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Pd AND Pt RECOVERY USING CHITOSAN GEL BEADS. II. INFLUENCE OF CHEMICAL MODIFICATIONS ON SORPTION PROPERTIES

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ABSTRACT

Chitosan is very efficient at removing precious metals from dilute acid solutions. Its sorption properties can be improved by the chemical modification of the polymer. Several methods have been tested for chitosan modification including poly(ethylene imine) (PEI)-grafting, hydrogenation of imine function on glutaraldehyde-cross-linked chitosan, and thiourea-grafting. Depending on the modification technique, the improvement in sorption performance may consist, in an increase in sorption capacity (PEI-grafted chitosan), a change in the stability of the sorbent

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(hydrogenation of imine linkage) or an increase in the selectivity of sorption in the presence of co-ions (thiourea derivatives of chitosan). Chitosan gel beads were chosen rather than the flaked material, since the gel beads have enhanced diffusion properties. The influence of drying and re-hydration of the beads are studied for some of these chitosan derivatives with regard to their diffusion properties.

Key Words: Platinum; Palladium; Chitosan; Glutaraldehyde cross-linking; Sorption isotherms; Sorption kinetics; Poly(ethylene-imine)-grafting; Thiourea-grafting; Sodium borohydride reduction

INTRODUCTION

Chitosan is efficient at removing precious and strategic metals from dilute acid (1–3). The protonation of chitosan in acid solutions induces interesting anion exchange properties, which are responsible for the extraction of metal anions. However, chitosan is soluble in acid solution, except in sulfuric acid, which consequently limits the possibility of using this biopolymer for the extraction of these metal ions from industrial solutions (4–6). The cross-linking of chitosan with glutaraldehyde increases the stability of chitosan in acid solutions. The reaction of chitosan with this bi-functional reagent leads to the formation of imine functions $>\text{C}=\text{N}-$ between the cross-linking agent and amine groups of the biopolymer. This results in a decrease in the number of available amine groups. The imine functions may be reduced by hydrogenation using sodium cyanoborohydride or sodium borohydride: the double linkage $>\text{C}=\text{N}-$ is replaced by a single linkage $>\text{C}=\text{N}$ in order to increase the reactivity of the nitrogen site (3,7,8). Ohga et al. (9) and Inoue et al. (10) protected amine groups by metal ion adsorption before the cross-linking treatment, and then desorbed the metal ions to prepare sorbents with high affinity for metal ions and greater stability in acid solutions. This technique has been also used for the preparation of a chitosan derivative that recognize planar metal ions in order to improve adsorption selectivity (8). Another technique to improve the sorption efficiency of chitosan, after a cross-linking treatment, consists in the incorporation of complementary amine functions. This procedure has been used by Kawamura et al. for the grafting of poly(ethylene imine) (PEI), on chitosan beads (11,12). They cross-linked chitosan beads with ethylene diglycidyl ether (another bi-functional reagent) and then reacted the derivative with epichlorohydrin, finally the product was reacted with PEI. In the present work,

the method used for the preparation of the beads was different: chitosan beads were brought into contact with PEI in a selected solvent and then rinsed. The PEI-impregnated beads were reacted with glutaraldehyde.

The grafting of new functional groups on chitosan in order to improve sorption selectivity and reactivity in complex media has been the subject of considerable research (3,13–16). Sulfur derivatives have been extensively studied due to the high reactivity of sulfur functions with metal ions (17). The sulfur derivatives used in this study were prepared by a two-step procedure consisting, in the preliminary reaction, of glutaraldehyde with thiourea followed by the reaction of the mixture with chitosan. Glutaraldehyde acts as a linker and a spacer between amine groups of chitosan and amine groups of thiourea.

These modifications were performed on chitosan gel beads in order to favor diffusion in the biopolymer. Previous studies have shown the favorable effect of this conditioning on sorption kinetics (6,18). Gel conditioning results in an expansion of the polymer network, an increase in the pore size, and a decrease in the crystallinity of the material, each of these beneficial effects give rise to better intraparticle diffusion. The effect of these modifications has been studied through conventional experiments: sorption kinetics and isotherms. For some of these derivatives, some experiments were compared after drying and re-hydration. Indeed, Part I of this work (23) has shown the influence of drying on the sorption rates.

MATERIAL AND METHODS

Material

The description of experimental procedures focuses on the preparation of derivatives, since the materials and the procedures used for the preparation and characterization of chitosan gel beads (raw material or dried products) have already been described (23).

Hydrogenation of Chitosan Gel Beads

The hydrogenation of imine functions in the cross-linked material was performed by dissolving 1 g of sodium borohydride in 100 mL of demineralized water. Wet cross-linked beads, of about 10 g, were then added to the solution and the slurry was agitated for 6 hr. The beads were then removed from the solution and rinsed several times with demineralized water. These beads were used as produced (BH) after drying/re-hydration. When relevant, a similar procedure was used for the hydrogenation of thiourea.

