated in the modeling. In order to evaluate the limiting step of the process various models have been tested.

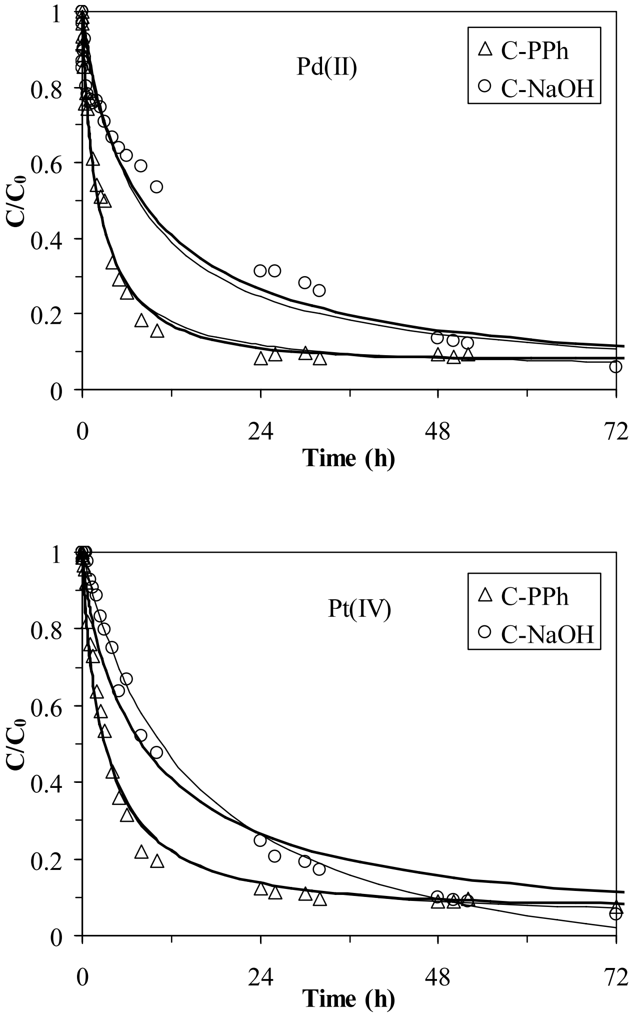


Fig. 6 Comparison of Pd(II) and Pt(IV) uptake kinetics for C-PPh and C-NaOH (pH 2; C_0: 30 $\mathrm{mg\,L^{-1}}$; SD: 200 $\mathrm{mg\,L^{-1}}$; Agitation: 400 rpm; *continuous thin line*: pseudo-second order rate equation; *continuous bold line*: intraparticle diffusion model)

Juang and Ju used the shrinking core model and the homogeneous diffusion model under specific control conditions (i.e., film mass transfer resistance, intraparticle diffusion resistance control and chemical rate control) for the description of Cu-EDTA complexes on polyaminated chitosan beads (Juang and Ju 1998). The driving equations are reported in Table 2. They were applied for checking the controlling steps: the linearization equation that best fits experimental data gives an indication on the controlling mechanism.

Figure 7 shows the plots obtained with these models for the different experimental conditions. In the case of C-PPh sorbent, the only equation that fits experimental data on a

Table 2 Linearization of kinetic models for homogeneous diffusion model (HDM) and shrinking core model (SCM) under film diffusion (FD), intraparticle diffusion (PD) and chemical reaction (CR) control

Model & controlling step	$f(X)$ (y-axis)	Time parameter (X, Y) (x-axis)
HDM-FD	$F(X) = -\ln(1 - \frac{q(t)}{q_{eq}})$	t
HDM-PD	$F(X) = -\ln(1 - (\frac{q(t)}{q_{eq}})^2)$	t
SCM-FD	$G(X) = \frac{q(t)}{q_{eq}}$	$\int_0^t C(t)dt$
SCM-PD	$G(X) = 3 - 3(1 - \frac{q(t)}{q_{eq}})^{2/3} - 2\frac{q(t)}{q_{eq}}$	$\int_0^t C(t)dt$
SCM-CR	$G(X) = 1 - (1 - \frac{q(t)}{q_{eq}})^{1/3}$	$\int_0^t C(t)dt$

(q_{eq} is the equilibrium concentration under specified experimental conditions)

sufficient large time range (or time-parameter range) was the SCM-CR equation. This result is consistent with the observation on SEM-EDAX that indicated a possible shrinking core mechanism. Additionally, the interaction of polyphosphate (which also acts as a spacer) with chitosan suggests that intraparticle diffusion was enhanced: the spacers at least partly avoided the collapse of the porous structure of the polymer. Different equations of chemical reactions have been tested (i.e., the pseudo-first order rate equation and the pseudo second-order rate equation). The pseudo-second order rate equation (2) systematically gave better results for the modeling of experimental data.

