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# Pd AND Pt RECOVERY USING CHITOSAN GEL BEADS. I. INFLUENCE OF THE DRYING PROCESS ON DIFFUSION PROPERTIES

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## ABSTRACT

Chitosan is very efficient at removing metal ions, especially precious metals. Sorption kinetics can be improved by the preparation of chitosan gel beads, using a coagulation procedure. However, this process leads to the formation of beads containing very high water yields, which prevent chitosan from being an economically competitive sorbent for large-scale industrial applications, for reasons linked to transport costs and handling. The air-drying of chitosan gel beads resulted in a decrease in the sorption rate, while the sorption performance at equilibrium was

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not influenced by the drying step. The influence of re-hydration was examined. The drying of beads saturated with saccharose was considered a simple alternative treatment, to prevent the restriction of the polymer network and improve sorption rate. The influence of these different treatments on both sorption kinetics and sorption isotherms was studied for the recovery of platinum and palladium from dilute solutions.

*Key Words*: Platinum; Palladium; Chitosan; Glutaraldehyde cross-linking; Sorption isotherms; Sorption kinetics; Drying process

## INTRODUCTION

The increasing industrial demand for precious metals due to their use in catalysis has focused research on the development of processes for their recovery from dilute solutions, spent catalysts, and waste materials (1). Solvent extraction, solvent-impregnated resin, and chelating resin systems have been developed for these applications (2–5). However, there is still a need to develop alternative sorbents specifically oriented toward the treatment of low-concentration solutions. Biosorption has been proposed as an alternative route to recover metal ions from dilute solutions and recently some studies have been focused on the sorption of strategic metals using fungal biomass (6), or biopolymers (7–9). Chitosan has been proved to be very efficient at removing metal ions especially precious metals (10,11). Chitosan is extracted by deacetylation of chitin, one of the most abundant biopolymers. This polymer is characterized by a high content of free amine groups, which are responsible for the sorption of metal ions through different mechanisms including chelation of metal cations at near neutral pH (12), and ion exchange of metal anions in acid solution (13). Indeed, chitosan is a unique material among natural polymers; in acid solution, it is protonated: the $pK_a$ of chitosan depends on the degree of deacetylation, but it tends toward 6.5 in the 80–90% deacetylation range (14). Metal anions can be adsorbed by ion exchange of counter anions in the vicinity of the protonated amine groups (15,16). Chitosan is soluble in acid solution, except in sulfuric acid solutions. Due to the competitor effect of sulfate and changes in the speciation of metal anions, sorption capacities are greatly reduced when treating sulfuric acid solutions (by one order of magnitude). For the treatment of hydrochloric acid solutions, it is necessary to reinforce the stability of the biopolymer using a cross-linking procedure. Several processes have been proposed for the cross-linking of chitosan, but the easiest and cheapest way consists of the Schiff base reaction between the aldehyde function of glutaraldehyde (the cross-linking agent) and the amine group of chitosan (17).

This reaction results in the formation of imine linkages between glutaraldehyde and chitosan. These new linkages prevent the hydrolysis of the polymer and increase its stability. However, it also results in a decrease in the proportion of free amine groups available for metal sorption, and a reduction in the accessibility to internal sites (18). Chitosan is also characterized by weak diffusion properties: long contact times are required to reach equilibrium. Sorption capacity can be controlled by sorbent particle size (19), especially in the case of the cross-linked material (18). However, the effect of diffusion properties can be diminished using chitosan gel beads. This procedure leads to both an expansion of the polymer network and a decrease in the residual crystallinity of the material. Chitosan gel beads can be obtained by a two-step procedure that consists of dissolving of chitosan in acetic acid solution and adding the resulting viscous solution drop-wise into an alkaline coagulating solution (NaOH, $1-2.5\,M$) (13,17,20). The main problem for a large-scale application using chitosan gel beads is the high water content of the beads (about 94–96%), which makes the transport, handling, and scaling-up of the process, economically noncompetitive.

Optimum sorption of platinum and palladium (in their chloro-complex forms) occurs at pH 2, in the presence of selected amounts of chloride anions to form hexachloroplatinate and tetrachloropalladate anionic species, which are highly adsorbable on protonated amine groups.

This work investigated the influence of the drying process on sorption performance (sorption isotherms and uptake kinetics). Previous studies have been carried out on the freeze-drying of chitosan gel beads (17,21); however, this process is expensive for the production of large amounts of sorbent. For this reason, the study focused on a simple drying process (oven-drying at 60°C). The influences of the re-hydration of the beads and the absorption of saccharose (before drying) were studied. Saturating the beads with saccharose was expected to maintain the porous structure of the polymer and prevent the collapse of the polymer network. The study also examined the influence of bead size and metal concentration on sorption kinetics and isotherms.

## MATERIALS AND METHODS

### Materials

Chitosan was supplied by Aber Technologies (Plouvien, France) as a flaked material, with a deacetylation percentage ca. 87%, defined by FTIR spectrometry. The mean molecular weight was measured at $125{,}000\,\mathrm{g\,mol^{-1}}$, using a size exclusion chromatography (SEC) method coupled with a differential refractometer and a multi-angle light scattering photometer. The moisture content of the chitosan was determined at ca. 10%.

$PdCl_2$, $H_2PtCl_6$ were supplied by Chem Pur, (Karlsruhe, Germany), other reagents (Glutaraldehyde (50% w/w in water), saccharose, NaOH, HCl, acetic acid) were purchased from Fluka AG, (Buchs, Switzerland).