PEI-Grafting

PEI-grafted beads (PEI-GA) were prepared according to the following procedure. Five grams of PEI (M_w : 600,000–1,000,000) were dissolved in 100 mL dimethylacetamide, 5 g (dry weight) of wet chitosan beads were then added under agitation for 16 hr. The impregnated beads were then separated from the solution and rinsed with 30 mL of dimethylacetamide. Three grams of glutaraldehyde (50% w/w in water) were dissolved in dimethylacetamide and then mixed with impregnated beads for 6 hr. Finally, the beads were rinsed several times with water.

Thiourea-Grafting

Two different thiourea derivatives were produced with increasing amounts of thiourea, using a procedure similar to the method previously used for the synthesis of thiourea derivatives of chitosan flakes (16). The 3:2:1 thiourea derivative was prepared by mixing 14.4 mL of glutaraldehyde (50% w/w, 8.5 mmol) with 9.6 g of thiourea (12 mmol) and 96 mL of demineralized water for 3 hr. Wet chitosan beads were then added (4.8 g, dry weight, 25 mmol-NH₂) and agitated for 16 hr. The modified beads were then removed from the solution, rinsed several times, and stored in water. For the 1:1:1: thiourea derivative, 4.8 mL of glutaraldehyde (3 mmol) was used and 4.8 g of thiourea (6 mmol) for 4.8 g (dry weight, 25 mmol-NH₂) of wet chitosan beads (all other experimental conditions were the same). Samples of these preparations were submitted to the hydrogenation procedure to prepare 3:2:1 BH and 1:1:1: BH samples.

Sorption Procedure

Experiments were performed at room temperature and the pH was adjusted to pH 2 using hydrochloric acid. 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 4 days. Filtrates were collected and analyzed using an inductively coupled plasma atomic emission spectrometer, ICP-AES (Jobin-Yvon, Longjumeau, France). The metal content of the beads was calculated using the mass balance equation, and the sorption capacity was determined in function of both the actual mass of chitosan in the sample—the increase in weight resulting from glutaraldehyde cross-linking, PEI grafting, and thiourea grafting was not taken into account—and the dry mass of the sorbent (including the substituents). The number of beads used for these experiments was adjusted in order to maintain identical amount of chitosan in each equivalent experiment. Some complementary experiments were carried out on the effect of chloride concentration on sorption capacity at equilibrium under selected experimental conditions.

For the study of sorption kinetics, a standard procedure was applied (6). One liter of solution at pH 2 was mixed with a constant weight of chitosan (independently of the weight increase resulting from chemical modification). The standard initial concentration was 20 mg metal L⁻¹. The determination of kinetic parameters was performed using the same equations as described in Part I (23).

RESULTS AND DISCUSSION

Characterization of Modified Chitosan Gel Beads

PEI-Grafting

Table 1 shows the main characteristics of chitosan beads obtained during PEI-grafting procedure. The impregnation of chitosan beads with the PEI-solution led to an increase in the dry weight of the sorbent of 18.8 mg (for 100 beads). After cross-linking with glutaraldehyde, the weight increased by 21.3 mg (for 100 beads), and chitosan represented only 52% of the final product (as compared with 74% for the reference, glutaraldehyde cross-linked chitosan beads). The cross-linking ratio (referred to the initial amount of chitosan—and amine functions in the beads—and calculated on the basis of the weight increase) went up from 0.6 (for reference beads) to 0.81 with PEI-grafted beads (PEI GA and PEI GA R). Since the amount of chitosan was unchanged in the different samples, the increase in the cross-linking ratio must have been due to direct interaction of glutaraldehyde functions with amine groups contained in PEI.

It is also interesting to observe that after PEI impregnation, the variation in the size of the beads between the initial size and the size of the beads after drying and re-hydration was comparable to the variation in size observed in the case of saccharose-dried beads (23). The reduction in the volume of the beads was only 55%, as compared with 49% in the case of saccharose-dried beads and 91.6% in the case of dried glutaraldehyde-cross-linked beads. It could be suggested that the presence of PEI in the porous network of the beads prevents the collapse of the structure that occurs with dried beads, as the presence of saccharose during the drying process prevents the marked reduction in the volume of the beads. However, in this case again, the re-hydration did not completely restore the porosity (and the volume) of the beads. It may influence sorption kinetics and induce diffusion limitations.

Thiourea-Grafting and Hydrogenation

The hydrogenation of the imine function (as the result of the reaction of sodium borohydride with imine functions—glutaraldehyde interaction with

Table I. Characteristics of PEI-Chitosan Gel Beads

Sample	DWC ^a	PW ^b	GW ^c	CLR ^d	D ^e	S _{exc} ^f	Characteristics
B	59.3	—	15.6	0.60	3.36 (± 0.12)	8.1	Glutar. Cross-linked beads
PEI	62.5	18.8	—	—	n.d. ^g	—	PEI-impregnated beads
PEI GA	83.8	18.8	21.3	0.81	3.50 (± 0.15)	8.8	PEI-grafted beads (with GA)
PEI GA R	83.8	18.8	21.3	0.81	2.58 (± 0.15)	4.8	PEI GA dried and rehydrated

For 100 beads.

