



## Mercury sorption on a thiocarbamoyl derivative of chitosan

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### ABSTRACT

The grafting of thiourea on chitosan backbone allows synthesizing a thiocarbamoyl derivative that was very efficient for mercury sorption in acidic solutions. Though the sorption capacity is not increased compared to raw chitosan in near neutral solutions, this modification allowed maintaining high sorption capacity (close to 2.3 mmol Hg g<sup>-1</sup>) at pH 2. Mercury sorption in acidic solutions is not affected by the presence of competitor metals (such as Zn(II), Pb(II), Cu(II), Cd(II), Ni(II)) or the presence of nitrate anions (even at concentration as high as 0.8 M). The presence of chloride or sulfate anions (0.8 M) decreased Hg(II) sorption capacity to 1 mmol Hg g<sup>-1</sup>. Kinetics are controlled by a combination of pseudo second-order reaction rate and resistance to intraparticle diffusion. Mercury desorption reached about 75% using thiourea (in HCl solution).

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### 1. Introduction

Due to the toxicity and accumulation effects of metals ions in the food chain, these micro-pollutants are extensively surveyed and the national and international regulations are becoming more and more drastic. The dramatic example of contamination in Minamata (Japan) showed the potential impact of the accumulation of mercury in the food chain on population health. Conventional processes for the recovery of mercury from industrial effluents consist in precipitation [1–4], cementation [5], ion exchange [6–9], solvent extraction [10–13] and adsorption [6,14–21]. Sorption processes may use synthetic resins but an increasing interest has been focused on biosorbents for the last decades. Biosorbents may consist of biomass [22–24], agriculture waste [22,25], biopolymers such as chitosan [26–30]. Chitosan ( $\beta$ -(1–4)-linked D-glucosamine) is obtained by the deacetylation of chitin ( $\beta$ -(1–4)-linked N-acetyl-D-glucosamine), one of the biopolymers the most abundant in nature. This biopolymer is characterized by its high ratio of amine groups, it is very efficient for metal binding through different mechanisms [31]. The binding of metal cations may occur by complexation on amine groups in near neutral solutions [32,33], while metal anions can bind to protonated amine groups in acidic solutions [34–36]. The intrinsic pK of amine groups in chitosan strongly depends on

the degree of acetylation and the degree of neutralization of amine groups. However, it is close to 6.5 with commercial samples (degree of acetylation close to 15%). The presence of chloride ions in the solution may induce the formation of chloro-anionic species that can bind to protonated amine groups [37,38]. Chitosan is soluble in acidic solution, except in sulfuric acid media; the biopolymer is thus frequently cross-linked for improving its stability in acidic solutions. Glutaraldehyde is a dialdehyde that contributes to establish supplementary linkages (Schiff's base reaction between aldehyde functions and amine groups) between the polymer chains and to stabilize the polymer in acidic media [32,33,39]. The cross-linking may reduce the availability and reactivity of amine functions for chelation [40], and in the case of ion exchange/electrostatic attraction mechanism the presence of anions strongly decreases sorption performance (competition effect) [41]. To prevent these limiting effects, a number of chitosan derivatives have been synthesized [38,42–45], with the objectives of increasing the density of reactive groups (aminated chitosan) [44,46,47], or to improve sorption selectivity (grafting of sulfur compounds for example). Different strategies have been developed including (a) the grafting of thiourea or other sulfur compounds (dithioamide, for example) through reaction with glutaraldehyde (as a linking agent) [48,49], <http://www.lwr.kth.se/English/OurSoftware/vminteq>, (b) the grafting of cysteine on chitosan backbone [50–52], and (c) the grafting of mercaptoacetamide [53]. The main drawback of these procedures is the limited pH range for efficient use or the lack of stability of the sulfur compounds (degradation of sulfur

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groups). Though most of the mercury-containing effluents at industrial scale are alkaline solutions (for example chlor-alkali industry), the recovery of mercury from acidic solutions is retaining attention in hydrometallurgy for example (processing of copper ores, for example) [54,55]. The present work describes a new procedure for the synthesis of a series of thiocarbamoyl derivatives of chitosan (including a cross-linking treatment with glutaraldehyde) and investigates their sorption properties for mercury. The reaction pathway is different to the procedures described in the literature (cysteine grafting, thiourea grafting through glutaraldehyde linkage, the grafting of mercaptoacetamide, etc.) and the procedure allows reaching high substitution degree. Apart of sorption isotherms, the influence of several parameters on sorption has been tested: pH (and effect of the acid used for pH control), presence of competitor ions on equilibrium (sorption isotherms) and influence of metal concentration, agitation speed and sorbent dosage (uptake kinetics). Finally the possibility to desorb mercury from loaded resin is investigated.

## 2. Materials and methods

### 2.1. Material

Chitosan was purchased from JSC “Sonat” (Moscow, Russia). Degree of acetylation (DA) was determined by  $^1\text{H}$  NMR spectroscopy to be 0.16; while the average molecular mass of  $2.5 \times 10^5 \text{ g mol}^{-1}$  was established using viscometry [56]. All other chemicals for sorbent synthesis were of analytical grade and were used without further purification.

For sorption experiments, metal salts were supplied by Fluka (Switzerland) as analytical grade salts (under the form of chloride salts).

### 2.2. Sorbent synthesis

Previous investigations at the I. Ya. Postovsky Institute of Organic Synthesis (U.D.R.A.S.) have contributed to select optimum conditions for thiol grafting. Varying the reaction temperature it appeared that below  $110^\circ\text{C}$ , the kinetics of the conversion was substantially reduced, while at temperature greater than  $150^\circ\text{C}$ , the partial degradation of the polymer matrix limited the efficiency of the synthesis. A temperature in the range  $110\text{--}130^\circ\text{C}$  appeared optimum. The reaction time was also varied: when the reaction time was lower than 4 h the substitution degree was low (less than 0.3); when the reaction time exceeded 6 h the substitution yields remained constant. A reaction time of 5 h was considered as the optimum. Actually, under optimal conditions the substitution yield varied between 0.5 and 1.1 depending on the ratio of reagents.

The modification of chitosan (thiocarbamoylation) was operated using the following procedure:

- 20 g (0.12 mol) of chitosan was mixed with 25.6 g (0.34 mol) of ammonium thiocyanate and 12.2 g (0.16 mol) of thiourea.
- The mixture was heated below  $130^\circ\text{C}$  for 10 min (formation of a gel-like mass).
- The gel was heated at  $130^\circ\text{C}$  for 4 h before being cooled.
- The gel was finally rinsed with water until the reaction of the water phase with ferric ions became negative (complete removal of unreacted  $\text{SCN}^-$ ), and air-dried.

The synthesis yield reached 22.8 g.

The cross-linking treatment was operated by contact of the thiocarbamoyl derivative with glutaraldehyde [57]. 16 g of thiocarbamoyl chitosan (10.6 mmol amine groups, degree of substitution DS: 0.68) were dispersed in 90 mL of water. The cross-linking solu-

tion was prepared by mixing 1.7 g of glutaraldehyde (25% solution, 4.48 mmol) with 30 mL of water. The cross-linking solution was mixed with the slurry (thiocarbamoyl chitosan) for 24 h at  $24^\circ\text{C}$ . The solid was thus filtered and dried at  $50^\circ\text{C}$ .

Two lots of sulfur derivative of chitosan have been prepared following the same procedure. They will be called S1 and S2 sorbents. These materials have been separated in two fractions: the first fraction has been used as synthesized; the second fraction of the sulfur derivative was chemically cross-linked with glutaraldehyde. Cross-linked materials have been called S1C and S2C, respectively.

### 2.3. Sorbent characterization

Element analysis was performed using an Elemental Analyzer Perkin Elmer. FT-IR spectra were recorded on a “Spectrum One” FT-IR spectrometer (Perkin Elmer) using (a) a Diffuse Reflectance Sampling Accessory (DRA); or (b) a Smart Orbit Accessory for Single-Reflection Attenuated Total Reflectance (ATR) (see [Additional material](#)). Solid-state  $^{13}\text{C}$  NMR spectra were registered on a spectrometer Bruker Avance AV-300 at 300 MHz.