## Chitosan Gel Bead Preparation

The procedure for the fabrication of gel beads has been described in previous papers (13,17,20). It consisted of a two-step procedure: chitosan flakes were ground and dissolved in acetic acid solution (a small quantity of excess acetic acid was used in order to entirely protonate the amine groups and decrease the viscosity of the solution). The viscous solution was then pumped and distributed drop-wise through a thin nozzle (diameter 0.6 mm) into an alkaline solution (NaOH 2.5 *M*). In order to control the size of particle beads, it was possible to inject airflow, at a controlled flow rate, in an appropriate system (made up of a concentric tube around the nozzle to drive airflow toward its base). The airflow made the chitosan drops fall down sooner than they would have fallen by their own weight. Three different sizes of beads were prepared, referred to as small (S), middle (M), and large (L). The chitosan drops coagulated in the alkaline solution and gave perfect spherical beads, whose diameter was measured. After 24 hr contact with the alkaline solution, beads were removed and rinsed several times with de-mineralized water till the pH did not vary. Two chitosan concentrations were tested, corresponding to w/w proportions of 4% (referred to as M4, middle size, 4% w/w chitosan concentration) and 6% (referred to as M6, middle size, 6% w/w chitosan concentration).

The cross-linking was performed by mixing for 16 hr, the appropriate amount of chitosan beads (calculated using the dry weight) with an aqueous solution of glutaraldehyde at an equimolar concentration (compared to the number of free amine groups in chitosan). The beads were then rinsed several times with water to remove unreacted glutaraldehyde. At each stage of the fabrication, samples (100 or 250 beads, depending on the size of the beads) were collected and dried at 105°C overnight, to compare water content and measure the weight of the bead for each fabrication procedure. The mean diameter of the beads was also determined for the final products. These measurements were performed in triplicate. The main characteristics of these beads are summarized in Table 1.

## Drying Procedure

After cross-linking, the appropriate number of chitosan gel beads (raw chitosan gel beads, B, this reference material is also called M4 for beads of

***Table 1.*** Characteristics of Chitosan Gel Beads

| Sample | WW | DW | ACP | DWC | GW | CLR | *D* | NBK | $S_{exc}$ |
|---|---|---|---|---|---|---|---|---|---|
| S4 | 0.356 | 12.3 | 3.5 | 18 | 5.7 | 0.77 | 1.52 ( ± 0.05) | 2033 | 14.8 |
| M4 | 1.1 | 43.7 | 4.0 | 59.3 | 15.6 | 0.60 | 3.36 ( ± 0.12) | 229 | 8.1 |
| L4 | 1.854 | 68 | 3.67 | 92.4 | 24.4 | 0.60 | 3.82 ( ± 0.11) | 148 | 6.8 |
| M6 | 1.16 | 74.8 | 6.5 | 102.4 | 27.6 | 0.61 | 3.30 ( ± 0.13) | 134 | 4.6 |
| DB[a] | | | | | | | 1.47 ( ± 0.04) | | 1.6 |
| RB[a] | | | | | | | 1.49 ( ± 0.04) | | 1.6 |
| Sa[a,b] | | | | 469.8 | | | 2.69 ( ± 0.02) | | 2.3 |

WW: Wet weight (g), DW: Dry weight (mg), ACP: Actual chitosan percentage (referred to wet weight) (%), DWC: Dry weight of cross-linked beads (mg), GW: Glutaraldehyde weight (mg), CLR: Cross-linking ratio (mol glutaraldehyde $\mathrm{mol}^{-1}$ $NH_2$), *D*: Diameter of beads (mm) (wet for S4, M4, L4, M6, RB—after re-hydration and Sa—after re-hydration; dried for DB), NBK: Number of beads used for kinetic experiments (for 1 L of solution), $S_{exc}$: External sorbent surface for kinetic experiment ($m^{-1}$), n.d.: not determined.

For 100 beads, except for small beads (S)—250 beads.

[a] Other parameters are similar to M.

[b] For Sa beads, DWC includes the weight of saccharose absorbed in the polymer network. The beads were submitted to re-hydration (saccharose was simultaneously released from the beads) before being dried again: the DWC was then 58 mg.

medium size with a chitosan content of 4%) (for kinetics and for sorption isotherms) was dried at 60°C in an oven till their weight became constant. These samples were referred to as dried samples (DB). Dried samples were also re-hydrated in water for two days (appropriate number of beads for kinetics and sorption isotherm experiments). This sample was referred to as re-hydrated chitosan beads (RB). Finally, another kind of sample was prepared: an appropriate number of cross-linked beads ($10\,g\,L^{-1}$, wet weight) was brought into contact with a concentrated saccharose solution ($145\,g\,L^{-1}$) for 30 min. The beads were then removed from the solution and dried in an oven at 60°C till their weight was constant. Finally, the beads were re-hydrated in water for two days and the saccharose was released. The beads were then used for sorption experiments, and referred to as saccharose samples (Sa).

## Sorption Procedure

Previous experiments had shown hat the optimum pH for palladium and platinum sorption on chitosan derivatives was ca. pH 2. Consequently, precious metal solutions were obtained by direct dilution of the salt in water and the pH was maintained at pH 2 with hydrochloric acid. The pH of the solutions did not vary significantly during the sorption (by less than 0.1 unit).

For sorption isotherms, increasing known numbers of beads were brought into contact with a fixed volume of solution at a known concentration (ca. 20 or 50 mg Metal $L^{-1}$) for four days. Filtrates were collected and analyzed using an inductively coupled plasma atomic emission spectrometer, ICP-AES JY 2000 (Jobin–Yvon, Longjumeau, France). The metal content in the beads was calculated using the mass balance equation, and the sorption capacity was determined in function of the actual mass of chitosan in the sample: unless specified, the increase in weight resulting from glutaraldehyde cross-linking was not taken into account. To take into account the total mass of the sorbent, the sorption capacity (on the basis of weight of chitosan) had to be multiplied by 0.68 for small beads and by 0.73 for medium- and large-size beads (mg Metal $g^{-1}$ sorbent). The number of beads used for these experiments was adjusted in order to maintain identical amounts of chitosan in each equivalent experiment.

For the study of sorption kinetics, a standard procedure was applied (13). One liter of solution at pH 2 was mixed with a constant weight of chitosan (independent of glutaraldehyde cross-linking). Consequently, the number of beads was different for each experimental set, depending on the chitosan concentration (M4 and M6), and chitosan particle size (S, M, and L) (reported in Table 1). Unless specified, the standard initial metal concentration was 20 mg Metal $L^{-1}$.