^a DWC: Dry weight of cross-linked beads (with PEI or without PEI) (mg).^b PW: PEI weight (mg).^c GW: Glutaraldehyde weight (mg).^d CLR: Cross-linking ratio (mol glutaraldehyde/mol-NH₂).^e D: Diameter of beads (mm).^f S_{exc}: external sorbent surface for kinetic experiment (m⁻¹).^g n.d.: not determined.

amine functions of chitosan) did not change the dry weight of chitosan beads (Table 2). Surprisingly, the diameter of the beads was increased by ca. 10%. Otherwise, other characteristics of cross-linked chitosan beads were not changed. We can assume the physical properties of the sorbents, after grafting of thiourea on the polymer beads, will not be changed by the complementary treatment with sodium borohydride.

The grafting of thiourea on chitosan (via the preliminary reaction of glutaraldehyde with thiourea) led to an increase in the dry weight of the beads by 30.15 mg (for 100 beads) instead of 15.6 mg in the case of the simple glutaraldehyde cross-linking. In the case of the 1:1:1 BH sorbent, the diameter was not changed compared to the reference beads (glutaraldehyde cross-linked beads), while in the case of the 3:2:1 BH derivative, the diameter increased by ca. 5%. For 3:2:1 BH sorbent, chitosan represented 59% of the total weight (instead of 74% in the reference material).

Influence of Chemical Modification of Chitosan Beads on Sorption Kinetics

PEI-Grafting

Figure 1 presents the influence of the grafting of PEI on chitosan beads on Pd and Pt sorption kinetics. While in the case of the Pt sorption the curves overlapped, in the case of Pd sorption the grafting of PEI significantly increased the sorption rate, especially in the second stage of the process, which is usually controlled by intraparticle diffusion or reaction velocity. This can be explained by the presence of extra sorption sites due to PEI chains inside the porous structure of the beads: increasing the number of sorption sites increases the velocity of metal removal. Moreover, these functions (from PEI chains) may be less sterically hindered than the sorption sites in the porous chitosan structure. The sorption rate for Pd and Pt are of the same order for PEI grafted beads: 6–8 hr were necessary to reach 90% of the equilibrium sorption for both Pd and Pt, while a larger contact time was required to reach the same sorption level in the case of glutaraldehyde cross-linked beads. Tables 3 and 4 present kinetic data for each system. The grafting of PEI increased the kinetic parameters (k and α) for Pd and Pt sorption on PEI derivatives. However, the modification of chitosan beads also led to an increase in the parameter k_0 , which was cited as a representative of the resistance to film diffusion: the greater the initial lag time, the stronger the resistance to film diffusion. The re-hydrated PEI beads gave a better sorption rate than simply cross-linked material for Pd sorption, however, as it occurred for dried and re-hydrated material (23), the restoration of diffusion properties was

Table 2. Characteristics of Thiourea-Chitosan Gel Beads and Beads Treated with Sodium Borohydride

Sample	DWC	G + T ^a	D	S_{exc}	Characteristics
B	59.3	15.6	3.36 (± 0.12)	8.1	Glutaraldehyde Cross-linked beads
BH	59.2	15.6	3.72 (± 0.19)	10.0	Cross-linked beads after hydrogenation
BH R	59.2	15.6			BH beads dried and rehydrated
1:1:1 BH			3.36 (± 0.04)	8.1	Thiourea grafted beads after hydrogenation ^b
3:2:1 BH	73.85	30.15	3.47 (± 0.12)	8.7	Thiourea grafted beads after hydrogenation ^c

For 100 beads.

^a G + T: weight of glutaraldehyde and thiourea (mg). Other symbols are described in Table 1.^b Low thiourea grafting.^c High thiourea grafting.

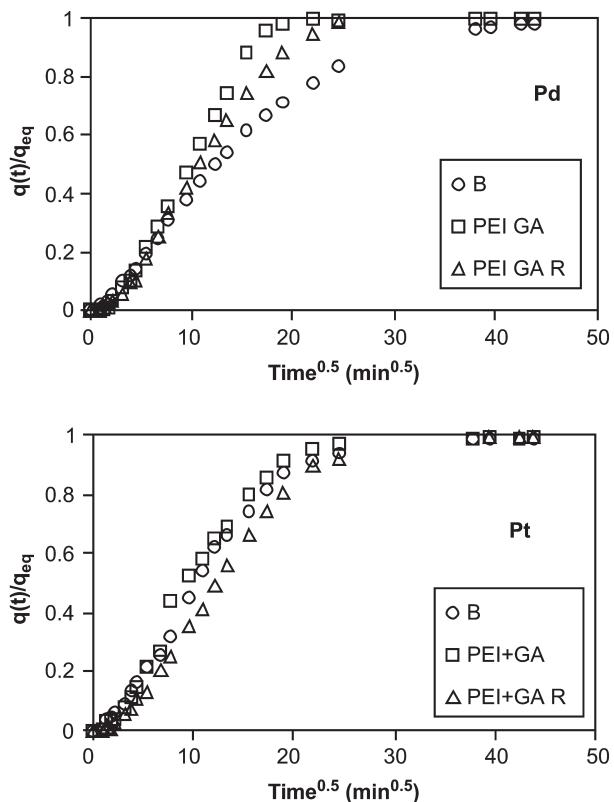


Figure 1. Influence of PEI-grafting on chitosan beads Pd (top) and Pt (bottom) sorption kinetics.

not complete after re-hydration. In the case of Pt sorption, the sorption rate was lower for PEI-grafted beads after re-hydration than simply cross-linked material.