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

and after integration:

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

After linearization:

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

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.

In Fig. 6 the continuous lines shows the modeling of experimental data with the pseudo-second order rate equation. The model fits relatively well experimental data, except in the strong curvature area, where several controlling mechanisms may be involved (including probably intraparticle diffusion resistance). Table 3 reports the parameters of the pseudo-second order rate equation. The sorption capacities at equilibrium were of the same order of magnitude for both Pd(II) and Pt(IV) and for both C-PPh and C-NaOH resins. Calculated values were close to experimental values. Regarding the values of the rate parameter (i.e., k_2), the constants for C-PPh sorbent were 5 to 6 times greater than those obtained with C-NaOH. This is a confirmation of the enhanced diffusion properties of C-PPh material.

In the case of C-NaOH the pseudo-second order rate equation was less efficient for describing the kinetic profiles, especially for Pd(II) sorption. This is consistent with the results on Fig. 7, where it appears that none of the individual models tested were satisfactory for the modeling of kinetic profiles (not only due to the long lag-time step). The sorption kinetics probably obeys a combination of limiting mechanisms, including intraparticle diffusion resistance as confirmed by the long contact time required for achieving the equilibrium.

The intraparticle diffusion coefficient (D_e, effective diffusivity, m^2 min^{-1}) has been determined using the Crank's equation, assuming the solid to be initially free of metal, external diffusion resistance not being limiting at long contact time (Crank 1975):

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

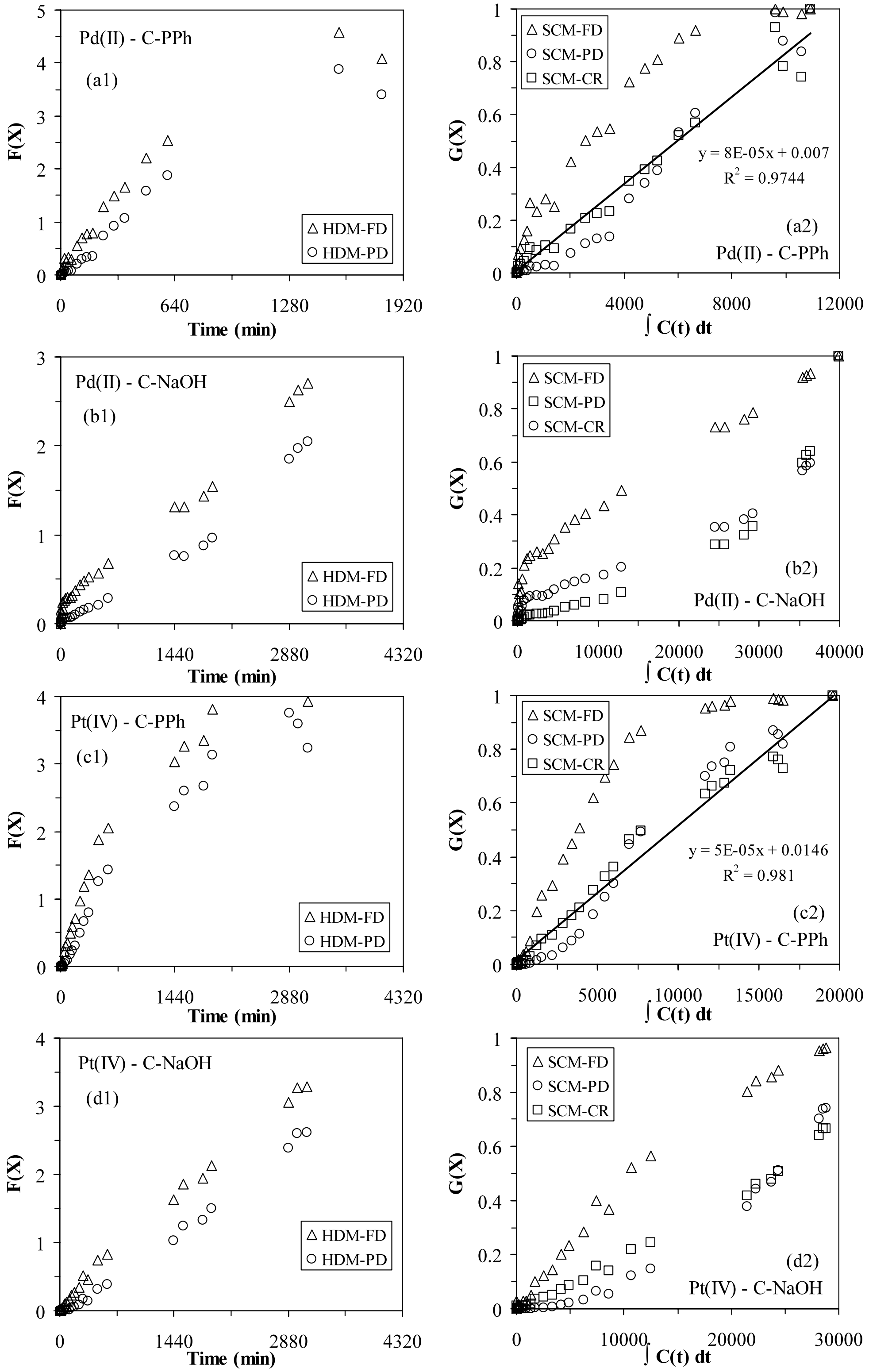
q_n non-zero roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad \text{with} \tag{3b}$$