## RESULTS AND DISCUSSION

### Characterization of Chitosan Gel Beads

Table 1 presents the main characteristics of chitosan beads. Despite an equimolar concentration of glutaraldehyde (compared to free amine content of chitosan beads), the cross-linking ratio was found to be 0.6, except for small beads for which the cross-linking ratio tended to 0.7 (calculated on the basis of weight increase). This indicates that the size of the beads influences the cross-linking procedure: small size increases the external surface while large size increases intraparticle diffusion resistance. Hsien and Rorrer have modeled glutaraldehyde cross-linking of chitosan using the shrinking core model (22). The progressive cross-linking of chitosan beads may lead to the formation of a heterogeneous material, in which glutaraldehyde diffusion into the particle may be restricted. Since glutaraldehyde is a bi-functional reagent, it can induce linkage with amine groups on both sides of the cross-linking molecule, but also single linkage, which leads to the presence of reducing ends that are responsible for the reduction of some metal ions (23). Moreover, Hsien and Rorrer (22) have highlighted the possibility of glutaraldehyde polymerizing in alkaline media (as can occur in beads when the rinsing step has not been sufficient to remove all the sodium hydroxide during the coagulation procedure). Consequently, it is difficult to establish an accurate cross-linking ratio for the different samples. However, it is possible to see that the cross-linking is reproducible since the cross-linking ratio was almost constant for M, L, and M6 samples. The actual chitosan percentage (also measured by dry weight) varied between 3.5 and 4%.

The drying of cross-linked chitosan beads led to a drastic decrease in the diameter of the particles: the final diameter was less than half the initial diameter. Based on the change in diameter, the volume of the bead was decreased by 91.6%, which is comparable to the water percentage in the beads (before drying): 96%. After re-hydration, the size of the beads was almost unchanged (below the level of significance). The drying of chitosan gel beads is irreversible. However, when the beads were saturated with saccharose prior to drying, after re-hydration, the final diameter was only reduced to 2.69 mm: a 20% decrease in the diameter, while the volume of the beads was almost halved.

### Sorption Kinetics

Influence of Particle Size and Initial Metal Concentration

Figures 1 and 2 show the sorption kinetics for Pd and Pt, respectively: the fractional approach to equilibrium (FATE) is plotted against the square root of

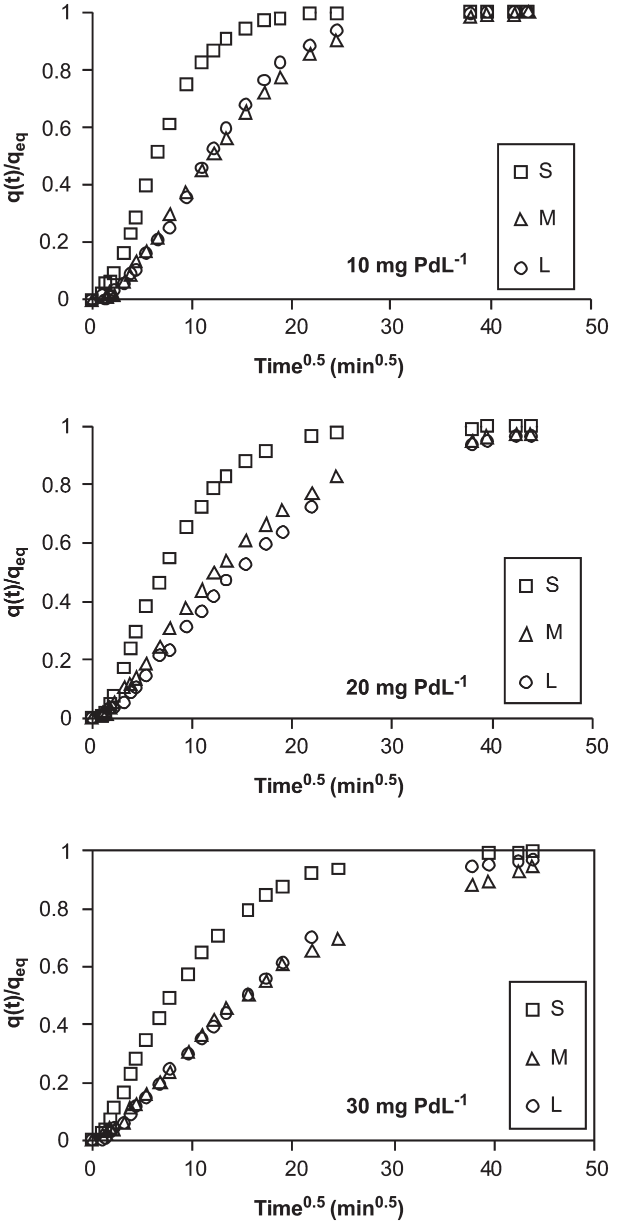

*Figure 1.* Influence of bead sizes (4% w/w concentration) and initial Pd concentration (10, 20, and 30 mg $L^{-1}$) on sorption kinetics.