Thiourea-Grafting and Hydrogenation

Figure 2 compares the sorption kinetics for beads modified by thiourea grafting and hydrogenation of imine functions for Pd and Pt recovery. Kinetic curves overlapped for both Pd and Pt sorption with simply cross-linked beads and thiourea derivatives, while in the case of the beads treated with sodium borohydride, the sorption was significantly slowed down, especially during the second stage of the sorption process (intraparticle and chemical reaction

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

Sample	$k \times 10^2$ (min $^{-0.5}$)	$k_0 \times 10^2$	R^2	$\alpha \times 10^3$	β	R^2
GA	4.42	4.70	0.998	3.64	2.93	0.976
PEI GA	6.07	9.25	0.990	7.07	3.00	0.999
PEI GA R	5.43	9.33	0.992	5.34	2.98	0.999
BH	3.23	1.85	0.997	2.43	2.93	0.972
BH R	2.83	3.90	0.992	1.98	2.96	0.983
1:1:1 BH	3.71	2.67	0.990	3.11	2.94	0.989
3:2:1 BH	3.97	1.40	0.995	3.97	2.93	0.976

controls). This result is consistent with previous conclusions concerning the influence of drying: the re-hydration improved diffusion properties but did not completely restore the sorption velocity of the original material. Tables 3 and 4 confirm these conclusions. The k parameter was slightly lower, but of the same order of magnitude, in the case of Pd sorption for thiourea derivatives, and almost equal to that of the reference material for Pt sorption. However, these parameters were significantly slower than those obtained with PEI grafted material. In the case of hydrogenated beads (without thiourea), the kinetic coefficients were significantly reduced, especially for re-hydrated materials, in agreement with Fig. 2. These trends are confirmed by the kinetic α parameters. Thiourea grafting increased sorption velocity but less than the grafting of PEI. Increasing thiourea concentration increased sorption velocity in the case of Pd sorption, while it decreased sorption rates for Pt sorption, however, there were no marked differences. The coefficient k_0 , which can be related to the initial lag time, and to the external diffusion resistance (connected with hydration mechanisms), was decreased in the case of Pd sorption when compared with the reference material

Table 4. Influence of Experimental Parameters on Kinetic Parameters for Pt Sorption on Chitosan Gel Beads

Sample	$K \times 10^2$ (min $^{-0.5}$)	$k_0 \times 10^2$	R^2	$\alpha \times 10^3$	β	R^2
GA	5.53	8.22	0.993	4.36	2.93	0.988
PEI GA	5.95	8.30	0.982	5.77	2.94	0.991
PEI GA R	4.73	9.78	0.995	4.29	2.99	0.999
BH	5.50	14.32	0.966	4.18	2.99	0.962
BH R	3.97	11.85	0.979	2.79	3.00	0.994
1:1:1 BH	5.32	10.32	0.994	5.19	2.98	0.992
3:2:1 BH	5.17	7.79	0.997	5.03	2.97	0.989

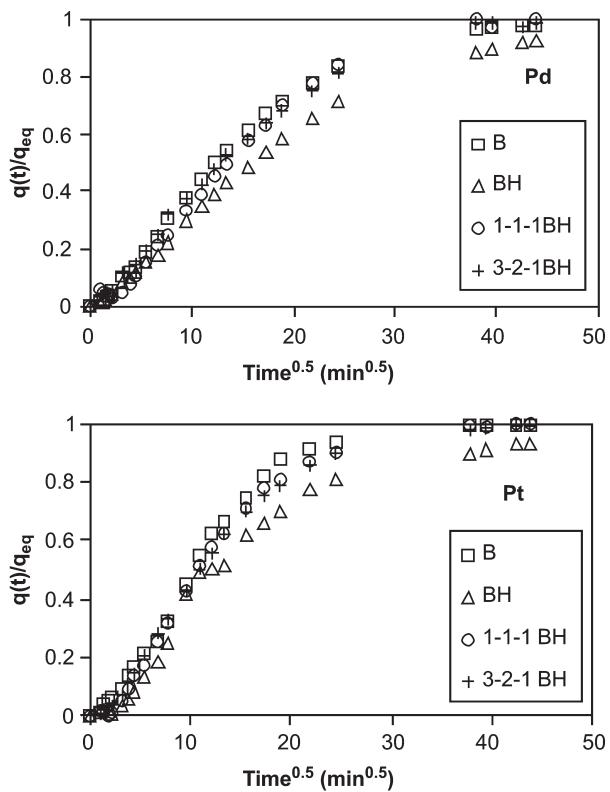


Figure 2. Influence of thiourea grafting and hydrogenation of chitosan beads on Pd (top) and Pt (bottom) sorption kinetics.

(and with PEI derivatives), while it was increased in the case of Pt sorption. In most cases, this coefficient was higher for Pt than for Pd uptake. It appeared that for sorption kinetics, the best modification was obtained with PEI grafting, due to better accessibility and the greater number of sorption sites.