### 2.4. Sorption and desorption experiments

The pH of initial solutions was controlled using NaOH and either  $\text{H}_2\text{SO}_4$  or HCl. The acid was changed to verify if the acid used can impact metal speciation and thus its sorption. The pH was not controlled during the sorption but it was measured at the end of each experiment.

Sorption isotherms were obtained by contact of a given amount of sorbent (i.e., 20 mg) with 150 mL of solution containing increasing concentrations of mercury (in the range 0–100 or 0–200  $\text{mg Hg L}^{-1}$ ) at target pH (pH 2, 5 and 7). A sample was collected after 4 days of agitation and filtered before being analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES JY 2000, Jobin Yvon, Longjumeau, France). The mass balance equation was used for the calculation of sorption capacity (metal concentration in the sorbent). The equilibrium pH was systematically measured at equilibrium. For the isotherm at pH 2, the equilibrium pH varied by less than 0.1 unit (between 1.9 and 2.1). For the isotherm at pH 5, the equilibrium systematically decreased in the range 3.7–4.3 when pH was controlled with sulfuric acid and in the range 3.3–4 when hydrochloric acid was used for initial pH control. Similar experimental procedures were used for the determination of sorption performance at equilibrium when investigating the effect of pH, the influence of the presence of competitor ions (metal salts or anions, which were directly added to metal solution as solid-state salts).

Kinetics was performed in batch reactor; the sorbent, at the appropriate sorbent dosage (SD), was added to 1 L of solution with known initial concentration. Samples were regularly collected, filtered and analyzed for plotting the relative metal concentration (residual concentration divided by the initial concentration) versus time. Experimental conditions (SD, metal concentration, sorbent type, etc.) were varied and the values of the parameters will be systematically reported in the caption of the figures.

The desorption of mercury from loaded sorbents has been studied in two steps: (a) the mass balance equation was used to evaluate the amount of mercury adsorbed on the sorbent ( $\text{SD: } 0.2 \text{ g L}^{-1}$ ;  $C_0$ :  $70 \text{ mg L}^{-1}$ , pH 2 controlled with sulfuric acid; contact time: 4 days); and (b) the loaded sorbent (after being rinsed with water) was mixed with the eluent solutions ( $\text{SD: } 0.4 \text{ g L}^{-1}$ ; contact time 2 h). The eluate was filtered and analyzed using ICP-AES. The comparison of the amounts of metal successively adsorbed and desorbed was used for the calculation of desorption efficiency.

**Table 1**  
Element analysis (%) of thiocarbamoyl chitosan samples (S1 and S2).

Sample	C	H	N	S	
S1	Anal.	38.34	6.23	9.97	9.29
	Calc.	38.40	6.07	10.19	9.74
S2	Anal.	37.79	6.32	9.63	8.47
	Calc.	37.52	6.28	9.78	8.86

All experiments were performed at room temperature (i.e.,  $20 \pm 1.5^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. Chemical characterization of thiocarbamoyl derivatives of chitosan

Elemental analysis was performed on thiocarbamoyl chitosan (before cross-linking treatment). Table 1 reports both the analytical results and the calculated values according to the structures suggested on Schemes 1 and 2. The substitution degrees deduced from proposed structures were 74% and 68%, respectively. The change in the substitution degree showed that the synthesis procedure did not allow perfect reproducibility, though the variation was less than 10%. The calculated values were close to the analytical results and the small variations may be attributed to parallel reactions involving the formation of additional groups such as  $\sim\text{NH}_2\cdot\text{HSCN}$  groups and, probably, the derivatives of thiobiuret  $\sim\text{NHCSCHCSNH}_2$ ,  $\sim\text{NHCSCHCSNH}\sim$ . Titrimetric analysis showed that the samples contained about 0.43 and 0.42 mequiv.  $-\text{NH}_2/\text{g}$  for S1 and S2, respectively (versus 0.46 and 0.45 mequiv.  $-\text{NH}_2/\text{g}$  for suggested structures).

Samples were characterized by FT-IR spectroscopy (Additional electronic material, AM1 and AM2) and the main bands were assigned (Table 2). The interpretation of the spectra is made difficult by the superimposition of several signals in close wavenumber ranges. For example a first broad and poorly resolved band around  $3300\text{ cm}^{-1}$  corresponds to the contribution of O–H stretching (from water molecule, and from intra- and intermolecular hydrogen bonds) and N–H stretching. Similarly some bands representative of thiourea are expected to appear at wavenumbers close to those observed with raw chitosan: in the range  $1050\text{--}1300\text{ cm}^{-1}$  (C=S stretching), in the range  $1590\text{--}1420\text{ cm}^{-1}$  (interaction C=S stretching with C–N stretching). Successful amidation is indicated by

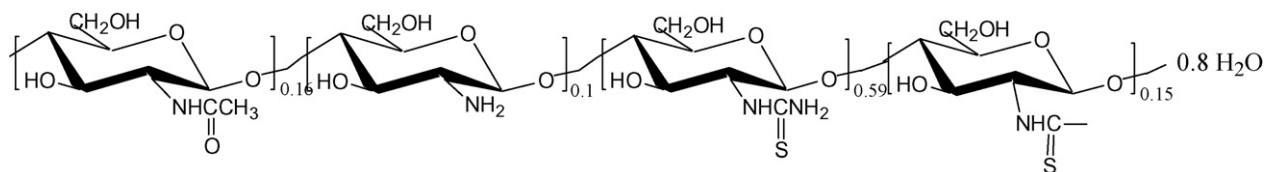
the appearance of the thiocarbonyl stretching band at  $1620\text{ cm}^{-1}$  and the appearance of the band typical of  $-\text{S}=\text{N}<$  groups at  $1404\text{ cm}^{-1}$ . In addition there is a small amount of  $\sim\text{NH}_2\cdot\text{HSCN}$  groups ( $2055\text{ cm}^{-1}$ ). The spectra of S1 and S1C sorbents before and after Hg sorption have been recorded (see Additional Material AM3). Various changes are observed after metal sorption in acidic solutions. Some of the modifications are attributable to the protonation of amine groups that contribute to modifying the environment of amine functions on the spectra (around  $1590\text{ cm}^{-1}$ ) others to metal binding. The intensity of the band at  $1400\text{--}1440\text{ cm}^{-1}$  was substantially decreased after mercury binding in both HCl and  $\text{H}_2\text{SO}_4$  solutions. This result confirms that sulfur groups were involved in metal binding. However, a lot of differences in the spectra before and after metal sorption were also observed in the environment of amine and amide groups (amide I band:  $1620\text{--}1660\text{ cm}^{-1}$ ; amide II band:  $1520\text{--}1560\text{ cm}^{-1}$ ; amide III band:  $1320\text{--}1340\text{ cm}^{-1}$ ) indicate that nitrogen-compounds can probably be involved in metal sorption.

The  $^{13}\text{C}$  NMR analysis (Additional electronic material AM4) showed the typical signals for C in the glucosamine/acetilglucosamine unit: C-2 signal (convoluted with C-6 signal) at 61 ppm, C-3 signal at 76 ppm, convoluted C-5 and C-4 signals at 83 ppm and the C-1 signal at 104 ppm. The signals at 24 and 175 ppm can be assigned to C in the acetyl groups present on the non-deacetylated fractions of the biopolymer. Additionally, a band appeared at 185 ppm; this is the band representative of the carbons in the thiourea group.