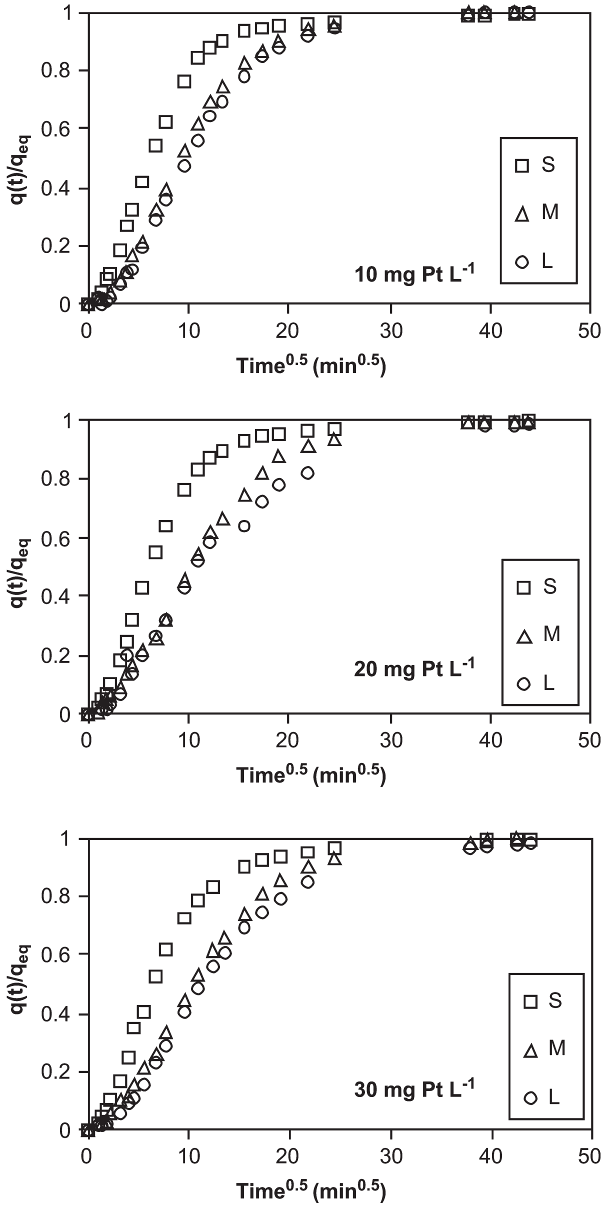

*Figure 2.* Influence of bead sizes (4% w/w concentration) and initial Pt concentration (10, 20, and 30 mg $L^{-1}$) on sorption kinetics.

time. The FATE is represented by $q(t)/q_{\mathrm{eq}}$, the ratio of the concentration in the sorbent at time $t$ to the equilibrium concentration in the solid. Morris and Weber used the plot of $q(t)$ vs. the square root of time for the calculation of sorption rate in the case of processes that are controlled by intraparticle diffusion (24). The curves for large particles are largely linear, except for the initial contact period (within the first 30 min) and for long contact time (higher than 6 hr). The initial section is concave in form, which can be explained by several mechanisms, including the sorption kinetics being controlled by external film mass transfer, while the final section may be controlled by a dual rate control, i.e., intraparticle diffusion and exchange reaction rate. The slope of the linear part of the curve may be used to give a relative sorption rate in order to compare the kinetics under differing experimental conditions. In the case of low-concentration solutions, the linear section was shortened, especially in the case of platinum sorption.

The size of the beads and the initial metal concentration were varied. As expected, sorption kinetics for Pd and Pt were faster with small particle size than with the largest beads. However, the difference between small and large beads increased with the initial concentration. The curves for middle and large size beads almost overlapped: the difference in particle diameter was only 0.3 mm.

In the case of Pd, the affinity of the sorbent for the metal was so high that even with a low concentration of sorbent (as low as $0.1\,\mathrm{g\,L^{-1}}$, dry weight) the residual concentration tended to 0. It is thus difficult to compare experiments at different initial concentrations, since the surface coverage is not the same for each of these experiments. With small beads, more than 95% of the metal was adsorbed within the first 4 hr, while increasing the initial concentration resulted in a progressive increase in the time required to reach the same level of extraction.

In the case of Pt sorption, small beads obviously reached equilibrium faster than middle and large size beads, but the differences were not so marked as they were with Pd sorption. Whatever the initial concentration is, the equilibrium was reached earlier than in the case of Pd sorption. It is also noticeable that independent of the initial concentration, the residual concentration did not tend to 0: it seems that under selected experimental conditions, a fraction of metal ions is not adsorbable.

Sorption kinetics may be controlled by several mechanisms, including film mass transfer resistance (FDC), intraparticle mass transfer resistance (PDC), or the actual exchange reaction rate. Hellferich has listed the influence of experimental parameters on the diffusion control of sorption kinetics (25). He showed that the ion-exchange rate (defined by the FATE) varies as a function of the reciprocal of squared diameter in the case of PDC, while it varies as a function of the reciprocal of particle diameter in the case of FDC. He pointed out that the concentration did not influence the FATE in the case of a process controlled by the PDC, while in the case of FDC, the FATE varies as a linear function of the concentration.

The linear sections of the curves were modeled using the following equation (24,26,27):

$$\text{FATE} = \frac{q(t)}{q_{\text{eq}}} = kt^{0.5} - k_o,$$

where $k$ is the rate constant ($\text{min}^{-1}$) and $k_o$ (the ordinate intercept) represents a parameter related to the concavity of the kinetic curve (the initial phase, which takes into account, external diffusion resistance). Corresponding parameters are summarized in Tables 2 and 3. The kinetic curves were also modeled using the pseudo-first order kinetic equation described by:

$$\ln C(t) = \alpha t + \beta,$$

where $\alpha$ and $\beta$ are the equation parameters ($\beta$ tends to $\ln C_0$). The first section of the curves was used for the determination of these parameters (i.e., for a contact time up to 4–5 hr): the coefficients are also summarized in Tables 2 and 3. This

***Table 2.*** Influence of Experimental Parameters on Kinetic Parameters for Pd Sorption on Chitosan Gel Beads

| Sample | Pd Concentration (mg Pd $\text{L}^{-1}$) | $k$ $10^2$ ($\text{min}^{-0.5}$) | $k_o$ $10^2$ | $R^2$ | $\alpha$ $10^3$ | $\beta$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| S4 | 10 | 7.81 | 5.54 | 0.984 | 12.01 | 2.21 | 0.987 |
| | 20 | 7.47 | 5.47 | 0.987 | 8.88 | 2.89 | 0.976 |
| | 30 | 6.19 | 2.15 | 0.988 | 6.62 | 3.27 | 0.954 |
| M4 | 10 | 4.74 | 8.17 | 0.997 | 3.68 | 2.23 | 0.991 |
| | 20 | 4.42 | 4.70 | 0.998 | 3.64 | 2.93 | 0.976 |
| | 30 | 3.59 | 3.67 | 0.997 | 2.72 | 3.34 | 0.968 |
| L4 | 10 | 4.95 | 9.79 | 0.995 | 4.59 | 2.29 | 0.998 |
| | 20 | 3.79 | 5.23 | 0.997 | 3.02 | 2.95 | 0.983 |
| | 30 | 3.54 | 4.14 | 0.998 | 2.46 | 3.37 | 0.979 |
| M6 | 10 | 5.61 | 19.19 | 0.996 | 4.90 | 2.32 | 0.996 |
| | 20 | 3.94 | 5.58 | 0.998 | 3.19 | 2.95 | 0.980 |
| | 30 | 3.64 | 6.88 | 0.998 | 2.64 | 3.36 | 0.983 |
| DB | 20 | 1.59 | 10.50 | 0.999 | 0.57 | 2.99 | 0.995 |
| RB | 20 | 3.01 | 19.79 | 0.997 | 1.23 | 2.99 | 0.996 |
| Sa | 20 | 3.38 | 5.82 | 0.997 | 2.28 | 2.96 | 0.979 |