Influence of Chemical Modification of Chitosan Beads on Sorption Isotherms

The sorption isotherms are given in function of both the actual mass of sorbent, and the mass of chitosan in the beads. Although it is not possible to allocate the metal ion adsorption between the chitosan and the compounds

grafted on the biopolymer, it appeared interesting to show how the modification of the biopolymer increases its volumetric sorption properties. Indeed, experiments were performed with fixed number of beads (representing the same volume of sorbent between glutaraldehyde cross-linked chitosan beads and modified beads). So, the sorption isotherms given in function of the actual mass of chitosan in the sorbent help to evaluate the impact of sorbent modification on the volumetric sorption capacity of the beads. This parameter is especially important for fixed-bed systems: the modification of the chitosan beads will increase the sorption efficiency and capacity of a volumetric unit of column.

PEI-Grafting

Figure 3 compares the Pd and Pt sorption isotherms for PEI materials to the sorption isotherms obtained on simply cross-linked sorbents. In the case of Pd uptake, the grafting of PEI led to an increase in sorption capacity from 360 to 810 mg Pd g⁻¹ chitosan. On the basis of the actual total mass of sorbent, the increase in sorption capacity was slightly lower: the maximum sorption capacity was increased from 270 to 420 mg Pd g⁻¹ sorbent.

In the case of Pt uptake, the grafting of PEI also led to an increase in sorption capacity, but it was slightly lower than that observed in the case of Pd sorption. The sorption capacity, on the basis of chitosan content, was increased from 550 to 1000 mg Pt g⁻¹ chitosan. When calculated on the basis of total sorbent mass, the sorption capacity was only increased from 400 to 520 mg Pt g⁻¹ sorbent. However, the figure suggested that the affinity of the sorbent for Pt, proportional to the initial slope of the curve, was enhanced by the grafting of PEI. This initial slope was not changed in the case of Pd sorption. So PEI grafting produced different changes in the sorption properties of chitosan depending on the metal: for Pd it increased the maximum sorption capacity, while for Pt it increased the affinity of chitosan for Pt.

Hundred beads contained 47.3 mg of chitosan; taking into account the deacetylation fraction of chitosan (87%), this amount represented 0.25 mmol of amine groups. On the other hand, PEI incorporation did not exceed 18.8 mg (for 100 beads), yet represented the addition of 0.36 mmol of amine groups. One would expect the sorption capacity to be doubled after PEI grafting if all the amine functions are available and reactive for metal anions. The ratio of primary, secondary, and tertiary amines in PEI is 1:2:1 (19), moreover, some of these amine groups may react with glutaraldehyde during the cross-linking step. This may cause a decrease in the number of reactive amine groups. Moreover, steric hindrance may decrease accessibility to some of these amine groups; it is thus difficult to directly correlate the addition of amine functions to the variation in sorption capacity. However, the comparison of maximum sorption capacity

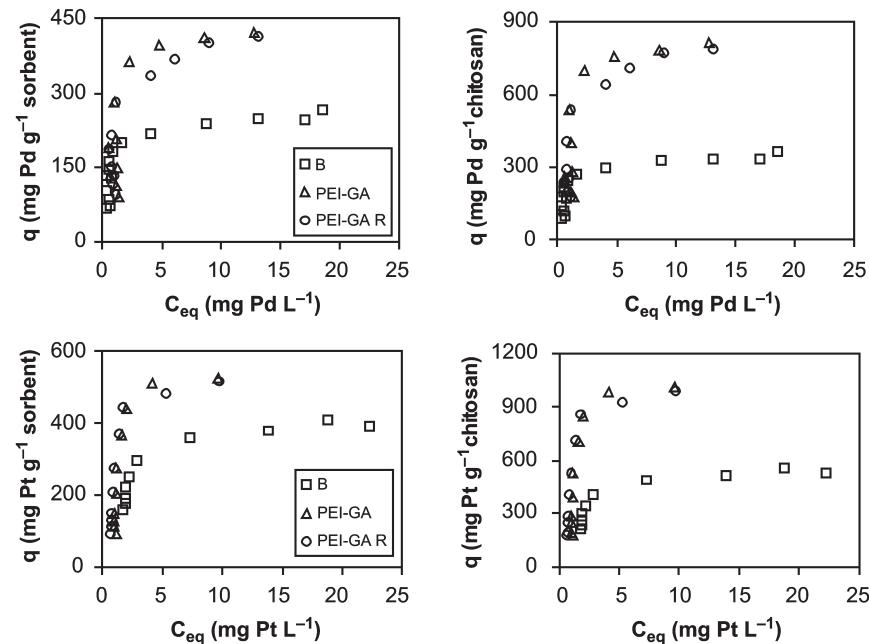


Figure 3. Influence of PEI-grafting on chitosan gel beads on Pd (top) and Pt (bottom) sorption isotherms.

showed that it increased by a factor of 2.25, while the theoretical increase in amine functions by PEI-grafting should be by a factor of 2.4. On the basis of the actual total mass of the sorbent, the increase is significantly lower (factor 1.6). PEI-grafting strongly increased the volumetric sorption capacity (referred to the constant fixed numbers of beads used in the experiments). On the basis of molar units, the sorption capacities of PEI-grafted chitosan beads were increased from 2.05 to 2.67 mmol Pt g⁻¹ sorbent (2.82 to 5.13 mmol Pt g⁻¹ chitosan) for Pt, and from 2.55 to 3.96 mmol Pd g⁻¹ sorbent (3.40 to 7.64 mmol Pd g⁻¹ chitosan).