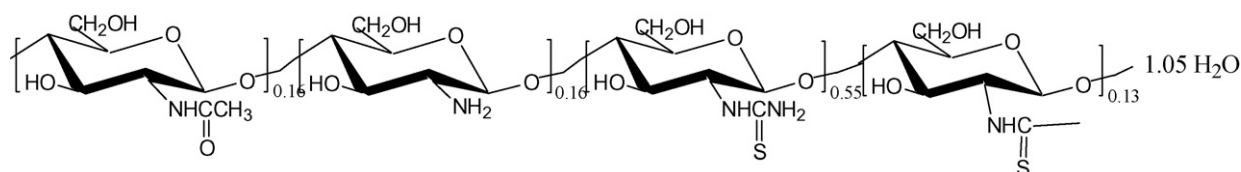
These results are consistent with the characterization of other thiocarbamoyl derivatives of chitosan. For example, Chen et al. reported the grafting of thiourea on chitosan for the binding of silver to prepare an antimicrobial agent [58]. They proceeded by interaction of chitosan with ammonium thiocyanate in alcoholic media. However, in this case the substitution degree was significantly lower (i.e., 0.035) than the values reached by the present method. Pestov et al. made derivated chitosan gels by reaction with lithium thiocyanate [59]. The degree of substitution reached with this procedure did not exceed 0.3. This means much lower than the levels reached with the present procedure: the substitution can increase up to 1.1 with the original method of thiocarbamoylation of chitosan in gel eutectic mixture  $\text{NH}_4\text{SCN}/\text{H}_2\text{NCSNH}_2$ . In the present work, with selected experimental conditions, the substitution degree ranged between 0.68 and 0.74.

#### 3.2. Influence of pH on sorption

Fig. 1a compares the sorption capacity for raw chitosan and thiocarbamoyl chitosan (before and after glutaraldehyde cross-linking)



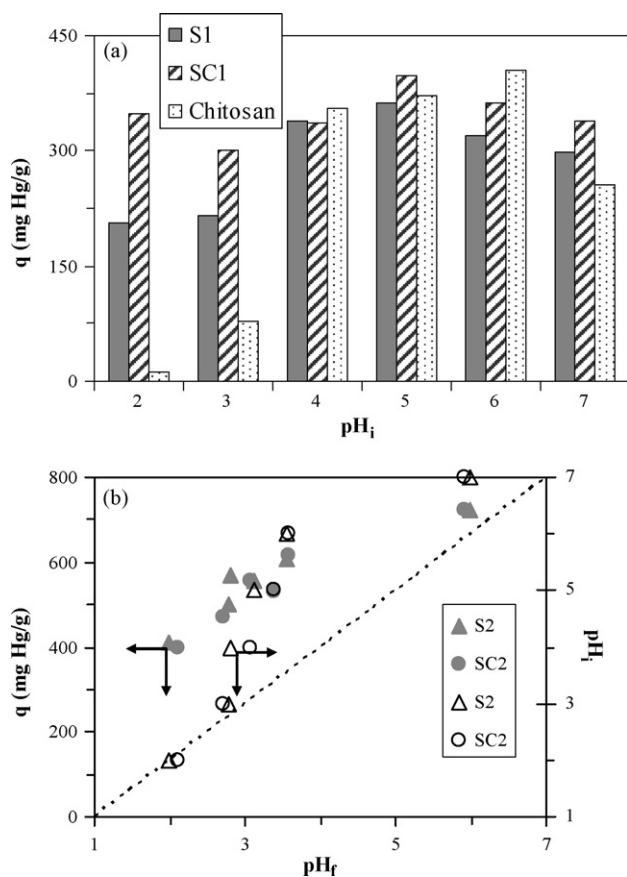
**Scheme 1.** Structure of S1 sample.



**Scheme 2.** Structure of S2 sample.

**Table 2**  
Assignment of FT-IR spectroscopy bands.

Chemical group/vibration band	Wavenumber (cm <sup>-1</sup> )		
	Range	S1	S2
$\nu_{OH}$ (O–H <sub>water</sub> + O–H Intra- and inter-H bonds) (+ $\nu_{NH}$ )	3200–3500	3327	3320
$\nu_{CH}$	2600–3000	2882, 2934	2888, 2935
$\nu_{NH}$	3269	Overlapped with $\nu_{OH}$	
$\nu_{CO} + \nu_{CN}$	1140–1160	1147	1148
	1025–1035	1027	1031
$\nu_{CO}$ (ring)	1060–1070	1063	1064
	890–900	899	899
$\nu_{CO}$ (conj. $\delta_{NH}$ ) (amide I)	1620–1675	1622	1623
$\delta_{NH}$ (conj. $\delta_{C=N}$ ) (amide II)	1520–1560	1537	1540
$\nu_{C=S}$ or $\nu_{CH_2}$	1414	1415	1416



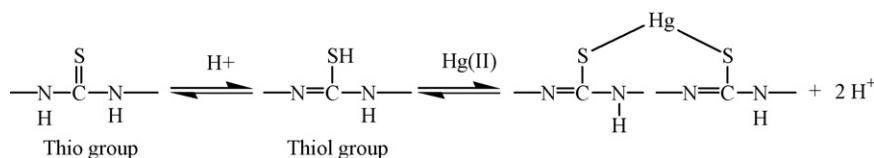
**Fig. 1.** Influence of pH on sorption capacity: (a) Hg(II) sorption capacity versus initial pH for chitosan, S1 and SC1 sorbents ( $C_0$ : 50 mg Hg L<sup>-1</sup>; sorbent dosage (SD): 67 mg L<sup>-1</sup>); (b) Hg(II) sorption capacity and initial pH versus equilibrium pH for S2 and SC2 sorbents ( $C_0$ : 100 mg Hg L<sup>-1</sup>; sorbent dosage (SD): 134 mg L<sup>-1</sup>) (pH controlled with sulfuric acid).

at different initial pHs. For pH between 4 and 6 mercury sorption capacity was comparable for all the resins: the variation did not exceed 10% (around 361 mg Hg g<sup>-1</sup>). The pH had a poor effect under selected experimental conditions and the sorbent capaci-

ties were comparable. It is noteworthy observing that raw chitosan lost most of its sorption efficiency when the pH decreased to pH 3 (and below) [6,44], contrary to the thiocarbamoyl derivatives that maintained a high sorption capacity even at pH 2. Pohl and Prusisz [16] showed that Duolite GT-73 (a resin bearing thiol groups) was very efficient for mercury binding in HCl solutions. Merrifield et al. [52] also prepared a thiol-grafted chitosan (cysteine immobilization on chitosan gel beads) and they showed that sorption efficiency increased with pH, though maintaining a sorption capacity close to 2 mmol Hg g<sup>-1</sup> at pH 2.2. Walcarus et al. [60] reached similar conclusions with thiol-functionalized mesoporous silicas. The sorption capacities are lower than the values cited by Donia et al. (i.e., 3.5 mmol Hg g<sup>-1</sup> at pH 2 and 4.5 mmol Hg g<sup>-1</sup> at pH 4.5) at using magnetic chelating resins prepared by copolymerization of bistiourea/thiourea/glutaraldehyde [61].

For the sample SC1 (cross-linked material) the sorption capacity remained in the range 300–340 mg Hg g<sup>-1</sup>, while the sorption capacity for the non-cross-linked material (i.e., S1) was close to 210 mg Hg g<sup>-1</sup>. Clearly the main interest of the thiocarbamoyl derivative of chitosan consists in extending the use of the sorbent to the sorption of mercury in acidic solutions. Indeed, in acidic solutions (controlled with sulfuric acid), mercury was present in the solution under the cationic form (Hg<sup>2+</sup>) that can be bound on chitosan through complexation mechanism: the competition of protons for interacting with amine groups reduces mercury binding on raw chitosan. Donia et al. [61] investigated mercury sorption on a magnetic chelating resin prepared by reaction of bistiourea, thiourea and glutaraldehyde. They suggest that in acidic solutions mercury binding occurs by complex formation between Hg(II) and deprotonated thiol forms: the thio functions are converted into thiol groups in acidic media (see Scheme 3). Additionally, in the case of HCl solutions, the formation of chloro-anionic mercury species led to the binding of HgCl<sub>3</sub><sup>-</sup> on protonated amine groups. Herrero et al. [62] pointed out the importance of mercury speciation on metal sorption using a marine macroalga: in the case of other transition metals the main limiting effect is the protonation/deprotonation of carboxylic groups (alginate compounds), while for mercury the acid base properties of the sorbent play a minor role compared to metal speciation.