***Table 3.*** Influence of Experimental Parameters on Kinetic Parameters for Pt Sorption on Chitosan Gel Beads

| Sample | Pt Concentration (mg Pt $L^{-1}$) | $k\ 10^2$ ($\min^{-0.5}$) | $k_o\ 10^2$ | $R^2$ | $\alpha\ 10^3$ | $\beta$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| S4 | 10 | 9.04 | 8.26 | 0.998 | 11.67 | 2.21 | 0.980 |
| | 20 | 8.75 | 7.62 | 0.989 | 11.83 | 2.90 | 0.978 |
| | 30 | 8.29 | 6.29 | 0.989 | 12.23 | 3.33 | 0.979 |
| M4 | 10 | 6.30 | 10.33 | 0.993 | 4.43 | 2.18 | 0.951 |
| | 20 | 5.53 | 8.22 | 0.993 | 4.36 | 2.93 | 0.988 |
| | 30 | 5.39 | 7.16 | 0.996 | 4.52 | 3.34 | 0.987 |
| L4 | 10 | 6.20 | 12.77 | 0.996 | 5.90 | 2.28 | 0.994 |
| | 20 | 5.34 | 7.77 | 0.983 | 5.78 | 2.97 | 0.977 |
| | 30 | 4.81 | 7.14 | 0.989 | 4.98 | 3.39 | 0.997 |
| M6 | 10 | 5.81 | 19.62 | 0.991 | 4.11 | 2.27 | 0.985 |
| | 20 | 5.46 | 14.85 | 0.997 | 3.90 | 2.94 | 0.987 |
| | 30 | 5.31 | 8.38 | 0.998 | 4.17 | 3.32 | 0.989 |
| DB | 20 | 1.56 | 9.84 | 0.995 | 0.60 | 3.01 | 0.990 |
| RB | 20 | 2.83 | 11.36 | 0.997 | 1.57 | 3.00 | 0.987 |
| Sa | 20 | 5.03 | 7.82 | 0.981 | 4.43 | 2.96 | 0.982 |

equation was frequently used for the determination of the external diffusion coefficient (when only the initial points, corresponding to the first minutes of contact, are taken into account) (28). More sophisticated models may be used for the simulation of experimental kinetic curves (29–31), including the Crank equation for infinite volume solution system (13,32). However, it has previously been observed by Ruiz et al. that when the sorption rate is very fast (case of Pt and Pd sorption), even this simple model failed to fit the kinetic curves for sorption (11). For this reason, the simplified models described above were preferred.

For Pd and Pt sorption, in each size fraction, increasing the concentration decreased the parameter $k$ but the variations were not very large. It is also interesting to observe that for Pt extraction, the coefficient was usually slightly higher than for Pd, when coefficients are compared for similar initial concentration. It is also true when results are compared based on molar concentrations. Indeed, since the molar mass of Pt is close to twice that of Pd, experiments at $C_0$: 20 mg Pd $L^{-1}$ are comparable to those performed with an initial concentration $C_0$: 10 mg Pt L$^{-1}$. It seems that Pt sorption is faster than Pd sorption. The parameter $k_o$, which was related to the external diffusion resistance, also decreased when the initial concentration of Pd and Pt was increased. The variations were, in the most cases, more marked for small beads than for other bead sizes. For this parameter, the values were also greater for Pt than for Pd. The parameter $\alpha$ also decreased with increasing initial concentration and the variations were not very marked for Pd. In the case of Pt, the variations were less marked, and for some experimental conditions, the variations were not continuous. The parameter $\beta$, as expected, tended to constant values representing the logarithm of the initial concentration, i.e., 2.3 (10 mg L$^{-1}$), 3.0 (20 mg L$^{-1}$), 3.4 (30 mg L$^{-1}$).

For constant initial Pd and Pt concentrations, the kinetic parameters $k$ and $\alpha$ were larger for small than for large beads, while the parameter $k_o$ increased with the size of the beads. It appeared that the variation in the sorption rates was proportional to the variations in the $S_{\text{exc}}$ (proportional to the square of diameter) for these different particle sizes. This indicates that PDC plays a significant part in the kinetic control of the sorption. According to Hellferich's rules, the weak effect of metal concentration confirms that sorption kinetics is mainly controlled by diffusion within the polymer beads, though the contribution of FDC cannot be totally ruled out. Fick's Law can be used to describe the sorption rate as a function of both the concentration gradients between the surface of the sorbent and the film surrounding the particle, and the surface area over which exchange takes place. The increase in $k_o$ with increasing particle size confirms this assumption. Increasing the particle size reduced $S_{\text{exc}}$ and consequently, reduced the initial sorption rate.