Sorption isotherms for PEI beads were not changed by the drying/re-hydration procedure. It confirms that the drying step controls the diffusion kinetics but does not change the recovery performance at equilibrium.

Thiourea-Grafting and Hydrogenation

On the basis of the total sorbent mass, the grafting of thiourea slightly increased sorption capacity at high residual palladium concentration from 266 to

330 mg Pd g⁻¹ sorbent, while at low initial concentration sorption capacity was decreased. The affinity of the sorbent for palladium decreased, perhaps due to a partial release of thiourea, which forms a complex with palladium ions, making the metal ions less adsorbable. This competitor effect is less detectable at high metal concentration. Relative to the actual chitosan mass, the increase in sorption capacity is more significant (360 to 560 mg Pd g⁻¹ chitosan) (see Fig. 4).

In the case of Pt sorption, thiourea-grafting slightly decreased sorption capacity from 400 to 380 mg Pt g⁻¹ sorbent. On the basis of chitosan content, the sorption capacity was slightly increased from 500 to 640 mg Pt g⁻¹ chitosan. In this case gain, the affinity, given by the slope of the isotherm at the origin, decreased after thiourea-grafting.

The hydrogenation procedure, resulting from the reaction of sodium borohydride, did not significantly change the sorption capacity and the affinity for both Pd and Pt uptake. The chemical modification is expected to transform imine functions into amine functions, and to stabilize the sorbent. Primary amines are very efficient in the case of cation complexation (chitin affinity for metal cations is drastically lower than that of chitosan); in this case, the hydrogenation of imine

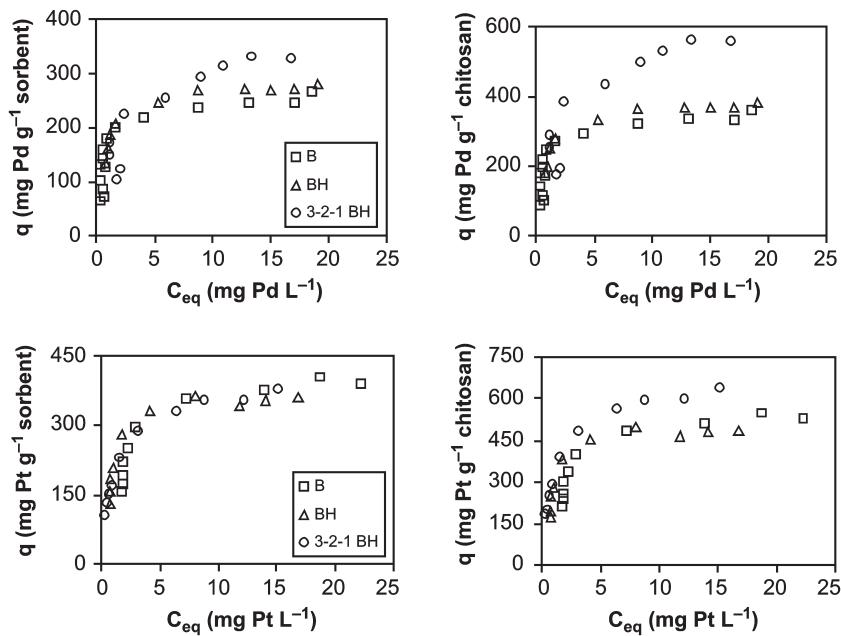


Figure 4. Influence of thiourea grafting and hydrogenation on chitosan beads on Pd (top) and Pt (bottom) sorption isotherms.

functions is expected to increase sorption capacity, however, in the case of anion-exchange process, the effect of the parameter is less significant.

Influence of Chloride Ions on Pt Sorption Isotherm Chitosan Beads

Figure 5 shows the influence of the presence of chloride ions (0.1 M) on platinum sorption. These results confirm previous studies that have shown that an excess of chloride ions leads to high levels of competition for metal sorption (16,20,21): in our study, the sorption capacity was reduced by 120 mg Pt g^{-1} (170 mg Pt g^{-1} chitosan). The influence of chloride ions may also be related to a change in the speciation of metal ions. The main interest in thiourea grafting is not only limited to an increase in sorption efficiency, but also this modification is assumed to decrease the sensitivity of the sorbent to environmental parameters such as pH and the presence of competitor ions or co-ions (16,21). Indeed, the grafting of thiourea on the chitosan backbone brings new sulfur functional groups that are very reactive for metal ions. While the original material adsorbed metal anions through anion exchange mechanisms, these new functions are suspected to chelate metal ions. Chelation mechanisms are less sensitive to pH and to the presence of co-ions (sulfate, chloride anions, for example).