A complementary experiment was performed on sample SC2 (before and after glutaraldehyde cross-linking) (Fig. 1b). On this lot the cross-linking did not influence sorption capacity, which linearly



**Scheme 3.** Hg(II) sorption mechanism on thio-based reactive groups (Donia et al. [61]).

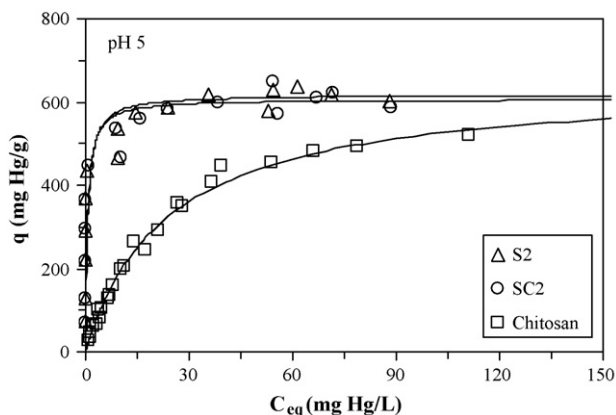


Fig. 2. Hg(II) sorption isotherms at pH 5 using chitosan, S2 and SC2 sorbents (pH controlled with sulfuric acid).

increased with the equilibrium pH in the range 1–4: the sorption capacity varied between 400 and 620 mg Hg g<sup>-1</sup>. It is noteworthy that the sorbent had a buffering effect at pH 3–3.6. Indeed, for low initial pH (i.e., pH 2 and 3) the equilibrium value was almost unchanged (lying close to the first bisector), while in the range pH 4–6, the equilibrium pH were systematically in the pH range 3–3.6 (above the first bisector). For initial pH 7, the pH tended to stabilize around pH 6, while the sorption capacity tended to level off at 800 mg Hg g<sup>-1</sup>. It is noticeable that at pH 7, mercury approaches the precipitation when concentration exceeds 80 mg L<sup>-1</sup>.

### 3.3. Sorption isotherms

The sorption isotherms for mercury have been compared for chitosan, S2 and SC2 sorbents at pH 5 (Fig. 2). The maximum sorption capacity was comparable for the three sorbents close to 600 mg Hg g<sup>-1</sup> (i.e., 3 mmol Hg g<sup>-1</sup>); this is consistent with the comments on the effect of pH (previous section). The sorption isotherm also confirms that S2 and SC2 gave similar sorption performance (the variation in sorption capacities did not exceed 5%). It is noteworthy that the affinity of the sorbent for Hg(II) was significantly increased by the modification of chitosan. Indeed, the initial slope of the curve, which represents the coefficient  $q_m \times b$  in the Langmuir equation, was significantly steeper in the case of thiocarbamoyl derivative. Modifying chitosan allows improving the efficiency of the sorbent at pH 5: the saturation level (comparable to the value reached with raw chitosan) was reached with a residual concentration much lower than in the case of raw biopolymer. This is another evidence of the interest of modifying chitosan. The shape of the sorption isotherms (appearance of a saturation plateau) suggests that the isotherm curve can be modeled using the Langmuir equation.

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

where  $q$  and  $q_m$  are the sorption capacities (mg Hg g<sup>-1</sup>) in equilibrium with concentration  $C_{eq}$  (mg Hg L<sup>-1</sup>) and at saturation of the monolayer, respectively;  $b$  is the affinity coefficient (L mg<sup>-1</sup>).

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

where  $k_F$  (mg<sup>1-(1/n)</sup> g<sup>-1</sup> L<sup>1/n</sup>) and  $n$  (non-dimensional) are the constants of the Freundlich equation. Table 3 reports the values of the parameters that were used for plotting the modeled curves (solid lines in Fig. 2, the parameters of the Langmuir equation have been used). The table confirms previous conclusions: the maximum sorption capacity is of the same order of magnitude, while the affini-

Table 3  
Modeling of sorption isotherms.

Sorbent	pH <sub>i</sub>	Langmuir equation—parameters		
		$q_m$	$b$	$R^2$
S2	2	459.5	0.153	0.993
SC2	2	459.9	0.154	0.995
S2	5	617.9	1.466	0.998
SC2	5	606.9	1.645	0.997
Chitosan	5	647.4	0.042	0.990
S2	7	1445.0	0.158	0.980
SC2	7	1271.2	0.195	0.990
Freundlich equation—parameters				
		$k$	$n$	$R^2$
S2	7	365.3	3.25	0.990
SC2	7	330.7	3.21	0.970

$q_m$ : mg Hg g<sup>-1</sup>;  $b$ : L mg<sup>-1</sup>;  $k$ : mg<sup>1-(1/n)</sup> g<sup>-1</sup> L<sup>1/n</sup>.

ty coefficient  $b$  was increased by a factor of 30–40 after chitosan modification.

The impact of initial pH (pH 2, 5 and 7) on the sorption isotherms was compared for sorbents S2 and SC2 (Fig. 3; the parameters of the Langmuir equation found in Table 3 have been used, except at pH 7 where the Freundlich equation was used for the modeling of the curves). At equilibrium, the pH was close to pH 2 for the most acidic solution, while it varied between pH 3.4 and 4.2 for the pH 5 series. This observation is consistent with results of the previous section. The experimental series at pH 7 were significantly affected by metal concentration in terms of pH variation: the equilibrium pH varied between pH 5 and 7.5 making difficult the accurate modeling of experimental data (simultaneous variation of pH and metal concentration). The contribution of potential hydrolysis and precipitation mechanisms at pH 7 for high metal concentration may explain the shape of the sorption isotherm that was significantly different to the asymptotic shape found with lower pH values. The dashed vertical line delimits the concentration range above which the precipitation may occur. Merrifield et al. [52] also observed a strong increase in sorption capacity at pH 7, probably due to precipitations mechanisms. Atia et al. [63] commented on the impact of the precipitation of Hg(OH)<sub>2</sub> on recovery performance. The shape of the isotherm suggests using the Freundlich (power-type equation) for the modeling of the curve (with the parameters reported in Table 3). At pH 2, the maximum sorption capacity was close to 460 mg Hg g<sup>-1</sup>, i.e., 2.3 mmol Hg g<sup>-1</sup>. At pH 5 (equilibrium pH close to 4), the maximum sorption capacity was close to 610 mg Hg g<sup>-1</sup>, i.e., 3 mmol Hg g<sup>-1</sup>. These values are consistent with the values cited by several researchers investigating sulfur-bearing sorbents.

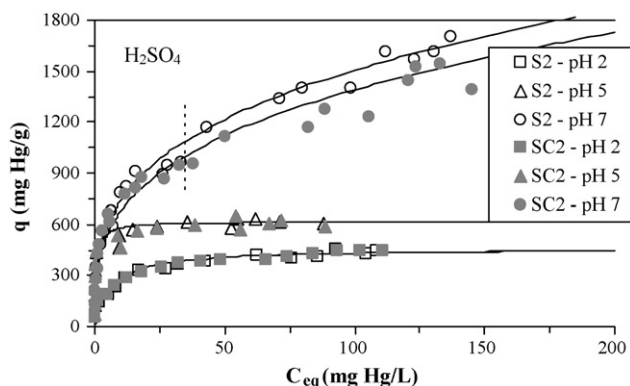


Fig. 3. Influence of pH on Hg(II) sorption isotherm using S2 and SC2 sorbents (pH controlled with sulfuric acid).

For example Donia et al. [48] cited a sorption capacity close to  $3 \text{ mmol Hg g}^{-1}$  at pH 5 for magnetic chitosan resin modified with thiourea and glutaraldehyde. Atia et al. [63] reported a sorption capacity close to  $3.2 \text{ mmol Hg g}^{-1}$  at pH 5 for a synthetic resin bearing both amine and mercaptan moieties. In the case of thiol-grafted chitosan gel beads, Merrifield et al. [52] cited sorption capacities of 2, 2.3,  $3.5 \text{ mmol Hg g}^{-1}$  at pH 2.2, 4 and 5, respectively. Higher sorption capacities ( $4.5\text{--}5 \text{ mmol Hg g}^{-1}$ ) were obtained at pH 5.2 by Neagu et al. [6] using quaternized resin (obtained by grafting of chloroacetamide). Jeon and Höll [44] prepared an aminated derivative of chitosan (reaction of ethylenediamine with chitosan through glutaraldehyde linkage): the maximum sorption capacity drastically decreased from  $2.2 \text{ mmol Hg g}^{-1}$  at pH 6 down to  $0.5 \text{ mmol Hg g}^{-1}$  at pH 4.