$$\frac{q}{VC_0} = \frac{1}{1+\alpha} \quad \text{and} \quad r \text{ being the radius of the particle} \tag{3c}$$

The equation was used with the Mathematica® package for the determination of the intraparticle diffusion coefficient. Applied to the kinetic profiles for C-NaOH sorbent the intraparticle diffusion coefficient was found to be 3.9×10^{-12} m^2 min^{-1} for Pd(II) and 3.5×10^{-12} m^2 min^{-1} for Pt(IV). These values should be compared to those obtained for C-PPh: 1.6×10^{-11} m^2 min^{-1} for Pd(II) and 2.5×10^{-11} m^2 min^{-1} for Pt(IV). These values are of the same order of magnitude than the values obtained with Cyphos IL-101 immobilized capsules (Vincent et al. 2008a, 2008b). Globally, the diffusion coefficients are of the same order for Pd(II) and Pt(IV) and there are 4 to 7 times greater for C-PPh than for C-NaOH, as another evidence of im-

Fig. 7 Application of linearization equations (Table 2) to experimental data for determination of controlling mechanisms



proved diffusion properties for the alternative sorbent. The simulated profiles are represented in Fig. 6 by the continuous bold line. For C-NaOH, in the case of Pd(II) the intraparticle diffusion model better approached experimental data than the pseudo-second order rate equation (though the curves were very close); in the case of Pt(IV) the intraparticle diffusion model does not improve the quality of the modeling. The lag-time phase probably induced significant discrepancies in the determination of the model constants. In the case of C-NaOH various resistance mechanisms are

Table 3 Parameters of the pseudo-second order rate equation

Sorbent	Metal	$q_{eq,\mathrm{exp}}$ (mg g^{-1})	$q_{eq,\mathrm{calc.}}$ (mg g^{-1})	$k_2 \times 10^5$ (mg g^{-1} min^{-1})	R^2
C-PPh	Pd(II)	134.4	139.7	6.1	0.999
C-PPh	Pt(IV)	135.2	141.3	4.2	0.999
C-NaOH	Pd(II)	152.1	158.5	1.4	0.980
C-NaOH	Pt(IV)	139.7	172.0	0.68	0.992

probably involved in the global control of mass transfer. For C-PPh, the modeling of experimental data with the intraparticle diffusion model was quite close to the curve generated with the pseudo-second order rate equation.

3.5 Desorption and sorbent recycling

A preliminary study allowed selecting thiourea (0.25 M) for Pd(II) desorption and thiourea (0.1 M) in HCl (2 M) solutions for Pt(IV) desorption. A contact time of 2 hours reveals sufficient for reaching desorption equilibrium: other contact times did not increase desorption efficiency. Figure 8 shows the sorption and desorption efficiency over 5 successive cycles. The response to sorption and desorption strongly depended on the sorbent and the metal. In the case of Pt(IV) and C-PPh, the performance for both sorption and desorption was almost constant, and even the sorption efficiency slightly increased along the cycles; the desorption efficiency was slightly lower than the sorption efficiency. For Pt(IV) and C-NaOH, sorption remained at the same level for the five cycles, while the desorption progressively increased but remained 10 to 20% below the sorption levels. For Pd(II) the results were less favorable. Previous studies on the sorption of Pd(II) and Pt(IV) in binary solutions using chitosan-based sorbents have shown that though the process cannot be selective enough for allowing metal separation the sorbents had a preference for Pd(II). In dynamic systems (fixed-bed columns), the breakthrough curves were characterized by the formation of an overshoot. Platinum ions were displaced from the sorbent by preferential sorption of palladium ions (Chassary et al. 2005). This preference is correlated to the "strength" of the interaction between protonated amine groups and metal anions. This could explain that the binding between protonated amine groups and Pt(IV) ions could be more easily reversed by thiourea than the bonds between reactive groups and Pd(II) ions.