Influence of Chloride Ions on Pd Sorption Using Thiourea Derivatives of Chitosan

In order to verify the effect of the presence of chloride anions on Pd sorption efficiency, several experiments were carried out with increasing chloride ion concentrations (Fig. 6). Although the presence of increasing concentrations of

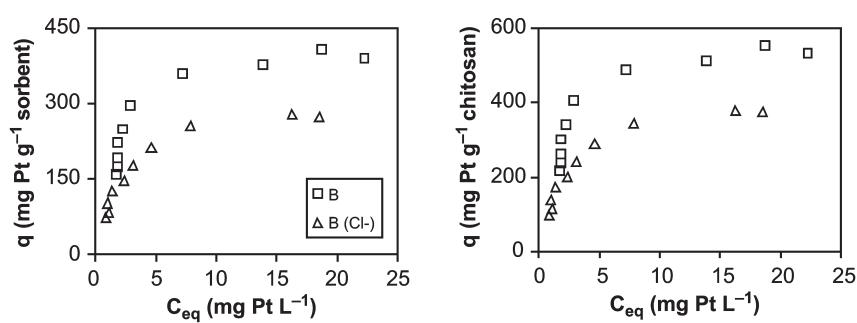


Figure 5. Influence of the presence of chloride ions (0.1 M) on Pt sorption isotherm.

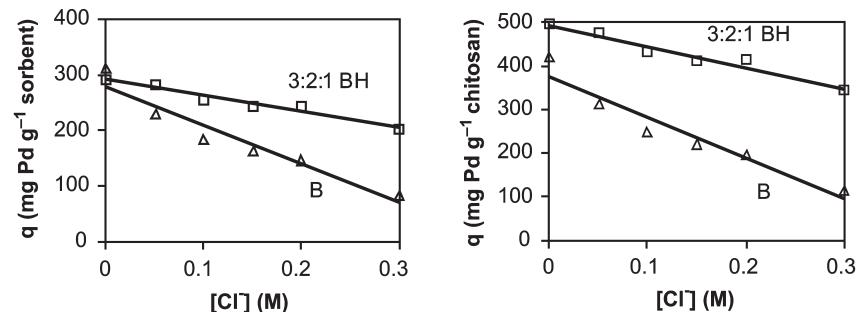


Figure 6. Influence of the concentration of chloride ions on Pd sorption capacity.

chloride may change the speciation of palladium in solution (20), the decrease in sorption could also be explained by heavy competition with chloride ions. The speciation, which is a function of pH and total metal concentration, can strongly affect metal sorption since it modifies the proportion of adsorbable species (22). However, in the present case, speciation is not changed enough to explain the large differences observed, and the effect of chloride ions is certainly due to their competitor effect. The figure compares the decrease in sorption capacity for reference material and thiourea grafted beads. While increasing chloride concentration to 0.3 M only reduced the sorption capacity by 30% in the case of the thiourea derivative, for glutaraldehyde cross-linked beads the sorption capacity was reduced by a factor of more than 3. This confirms the interest of thiourea derivatives for the sorption of palladium in complex media.

CONCLUSION

The incorporation of PEI in chitosan gel beads is assumed to produce new primary, secondary, and tertiary amine functions that increase the reactivity of the sorbent for metal ions. Its inclusion allows the low relative density of sorbing functions to be increased (the wet chitosan beads contain more than 95% of water). Another interesting effect of PEI incorporation was observed on rehydrated beads: it increases the sorption rates. The influence of PEI on sorption kinetics is similar to the effect of the presence of saccharose in the beads during the drying step: it maintains the structure of the polymer; it prevents the collapse of the porous network and improves diffusion properties after re-hydration.

The reaction of cross-linked beads with sodium borohydride is assumed to hydrogenate imine functions and to stabilize the beads. Actually, this treatment limits sorption performances for both equilibrium and kinetics. More interesting

is the grafting of thiourea that gives new chelating functionalities to the sorbent. It makes the polymer less sensitive to the presence of chloride ions.

The increase in sorption properties is approximately proportional to the number of PEI groups that have been incorporated in the sorbent: it seems that almost all the new functional sites are active (primary/secondary/tertiary amine in PEI) and accessible for metal ions. The simultaneous grafting of PEI and thiourea is currently investigated.