The difference in the sorption capacity with increasing pH may be explained by the contribution of additional reactive groups (amine functions for example) at pH 4–5. Indeed, the reactivity of sulfur groups (complexation) is less influenced by the pH than the reactivity of other groups such as amine groups [64]. The thiocarbonyl derivative of chitosan contains both free amine and sulfur groups. In acidic solutions the protonation of amine groups drastically reduces their ability to complex mercury, as shown in Fig. 1a (sorption capacity for raw chitosan at pH 2 was negligible). At pH 2, the sorption is thus only due to sulfur groups; Table 1 shows that S content was close to  $2.7 \text{ mmol S g}^{-1}$ . This is about 20% higher than the maximum sorption capacity reached at pH 2: a part of sulfur groups are not available for reacting with mercury. At pH 5 (decreasing to 4 at equilibrium) both sulfur and amine groups may contribute to mercury binding. Most of the binding may proceed through interactions with sulfur groups ( $\sim 2.3 \text{ mmol g}^{-1}$ ) with a contribution of free amine groups. Based on N content and the suggested structure (Schemes 1 and 2), the amount of free  $\text{-NH}_2$  groups should be close to  $1 \text{ mmol g}^{-1}$ . At pH 5 (equilibrium pH close to 5.3) the sorption capacity of raw chitosan was close to  $3 \text{ mmol Hg g}^{-1}$  (Fig. 2), it is expected that decreasing the pH to 4 causes the protonation of amine groups and thus a substantial decrease of the binding efficiency of these groups. This partial decrease in binding efficiency of amine groups at pH 4–4.5 may explain that the sorption capacity only increased from 2.3 to  $3 \text{ mmol Hg g}^{-1}$  when increasing the pH of the solution from 2 to 5 (equilibrium value 4–4.5).

Comparing the amount of amine groups (determined by titrimetric analysis, i.e.,  $0.42 \text{ mmol -NH}_2 \text{ g}^{-1}$ ), and the amount of sulfur groups (determined by elemental analysis, i.e.,  $2.65 \text{ mmol S g}^{-1}$ ) to the sorption capacity (close to  $2.3\text{--}3 \text{ mmol Hg g}^{-1}$ ) it appears that most of the metal was sorbed on sulfur groups with a possible contribution of amine groups. In lightly acidic solutions (i.e., pH 5) amine groups can interact by complexation additionally to sulfur groups: the sorption capacity reached up to  $3 \text{ mmol Hg g}^{-1}$ . This sorption capacity is close to the total of reactive groups (i.e., amine and sulfur groups). In acidic solutions (i.e., pH 2) the protonation of amine groups limit their capacity to bind mercury by complexation. The formation of chloro-anionic species (in HCl solutions) makes possible their interactions with protonated amine groups, but probably with a lower affinity compared to complexation strength ( $\text{-NH}_2/\text{Hg}$ ). On the opposite hand the stability constant of mercury with thiourea is almost independent of pH; this means that the potential of sulfur groups for interacting with mercury was maintained at pH 2. These observations may explain that the sorption capacity decreased to  $2.3 \text{ mmol Hg g}^{-1}$ ; this also means that some of these groups are not fully accessible or available for reacting with mercury.

The influence of the acid used for pH control (either sulfuric acid or hydrochloric acid) was tested (not shown, to be checked in Additional electronic material, AM5). The speciation of metal

ions is strongly affected by the composition of the solution. In the present case changing the acid used for pH control affected the speciation of mercury in solution due to the formation of complexes between the metal and chloride ions (for HCl solutions). Using Medusa (Puigdomenech [65]) and MINTEQA2 (Gustafsson [66]) softwares allowed identifying the predominant species. At pH 5, regardless of the acid used for pH control, the predominant species is  $\text{HgCl}_2$  (around 87%); though some chloride complexes can exist in HCl media their proportion remain negligible compared to the second species,  $\text{HgClOH}$  (10–12%). At pH 2, the differences are more marked for HCl and  $\text{H}_2\text{SO}_4$  solutions. In HCl solutions,  $\text{HgCl}_2$  represent about 90–92% of total mercury species, while the fraction of  $\text{HgCl}_3^-$  is close to 8–9%. In sulfuric acid solutions,  $\text{HgCl}_2$  counts for 98–99%, remaining species are  $\text{HgCl}^+$ . This means that at pH 2, in HCl solutions, there is the possibility for the sorbent to bind mercury species (chloro-anionic forms) by ion exchange with protonated amine groups while in sulfuric acid solutions, the speciation of mercury is not favorable for this electrostatic attraction mechanism. However, the fraction of amine groups (on the total of reactive groups) and the change in the speciation of mercury are probably not large enough to cause dramatic variations in the sorption capacity for mercury (as confirmed in Additional section AM5).

Changing the acid did not significantly varied the sorption isotherms. Using hydrochloric acid contributes to the formation of chloroanionic mercury species ( $\text{HgCl}_3^-$ ,  $\text{HgCl}_4^{2-}$ ) that can be sorbed on chitosan through ion exchange with protonated amine groups. In the case of polyaminated chitosan resins Kawamura et al. [67] showed that mercury can be sorbed by complexation at near neutral pH while in acid solutions sorption proceeds by electrostatic attraction and ion exchange (with mercury in the form of chloro-complexes). In sulfuric acid solutions chloro-mercuric species are not formed and sorption capacities were significantly lower than in HCl solutions. Here, the contribution of amine groups is significantly lower than the contribution of sulfur compounds, which are not influenced by the speciation of mercury; the weak effect of the acid is thus understandable. This conclusion is consistent with the comments of Merrifield et al. [52], who observed that the speciation of mercury (in the presence of chloride anions) did not influence sorption capacity when using thiol-grafted chitosan.

#### 3.4. Interference of competitor ions

Industrial effluents systematically contain a series of other elements: metals ions, anions. To evaluate the interest of a sorbent it is thus important to check how the presence of competitor ions may impact sorption performance and if the sorbent is selective. Various metals (Cu(II), Zn(II), Ni(II), Cd(II) and Pb(II)) and

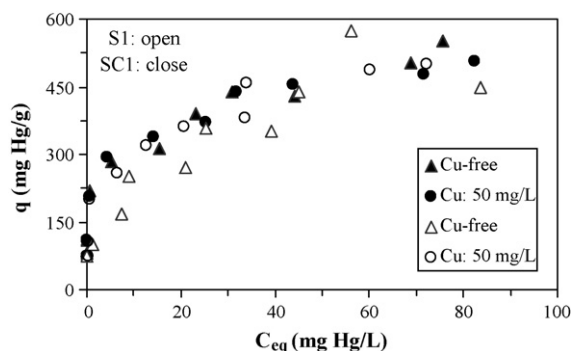
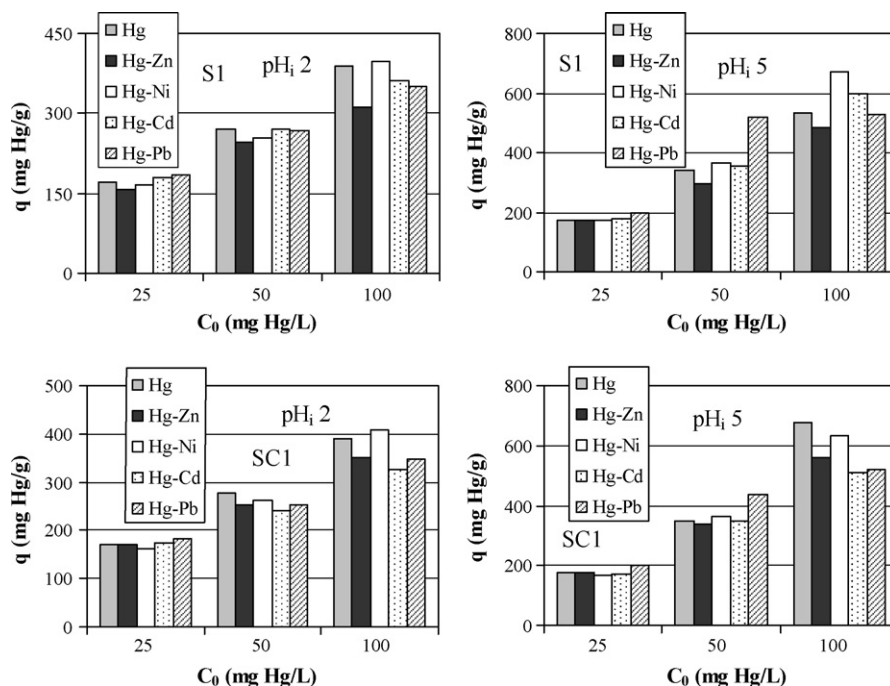


Fig. 4. Influence of Cu(II) on Hg(II) sorption isotherm for S1 and SC1 sorbents (initial Cu concentration:  $50 \text{ mg L}^{-1}$ ; SD:  $20 \text{ mg}/150 \text{ mL}$ ; pH 2 controlled with sulfuric acid).