## Influence of Chitosan Concentration

Figure 3 compares the sorption kinetics for middle size beads with different concentrations of chitosan. The increase in the concentration of chitosan did not change the particle size but, since the experiments were performed at constant mass of chitosan, the number, and consequently the $S_{\text{exc}}$ were decreased using high chitosan concentration beads. The $S_{\text{exc}}$ was halved. The sorption kinetics, which is independent of the change in chitosan concentration and $S_{\text{exc}}$ confirms that the FDC was not the main controlling step. On the other hand, one would expect a change in the intraparticle diffusion characteristics of the sorbent with increasing density of the polymer network (comparable volume of the beads for an increase in the dry mass). The porous volume, calculated based on water content in the beads, would be almost halved. The increase in the density of the porous network would restrict intraparticle diffusion as it occurs with increased cross-linking or macroreticular structure. Figure 3 invalidates this hypothesis: the

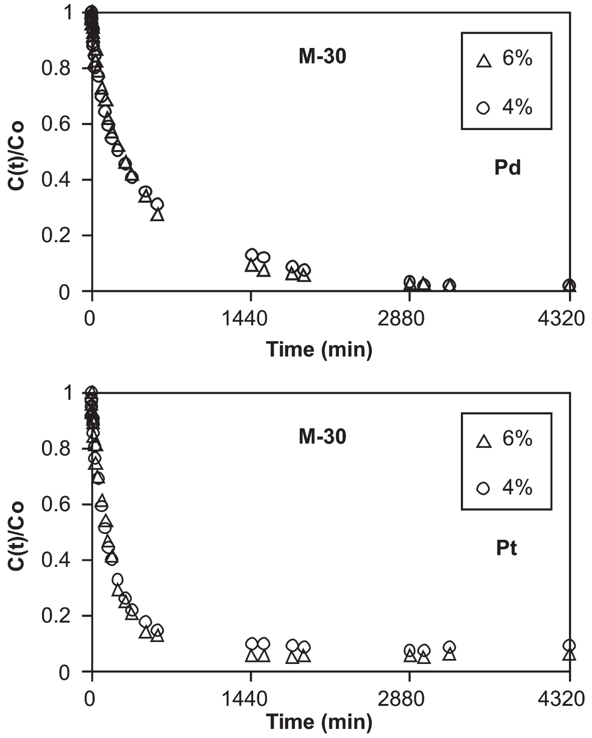

***Figure 3.*** Influence of chitosan concentration in the beads on Pd (top) and Pt (bottom) sorption kinetics (initial metal concentration: 30 mg Metal $L^{-1}$).

PDC was not influenced by this density parameter. The coefficients in Tables 2 and 3 confirm these trends: the coefficients $k$ and $\alpha$ were of the same order of magnitude as for comparable beads at lower chitosan content. The only significant change was observed for the parameter $k_o$, which slightly increased with chitosan content.

### Influence of Drying Procedure

Another way to influence the packing density of the polymer is drying. Figure 4 compares sorption kinetics for beads that were submitted to different drying treatments: raw beads (B), dried beads (DB), dried beads that were re-hydrated (RB), and re-hydrated saccharose beads (after drying in the presence of saccharose, Sa). This figure clearly shows that drying, and re-conditioning if it

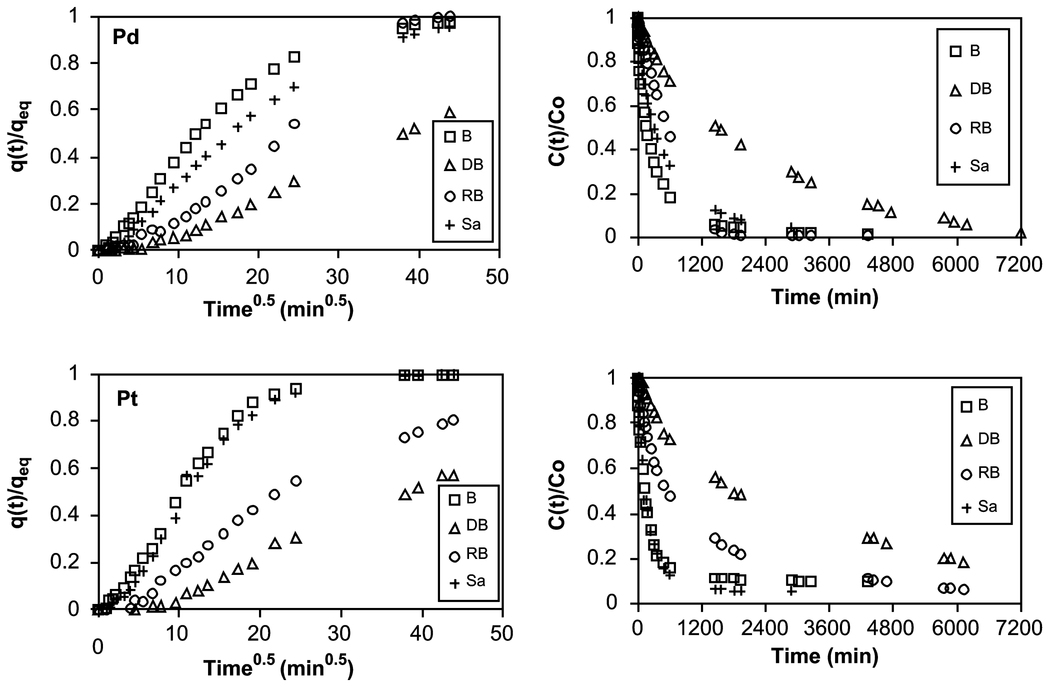

*Figure 4.* Influence of drying process on Pd (top) and Pt (bottom) sorption kinetics (initial metal concentration: 20 mg Metal $L^{-1}$).