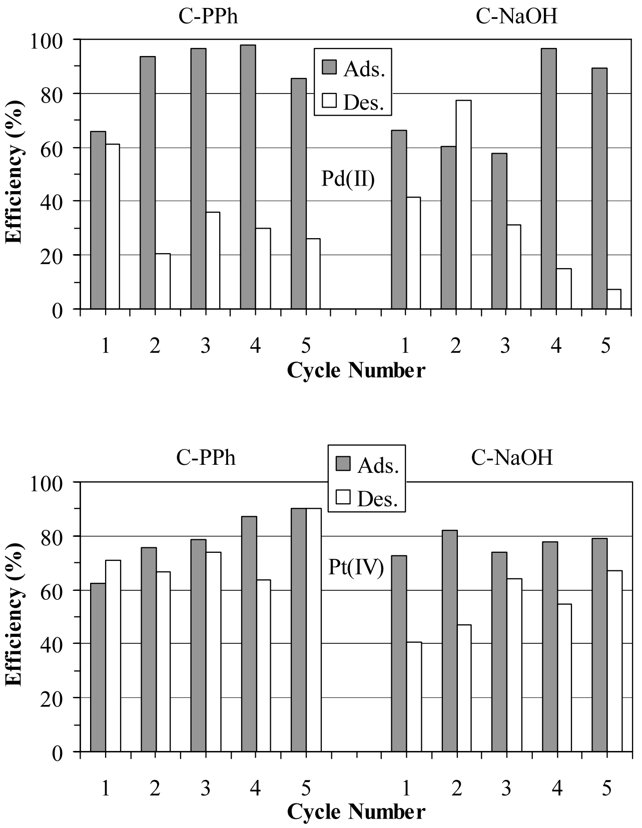


Fig. 8 Sorption/desorption cycles for C-PPh and C-NaOH applied to Pd(II) and Pt(IV) recovery (Adsorption: pH 2; SD: 250 mg L^{-1}; C_0(Pd): 50 mg L^{-1} or C_0(Pt): 100 mg L^{-1}; contact time: 3 days. Desorption: SD: 250 mg L^{-1}; contact time: 2 h, eluent: 0.25 M thiourea for Pd(II), 0.1 M thiourea in 2 M HCl for Pt(IV))

Sorption efficiency remained at high levels for C-PPh while desorption was very low: the progressive saturation of the biosorbent will limit in due course the sorption efficiency. For C-NaOH, adsorption levels strongly varied along the cycles (high levels were reached for the last two cycles) and the desorption efficiency strongly decreased (less than 20% for the last two cycles). These results indicate that:

(a) the sorbent can be re-used but for a limited number of cycles,
(b) the sorbents are more suitable for Pt(IV) recovery than for Pd(II) removal,
(c) C-PPh is generally more recyclable than C-NaOH.

4 Conclusion

The alternative manufacturing procedure (i.e., polyphosphate ionotropic gelation versus alkaline neutralization) does not change globally the sorption capacities at equilibrium but improved diffusion behavior as evidenced by kinetic profiles (carried out under similar experimental conditions). The drying of the hydrogels is less kinetically-impacting when the chitosan gel was prepared by ionotropic gelation. This is probably due to the presence of polyphosphate in the porous network that contributes to play a role of spacer but also to manage repulsion forces and capillary forces during the drying step. Sorption capacities at equilibrium remains quite high at pH 2: the electrostatic attraction mechanism (chloro-anionic metal species reacting with protonated amine groups) is more sensitive to the composition of the solution (HCl concentration, presence of an excess of chloride anions) than conventional chelating resins. Compared to other resins, which are able to bind these metal ions in more acidic solutions, these materials are probably not appropriate for the recovery of these metals from highly acidic leachates that can be found in industry. However, an increasing number of papers have been recently published on the use of biopolymers for supported catalysis: ionotropic gelation using polyphosphate as the cross-linking agent may be an alternate process for a better management of diffusion issues for these supported catalysts. The desorption of sorbed metals is possible using a strong complexing agent such as thiourea (alone or in HCl solution). However, the desorption of metal ions progressively decreased along sorption/desorption cycles making the re-use of the resins possible though for a limited number of steps.

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