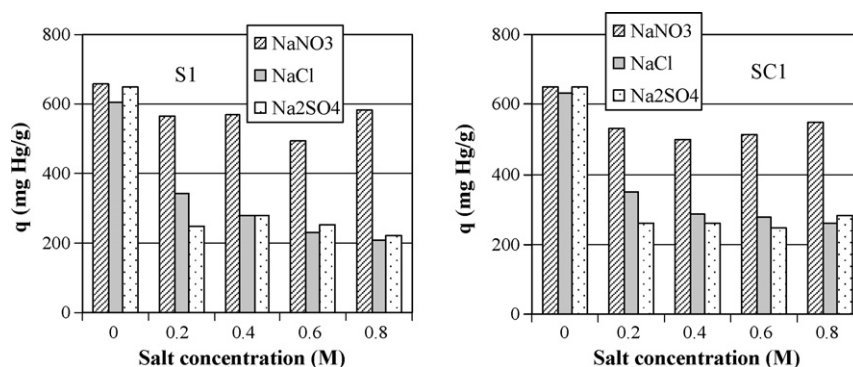


**Fig. 5.** Influence of pH and Hg(II) concentration on sorption capacity in the presence of 50 mg metal  $L^{-1}$  (Zn(II), Ni(II), Cd(II) and Pb(II)) for S1 and SC1 sorbents (SD: 20 mg/150 mL).

anions such as  $NO_3^-$ ,  $Cl^-$  and  $SO_4^{2-}$  have been tested for their impact on Hg(II) sorption. Fig. 4 shows that at pH 2 the sorption isotherms for both S1 and SC1 sorbents were not affected by the presence of Cu(II) at the concentration of 50 mg  $L^{-1}$ . In the case of Hg(II)/Cu(II) binary mixtures, Vieira et al. [39] showed that chitosan membranes have a greater affinity for mercury than for copper. In the case of macroalga, Herrero et al. [62] showed that high copper concentration (0.5–1 g  $L^{-1}$ ) may cause a 20% decrease of sorption capacity. Atia et al. [63] showed that a resin bearing amine-mercaptan groups had a stronger affinity for Hg(II) than for metals such as Cd(II), Zn(II), Cu(II), Pb(II) with sorption capacities lower than 0.2 mmol metal  $g^{-1}$  (compared to 2 mmol Hg  $g^{-1}$ ).

Fig. 5 compares (for different initial concentrations of mercury) the sorption capacity of the metal in the presence of various metals; the concentration of competitor metals was set at 50 mg metal  $L^{-1}$ . These are not complete isotherms; however, these preliminary results are sufficient to reach a first conclusion on the general trends followed by the sorption of mercury in the presence of Zn(II), Ni(II), Cd(II) and Pb(II). It is interesting to observe that the impact of these metal ions did not interfere much on mercury binding. The trends

are globally the same at pH 2 and pH 5 for both S1 and SC1 resins: variations observed in both negative and positive sense did not exceed 10% around the average value (calculated among the five values: Hg(II) single solutions and binary solutions). Since sulfur functions are very reactive for a number of base metals a greater impact of competitor metals was expectable: at low mercury concentration the number of reactive groups allows the simultaneous sorption of competitor metals; however, at high mercury concentration (i.e., 100 mg  $Hg L^{-1}$ ), the amount of reactive groups is not sufficient for allowing the simultaneous binding of Hg and competitor metals on vicinal sulfur sites. This means that the sorbent had a preference for Hg(II) over other selected metal cations. According Pearson's theory (HSAB – hard and soft acid and base theory – soft ligands attract soft metals and hard ligands attract hard metals), sulfur groups are classified as soft ligands and may react with soft acids such as Hg(II) and Cd(II) [68]. Mercury is considered as a soft acid that has a strong affinity for sulfur ligands. On the contrary Zn(II), Pb(II), Cu(II), Ni(II) are classified as borderline metals that have less affinity for sulfur ligands (compared to soft acids like Hg(II)). This may explain that in bi-component solutions mercury sorption was not affected by the presence of these metal ions.



**Fig. 6.** Influence of the concentration of anions on Hg(II) sorption capacity (initial Hg(II) concentration: 100 mg  $L^{-1}$ ; SD: 20 mg/150 mL; pH 2 controlled with sulfuric acid).

No explanation was found concerning the limited impact of Cd(II), which is also part of the soft acids. The softness of Hg(II) is the double of the value attributed to Cd(II) [69]; this probably explains that Cd(II) did not interfere significantly on Hg binding, at least under selected experimental conditions. Cu(II), Ni(II) and Zn(II) are part of the so-called borderline elements that are characterized by a lower affinity for soft ligands such as sulfur groups. These results are consistent with those obtained by Oktar et al. [70] for the sorption of mercury using polymer-supported hydroxyethyl sulfonamides in the presence of Zn(II), Cd(II) and Fe(II), which can be present in mercury-containing ores. Donia et al. [48] tested the sorption of mercury in the presence of Cu(II), Pb(II), Cd(II), Zn(II) on magnetic chitosan resins modified with Schiff's base derived from thiourea and glutaraldehyde. They showed that Hg(II) was preferentially sorbed.

The addition of increasing concentrations of anions had more significant impact on Hg(II) sorption by S1 and SC1 sorbents, as shown in Fig. 6. With S1 sorbent, the addition of nitrate anions hardly affected (by less than 15%) metal sorption (sorption capacity for Hg(II) sorption:  $637 \pm 25 \text{ mg Hg g}^{-1}$  versus  $553 \pm 34 \text{ mg Hg g}^{-1}$  in the presence of increasing amounts of nitrate anions). Similar trend was observed for SC1 sorbent, with a decrease in sorption capacity close to 19% (sorption capacity for Hg(II) sorption:  $644 \pm 8 \text{ mg Hg g}^{-1}$  versus  $522 \pm 19 \text{ mg Hg g}^{-1}$  in the presence of increasing amounts of nitrate anions). The presence of chloride and sulfate anions had a more significant impact; the sorption capacity strongly decreased in the presence of 0.2 M of either chloride or sulfate anions (from  $640 \text{ mg Hg g}^{-1}$  to 340 and  $260 \text{ mg Hg g}^{-1}$  for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , respectively). At higher concentration of competitor anions the decrease in sorption capacity tended to stabilize, especially in the case of SC1 sorbent (for which the concentration of both nitrate and sulfate anions did not vary above 0.2 M). These results are consistent with those obtained by Atia et al. [63], who compared sorption capacities from solutions prepared in sulfuric acid, nitric acid and hydrochloric acid solutions at pH 1–3. Sulfuric acid revealed unfavorable for mercury sorption, while for nitric and hydrochloric acids the positive or negative effects depend on the type of salt used for the preparation of the solution (mercury chloride or mercury nitrate).