took place, strongly influenced palladium and platinum extraction rates. The shape of the sorption kinetic curves is radically different for dried beads than the raw beads. The DB and RB are characterized by a long initial period for which the sorbent was almost unable to uptake metal ions. This period lasted between 30 and 75 min depending on the metal for DB and between 20 and 30 min for RB. Moreover, the slope of the sorption kinetic curve was significantly lower than that of B. The intraparticle diffusion resistance was strongly increased after drying. This may be explained by several reasons, including (a) a restriction in the porous volume of the beads; (b) a decrease in the size of the pores, which may control the diffusion of metal ions, as has been observed for other metal ions (18,19); (c) an increase in the crystallinity of the material. Indeed, Piron et al. have shown that the dissolving of chitosan results in a decrease in the residual crystallinity of chitosan (33,34). The crystallinity parameter is a key-parameter in the accessibility to internal sites for both water and metal ions, and many studies have shown that decreasing the crystallinity results in improved metal ion sorption properties (35). Kurita et al. (36) studied the cross-linking of water-soluble chitin samples with glutaraldehyde and observed that the resulting products were amorphous similar to the original water-soluble chitin, while the raw material (uncross-linked), submitted to dissolving, developed a high degree of crystallinity on drying. Kurita et al. (37) observed similar trends with chitosan cross-linked with glutaraldehyde. These studies correlated the copper sorption to the crystallinity of the materials. An optimum in the aldehyde/amine ratio has been found: copper sorption increases with the cross-linking ratio upto a maximum and then decreases again. The initial increase in metal ion adsorption was attributed to the low levels of cross-linking in the precipitate preventing formation of closely packed chain arrangements without any great reduction in the swelling capacity. At higher levels of cross-linking, the precipitates (for the water-soluble chitin samples) had lower swelling capacities, and hence lower accessibilities, because of the more extensive three-dimensional network and also of the more hydrophobic character with increase in the glutaraldehyde content (38). Piron et al. have shown also that the drying step partially restores the original crystallinity of the material, except when the sorbent is freeze-dried (33,34). Re-hydration allows the sorption kinetics to be increased, however, under the conditions selected for these experiments, it was not sufficient to compensate for the diffusion restrictions, especially because the drying, under uncontrolled conditions, is almost irreversible, as confirmed by the unchanged bead diameter. For these reasons, wettability and intraparticle diffusion in the porous network were greatly reduced. This is confirmed by the parameters listed in Tables 2 and 3. Re-hydration causes the parameters $k$ and $\alpha$ to be almost doubled for Pd and Pt sorption. Surprisingly, the parameter $k_o$ was also increased after re-hydration, though a decrease in the re-hydration time and external diffusion resistance was expected. The parameters were significantly less favorable than for raw beads (B): lower $k$, lower $\alpha$, and higher $k_o$. Similar behavior was observed for Pd and Pt sorption.

In the case of beads that were pre-treated with saccharose, the kinetic curves were significantly improved: the shape and the relative position were close to those obtained with raw beads. The lag time was reduced and the slope of the kinetic curves was significantly increased. In the case of Pt sorption, the sorption kinetic curves almost overlapped for B and Sa sorbents. On the other hand, for Pd the diffusion properties were not completely restored: though the equilibrium concentration was comparable, the time required to reach the equilibrium was increased. Tables 2 and 3 confirm these conclusions. The presence of saccharose during the drying step increased kinetic parameters, $k$ and $\alpha$, while the "time lag parameter," $k_o$ was decreased. It is interesting to observe that the parameters for Sa sorbent are comparable to that of B sorbent for Pt sorption, and just slightly lower for Pd sorption: but the same order of magnitude was obtained. The incorporation of saccharose during the drying step allowed the beads to partly maintain their structure: the network was not so shrunk as it occurred in absence of the sugar. In the absence of saccharose, new bonds may be formed between the chains of the polymer during the shrinking, which made re-hydration impossible. The presence of saccharose prevented these linkages becoming established between nearest polymer chains, and re-hydration was therefore possible. The bead diameter was increased from 1.49 to 2.69 mm. The re-hydration was not complete (in comparison to the initial diameter of the beads) but restored a part of the initial volume of the beads: ca. 60% of the volume of the bead lost during the drying step under uncontrolled conditions was restored.

## Sorption Isotherms

### Influence of Particle Size and Chitosan Concentration in the Beads

Figure 5 shows the sorption isotherms for Pd and Pt using different bead sizes. Both curves were characterized by a steep increase in the sorption capacity at low concentrations followed by a saturation plateau. Such typical curves can be modeled using the Langmuir equation. However, the sorption curves were significantly different for Pd and Pt. For Pd sorption, the curve was almost vertical at low concentrations (below 2 mg Pd $L^{-1}$), and the plateau was reached at ca. 5 mg Pd $L^{-1}$, while for Pt, at low residual concentrations, the sorption was very weak and the sorption curve began to get steeper for a residual concentration above 1 mg Pt $L^{-1}$. This is consistent with the above results on kinetics, which have shown that the equilibrium concentration was usually higher than 1 mg Pt $L^{-1}$. Similar trends have been observed in the case of the sorption of molybdate and vanadate (39,40). Depending on the speciation, which in turn

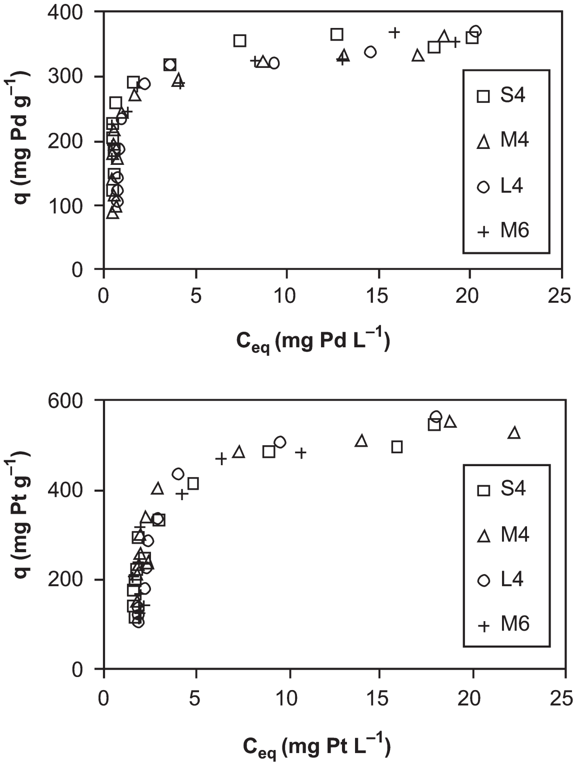

***Figure 5.*** Influence of bead size and chitosan concentration in the beads on Pd (top) and Pt (bottom) sorption isotherms.