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REFERENCES

1. Baba, Y.; Hirakawa, H. Selective Adsorption of Palladium(II), Platinum(IV) and Mercury(II) on a New Chitosan Derivative Possessing Pyridil Group. *Chem. Lett.* **1992**, 1905–1908.
2. Guibal, E.; Larkin, A.; Vincent, T.; Tobin, J.M. Chitosan Sorbents for Platinum Sorption from Dilute Solutions. *Ind. Eng. Chem. Res.* **1999**, *38*, 401–412.
3. Wan Ngah, W.S.; Liang, K.H. Adsorption of Gold(III) onto Chitosan and *N*-Carboxymethyl Chitosan: Equilibrium Studies. *Ind. Eng. Chem. Res.* **1999**, *38* (4), 1411–1414.
4. Hsien, T.-Y.; Rorrer, G.L. Effects of Acylation and Crosslinking on the Material Properties and Cadmium Ion Adsorption Capacity of Porous Chitosan Beads. *Sep. Sci. Technol.* **1995**, *30* (12), 2455–2475.
5. Hsien, T.-Y.; Rorrer, G.L. Heterogeneous Cross-Linking of Chitosan Gel Beads: Kinetics, Modeling and Influence on Cadmium Ion Adsorption Capacity. *Ind. Eng. Chem. Res.* **1997**, *36* (9), 3631–3638.
6. Guibal, E.; Milot, C.; Tobin, J.M. Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic Studies. *Ind. Eng. Chem. Res.* **1998**, *37* (4), 1454–1463.
7. Muzzarelli, R.A.A. Removal of Uranium from Solutions and Brines by a Derivative of Chitosan and Ascorbic Acid. *Carbohydr. Polym.* **1985**, *5*, 85–89.

8. Baba, Y.; Masaaki, K.; Kawano, Y. Synthesis of Chitosan Derivative Recognizing Planar Metal Ion and Its Selective Adsorption Equilibria of Copper(II) over Iron(III). *React. Funct. Polym.* **1998**, *36*, 167–172.
9. Ohga, K.; Kurauchi, Y.; Yanase, H. Adsorption of Cu^{2+} or Hg^{2+} Ion on Resin Prepared by Cross-Linking Metal-Complexed Chitosan. *Bull. Chem. Soc. Jpn* **1987**, *60*, 444–446.
10. Inoue, K.; Baba, Y.; Yoshizuka, Y. Adsorption of Metal Ions on Chitosan and Crosslinked Copper(II)-Complexed Chitosan. *Bull. Chem. Soc. Jpn* **1993**, *66*, 2915–2921.
11. Kawamura, Y.; Mitsushashi, M.; Tanibe, H.; Yoshida, H. Adsorption of Metal Ions on Polyaminated Highly Porous Chitosan Chelating Resin. *Ind. Eng. Chem. Res.* **1993**, *32* (2), 386–391.
12. Kawamura, Y.; Yoshida, H.; Asai, S.; Tanibe, H. Breakthrough Curve for Adsorption of Mercury(II) on Polyaminated Highly Porous Chitosan Beads. *Water Sci. Technol.* **1997**, *35* (7), 97–105.
13. Muzzarelli, R.A.A.; Tanfani, F. *N*-(*o*-Carboxybenzyl) Chitosan, *N*-Carboxymethyl chitosan and Dithiocarbamate Chitosan: New Chelating Derivatives of Chitosan. *Pure Appl. Chem.* **1982**, *54* (11), 2141–2150.
14. Argüelles-Monal, W.; Peniche-Covas, C. Preparation and Characterization of a Mercaptan Derivative of Chitosan for the Removal of Mercury from Brines. *Makromol. Chem.* **1993**, *207*, 1–8.
15. Asakawa, T.; Inoue, K.; Tanaka, T. Adsorption of Silver on Dithiocarbamate Type of Chemically Modified Chitosan. *Kagaku Kogaku Ronbunshu* **2000**, *26* (3), 321–326.
16. Guibal, E.; Vincent, T.; Navarro Mendoza, R. Synthesis and Characterization of a Thiourea Derivative of Chitosan for Platinum Recovery. *J. Appl. Polym. Sci.* **2000**, *75*, 119–134.
17. Saha, B.; Iglesias, M.; Cumming, I.W.; Streat, M. Sorption of Trace Heavy Metals by Thiol Containing Chelating Resins. *Solvent. Extr. Ion Exch.* **2000**, *18* (1), 133–167.
18. Milot, C.; McBrien, J.; Allen, S.; Guibal, E. Influence of Physicochemical and Structural Characteristics of Chitosan Flakes on Molybdate Sorption. *J. Appl. Polym. Sci.* **1998**, *68*, 571–580.
19. Juang, R.-S.; Ju, C.-Y. Equilibrium Sorption of Copper(II)-Ethylenediaminetetraacetic Acid Chelates onto Cross-Linked Polyaminated Chitosan Beads. *Ind. Eng. Chem. Res.* **1997**, *36* (12), 5403–5409.
20. Ruiz, M.; Sastre, A.M.; Guibal, E. Palladium Sorption on Glutaraldehyde-Crosslinked Chitosan. *React. Funct. Polym.* **2000**, *45*, 155–173.
21. Guibal, E.; Von Offenberg Sweeney, N.; Vincent, T.; Tobin, J.M. Sulfur Derivatives of Chitosan for Palladium Sorption. *React. Funct. Polym.* **2002**, *50* (2), 149–163.

22. Guibal, E.; Milot, C.; Roussy, J. Influence of Hydrolysis Mechanisms on Molybdate Sorption Isotherms Using Chitosan. *Sep. Sci. Technol.* **2000**, *35* (7), 1021–1038.
23. Ruiz, M.; Sastre, A.; Guibal, E. Pd and Pt Recovery Using Chitosan Gel Beads. I. Influence of the Drying Process on Diffusion Properties. *Sep. Sci. Technol.* **2002**, *37* (9), 2143–2166.

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