### 3.5. Uptake kinetics

#### 3.5.1. Identification of controlling steps

The sorption kinetics may be controlled by various diffusion mechanisms: (a) bulk diffusion, (b) film diffusion, and (c) intraparticle diffusion. In most cases, binding on sorbents is controlled by diffusion mechanisms rather than the reaction rate; though some systems have been shown to be governed by a reaction mechanism in relation with the parallel ionic reactions (which change the speciation of the ions involved in the principal reaction). Since the pioneering work on dynamics of ion exchange processes by Streat [71] and Helfferich [72], Juang and Ju [73] discussed a series of simplified modeling systems derived from the homogeneous diffusion model (HDM) and shrinking core model (SCM). The HDM involves counterdiffusion of exchangeable species in quasi homogeneous media, with a contribution from film diffusion (HDM-FD) and/or particle diffusion (HDM-PD). Solute molecules and exchangeable species (immobilized on the resin) follow a similar diffusion mechanism (though in the opposite direction). In the case of the SCM, a sharp virtual boundary exists between the reacted shell of the particle and the unreacted core, and this boundary moves towards the center of the particle [74,75]. This model was developed with different systems depending on the controlling step: film diffusion (SCM-FD), particle diffusion (SCM-PD) and chemical reaction rate (SCM-CR) [73]. A number of mathematical equations have been

developed to simulate these mechanisms, they are listed below:

#### Homogeneous Diffusion Models

$$\text{Film Diffusion : } F_1(X) = -\ln(1-X) = f(t) \quad (3)$$

$$\text{Particle Diffusion : } F_2(X) = -\ln(1-X^2) = f(t) \quad (4)$$

#### Shrinking Core Models

$$\text{Film Diffusion : } G_1(X) = X = g\left(\int_0^t C(t) dt\right) \quad (5)$$

$$\begin{aligned} \text{Particle Diffusion : } G_2(X) &= 3 - 3(1-X)^{2/3} - 2X \\ &= g\left(\int_0^t C(t) dt\right) \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Chemical Reaction Rate : } G_3(X) &= 1 - (1-X)^{1/3} \\ &= g\left(\int_0^t C(t) dt\right) \end{aligned} \quad (7)$$

where  $X$  is the fractional approach to equilibrium, i.e.,  $q(t)/q_{eq}$ . Plotting  $F_i$  and  $G_i$  functions versus time and the integral term (respectively) determined the most appropriate mechanism for describing the controlling step. The predominant limiting step is usually identified as the modeled curve that best fit experimental data (approaching the straight line). Fig. 7a shows that none of

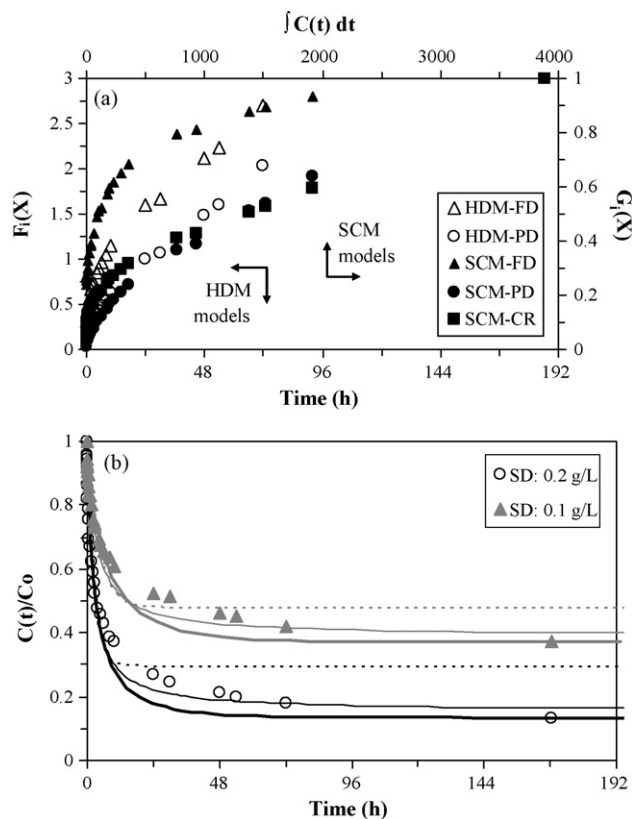


Fig. 7. Modeling of kinetic profiles. (a) Homogeneous diffusion and shrinking core models (S2 sorbent; pH 2 controlled with sulfuric acid; SD:  $0.1 \text{ g L}^{-1}$ ;  $C_0$ :  $50 \text{ mg Hg L}^{-1}$ ;  $v$ : 350 rpm); (b) intraparticle diffusion model (Crank's equation: bold line), pseudo first-order equation (dashed line) and pseudo second-order equation (continuous line) (S2 sorbent; pH 2 controlled with sulfuric acid; SD: 0.1 and  $0.2 \text{ g L}^{-1}$ ;  $C_0$ :  $50 \text{ mg Hg L}^{-1}$ ;  $v$ : 350 rpm).



the combinations allowed fitting experimental data. The sorption is probably controlled by the simultaneous contribution of different mechanisms (i.e., intraparticle diffusion and reaction rate).

Three other models were also tested for the description of kinetic profiles based on the pseudo first-order equation (the so-called Lagergren equation), on the pseudo second-order equation described by Ho [76], and on the intraparticle diffusion equation defined by Crank [77].

$$\text{Pseudo first-order equation: } \frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

$$\text{After integration of Eq. (8): } \frac{q_t}{q_e} = (1 - \text{Exp}[-k_1 t]) \quad (9)$$

$$\text{Pseudo second-order equation: } \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

$$\text{After integration of Eq. (10): } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (11)$$

where  $q_e$  is the amount of metal ion sorbed at equilibrium ( $\text{mg Hg g}^{-1}$ ),  $q_t$  is the amount of metal sorbed ( $\text{mg Hg g}^{-1}$ ) at any time,  $t$ , and  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the pseudo first-order and the pseudo second-order rate constants. The parameters  $q_e$ ,  $k_1$  and  $k_2$  are pseudo-constants, depending on experimental conditions; they were obtained by non-linear regression analysis using the Math Package Mathematica®.

The modeling of sorption kinetics requires taking simultaneously into account film diffusion, intraparticle diffusion and equilibrium distribution (boundary condition at the interface) for an accurate simulation of experimental data. This approach requires a complete knowledge of sorbent characteristics (including homogeneity of the material) and requires extensive and complex numerical analysis. Simplifying hypotheses on the characteristics of the sorbent obviously induce discrepancy in the modeling and in a first approach we decided to separate film diffusion from intraparticle diffusion. The poor effect of agitation speed on the kinetic profiles indicated that this mechanism hardly contributed to mass transfer resistance (not shown, see [Additional electronic material section, AM6](#)). Table 4 shows that the kinetic parameter (kinetic rate for the pseudo second-order equation) was almost unchanged when increasing agitation speed. For this reason, film diffusion was neglected and the intraparticle diffusion coefficient ( $D_e$ , effective diffusivity,  $\text{m}^2 \text{s}^{-1}$ ) was determined using Crank's equation, assuming the solid to be initially free of metal

[77]:

$$\frac{q(t)}{q_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1) \exp((-D_e q_n^2 t)/r^2)}{9 + 9\alpha + q_n^2 \alpha^2} = \text{FATE} \quad (12)$$

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

And  $q_n$  are the non-zero roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (13)$$

with

$$\frac{q_{eq}}{VC_0} = \frac{1}{1 + \alpha} \quad (14)$$

Fig. 7b shows the comparison of the modeling of two experimental series with these three kinetic models. These trends have been systematically observed: (a) the intraparticle diffusion equation allowed a good simulation of the initial section of the curve and the equilibrium section but failed to describe the intermediary stage; (b) the pseudo first-order equation only fitted well the initial section of the kinetic curve; and (c) the pseudo second-order equation was the best model for describing the kinetics over the first 48 h but failed at describing the final stage (probably controlled by the resistance to intraparticle diffusion). This probably means that a correct modeling would require taking into account both the pseudo second-order equation and the intraparticle diffusion at the expense of strong numerical calculations. The intraparticle diffusion coefficient was determined for the curves shown in Fig. 7b:  $8.8 \times 10^{-13} \text{ m}^2 \text{ min}^{-1}$  and  $7.4 \times 10^{-13} \text{ m}^2 \text{ min}^{-1}$  for S2 sorbent at sorbent dosages of 0.1 and 0.2  $\text{g L}^{-1}$ , respectively. These values are several order of magnitude lowers than the self-diffusivity coefficients cited by Marcus [69] for the most common metal ions (i.e., in the range  $3\text{--}12 \times 10^{-8} \text{ m}^2 \text{ min}^{-1}$ ).