depends on metal concentration and pH, the metal ions can be present in solutions in either non- or less-adsorbable ionic forms. As a consequence, at low metal concentrations, the predominance of nonadsorbable species leads to a very low sorption level, while an increase in the residual concentration results in the formation of more adsorbable species, and the sorption capacity increases. A similar interpretation could be suggested in the case of Pt sorption using these sorbents. The lower slope of the Pt sorption isotherm curve in comparison to Pd sorption isotherm confirmed this hypothesis. The plateau was reached at a residual concentration of 10 mg Pt L$^{-1}$. The sorption isotherms for Pd and Pt can be described, respectively, as almost irreversible and very favorable. The maximum sorption capacities for Pd and Pt were ca. 360 mg Pd g$^{-1}$ (266 mg Pd g$^{-1}$ sorbent), and 530 mg Pt g$^{-1}$ (392 mg Pt g$^{-1}$ sorbent), respectively. On the basis of molar units, the maximum sorption capacities were 3.4 mmol Pd g$^{-1}$

(2.5 mmol Pd $g^{-1}$ sorbent), and 2.7 mmol Pt $g^{-1}$ (2.0 mmol Pd $g^{-1}$ sorbent). Based on the deacetylation degree of the chitosan used in this study (87%), 1 g of chitosan contained ca. 6 mmol of nitrogen and 5.2 mmol of $—NH_2$, neglecting the fraction of amine groups involved in imine linkages with glutaraldehyde; the maximum molar ratio between Pd/Pt and nitrogen was 0.57 and 0.45, respectively, and the ratio Pd/Pt vs. amine groups were 0.65 and 0.52, respectively.

It is interesting to observe that for Pd and Pt sorption, the size of the beads did not significantly influence the sorption capacity. Particle diameter influenced the sorption kinetics but not the equilibrium. For middle size beads, increasing the concentration of chitosan in the beads did not change the shape of the sorption isotherms for Pd and Pt. This parameter did not influence the kinetics and the equilibrium in the sorption. Potential diffusion restrictions, related to particle size and chitosan concentration, did not influence sorption at equilibrium.

## Influence of Drying Process

Figure 6 compares the sorption isotherms for beads submitted to different drying procedures, with those of raw beads (B). The drying of chitosan beads resulted in similar Pd sorption isotherms: the same steep increase in sorption capacity was observed as for raw beads, however, at large residual concentrations (on the plateau), the maximum sorption capacity was slightly decreased (by ca. 10%). This decrease can be related to an insufficient contact time to reach the equilibrium, since sorption kinetics have already shown that at high concentrations of dry beads, the time required to reach the equilibrium is significantly higher than that of raw beads. In the case of RB, the same behavior was observed and can be explained by the same reason. On the other hand, in the case of saccharose-treated beads (Sa), the sorption isotherm overlapped perfectly with that of raw beads (B). The Sa beads were less sensitive to diffusion limitations and the equilibrium was reached within the contact time selected for sorption isotherms. Drying in presence of saccharose significantly improved sorption performance.

For Pt, results were more contrasting. For saccharose-treated beads, the sorption isotherm also overlapped with that of raw beads. For RB, the sorption capacity was slightly lower than that obtained with Sa and B, but the change was not very marked in comparison to DB. Indeed, for dried beads, sorption capacity was halved, even at low residual concentration (5–10 mg Pt $L^{-1}$). This can be explained by the very long sorption kinetics, which require a long contact time. Since the contact time for sorption isotherms was limited to four days, the equilibrium was not really reached but such a large decrease in sorption capacity may be related to difficult access to internal sorption sites, resulting from

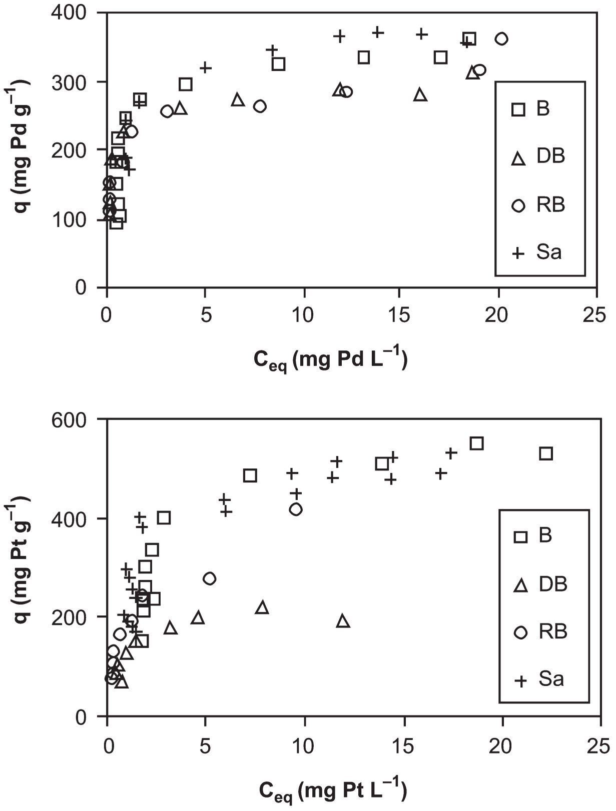

***Figure 6.*** Influence of drying process on Pd (top) and Pt (bottom) sorption isotherms.

uncontrolled drying. Indeed, the material was more crystalline in comparison with raw beads or beads dried under controlled conditions.

## CONCLUSIONS

These results confirm that diffusion resistance represents a key parameter in the design of chitosan sorbents. Gel bead conditioning is very efficient at increasing sorption kinetics and uptake performances. However, for large-scale use, chitosan gel beads containing high water percentage cannot be easily handled and transported; it is thus necessary to optimize the drying process. Previous studies have shown that the freeze-drying process is an efficient but very expensive method to achieve the drying whilst maintaining sorption performance. When uncontrolled conditions are selected for the drying, sorption rates are greatly reduced. Preliminary re-hydration of the beads partly restores diffusion properties, however, since the drying is irreversible, kinetics are still affected by intraparticle diffusion limitations. The drying results in a strong irreversible reduction in the size of the beads, which may result in a decrease in the porous volume, pore size, and in an increase in the polymer crystallinity. On the other hand, using saccharose to maintain the volumetric structure of the beads significantly improves sorption performance and enhances sorption kinetics. The saccharose pre-treatment prevents the collapse of the structure and limits the volume variation. Sorption kinetics and isotherms are thus maintained at a level close to that of raw beads.

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