Unfavorable experimental conditions (excess of metal versus sorption sites) have been selected in order to make possible the identification of limiting parameters. For these reasons the time required for achieving the complete recovery of mercury or for reaching the equilibrium was quite long (up to 3–4 days of contact). In many studies dealing with metal sorption or dye sorption on chitosan authors are claiming for fast sorption kinetics, underestimating the contribution of the resistance to intraparticle diffusion due to large excess of sorbent (the sorption being limited to external layers).

**Table 4**  
Kinetic parameters—pseudo second-order equation (Eq. (11)).

Resin type	$C_0$ ( $\text{mg L}^{-1}$ )	$\nu$ (rpm)	SD ( $\text{g L}^{-1}$ )	$q_{exp}$ ( $\text{mg Hg g}^{-1}$ )	$q_e$ ( $\text{mg Hg g}^{-1}$ )	$k_2 \times 10^5$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	EV $\times 10^5$
S2	50	350	0.1	321.5	318.2	1.54	7.6
S2	50	350	0.2	220.5	219.5	3.47	4.7
S2	50	350	0.3	156.8	159.5	10.53	0.3
SC2	50	350	0.1	318.2	321.9	0.88	12.8
SC2	50	350	0.2	216.5	214.2	4.10	72.4
S1	25	350	0.3	76.3	76.9	59.2	0.5
S1	50	350	0.3	156.4	159.1	10.40	0.3
S1	100	350	0.3	283.1	285.4	3.80	0.4
S2	25	350	0.3	84.2	84.3	26.4	0.5
S2	100	350	0.3	258.7	244.7	3.90	2.9
SC1	16	350	0.3	53.9	54.1	132.2	0.2
SC1	32	350	0.3	106.9	108.5	17.0	0.8
SC1	64	350	0.3	191.3	191.7	6.38	1.7
SC2	25	350	0.3	72.1	73.1	21.3	7.2
SC2	50	350	0.3	152.3	154.2	3.55	6.8
SC2	100	350	0.3	254.0	251.6	2.74	5.5
S2	50	500	0.2	193.2	192.7	4.92	2.8
SC2	50	500	0.2	191.2	192.8	4.3	4.2

EV: estimated error variance.

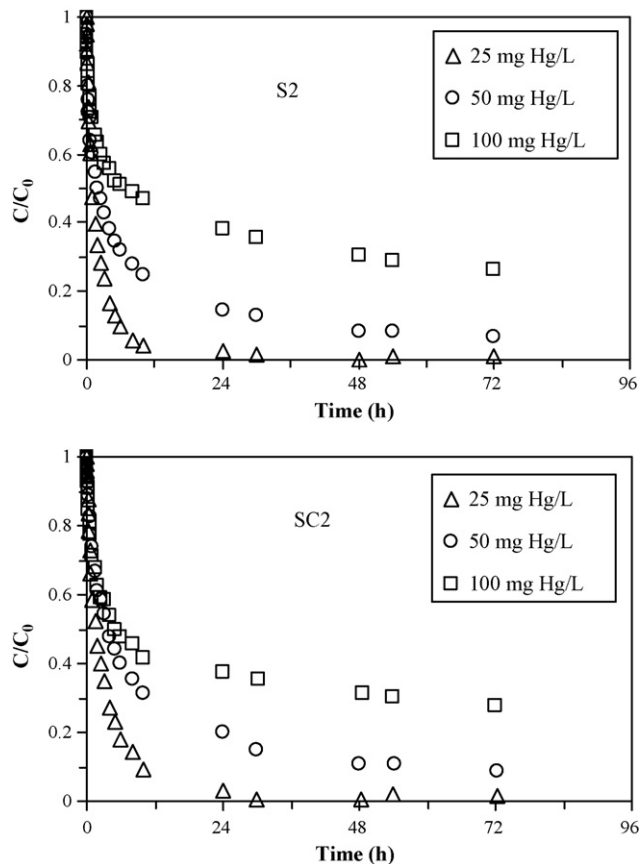


Fig. 8. Influence of Hg(II) concentration on kinetic profile (S2 and SC2 sorbents; pH 2 controlled with sulfuric acid;  $v$ : 350 rpm; SD:  $0.3 \text{ g L}^{-1}$ ).

### 3.5.2. Influence of experimental parameters

The investigation on the effect of metal concentration (Fig. 8) and SD (Fig. 9) shows that increasing the ratio SD/metal concentration allowed reaching the complete recovery of the metal within a few hours. The half-reaction time (time required for reaching 50% of total sorption) increased with metal concentration but even in excess of metal (i.e.,  $100 \text{ mg Hg L}^{-1}$  for SD:  $0.3 \text{ g L}^{-1}$ ) the half-reaction was less than 90 min. Table 4 shows that when the initial concentration increases the kinetic rate ( $k_2$ ) decreases by a factor 15–20 and by a factor close to 7 for S2 and SC2 sorbents. Fig. 9 shows that for a given metal concentration (i.e.,  $50 \text{ mg Hg L}^{-1}$ ) increasing sorbent dosage linearly decreased the half-reaction time: 5 h at SD:

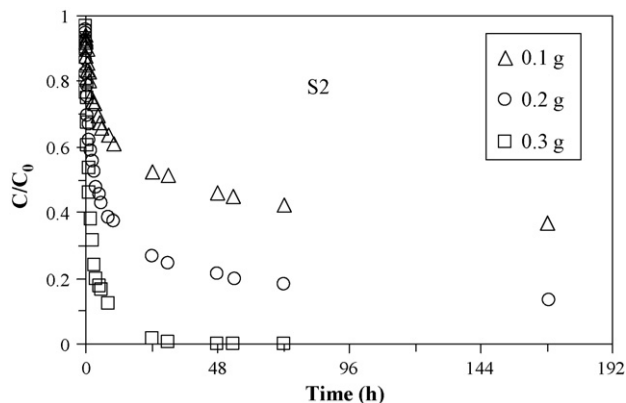


Fig. 9. Influence of sorbent dosage on kinetic profile (S2 sorbent; pH 2 controlled with sulfuric acid;  $v$ : 350 rpm;  $C_0$ :  $50 \text{ mg L}^{-1}$ ).

$0.1 \text{ g L}^{-1}$ , 3 h at SD:  $0.2 \text{ g L}^{-1}$ , and down to 1 h at SD:  $0.3 \text{ g L}^{-1}$ ). This is confirmed by the increase of the reaction rate (pseudo second-order equation) as shown in Table 4. Though these results are logical they point out the strong contribution of the resistance to intra-particle diffusion in the control of the kinetics. Indeed, increasing the sorbent dosage simultaneously increases the external surface area available for metal sorption, and the sorption is faster than in the case where metal ions have to be bound on less accessible internal sites. The sorbents were only available in the diameter range of  $125\text{--}250 \mu\text{m}$ . Investigating different particle size would probably bring complementary information on the contribution of diffusion properties.

In the case of magnetic chitosan resin obtained by immobilization of thiourea, Donia et al. [48] obtained at pH 5 with a  $20 \text{ mM Hg(II)}$  solution a pseudo second-order rate constant close to  $1.2 \times 10^{-4} \text{ g mmol}^{-1} \text{ min}^{-1}$ . This value is consistent with the values reported in Table 4. Merrifield et al. [52] discussed the sorption kinetics of mercury on thiol-modified chitosan gel beads; they observed that at low agitation speed (below 75 rpm) the kinetics was controlled by the resistance to film diffusion, as evidenced by the first-order dependence of uptake on time. At agitation speed higher than 150 rpm, they concluded on the predominance of pore diffusion resistance on kinetic control: the uptake did not depend on agitation. Manohar et al. [20] immobilized mercapto-benzimidazole on clay and used this sorbent for mercury sorption. The sorption capacities were much lower than the values obtained with this chitosan derivative (less than  $50 \text{ mg Hg g}^{-1}$ ). They found that the kinetics can be modeled using the pseudo second-order equation. They found that the kinetic rate decreased with increasing metal concentration but with values ( $1\text{--}3 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ ) much greater than those obtained with the present system. This is another evidence of the strong impact of the resistance to intra-particle diffusion. The modified clay was characterized by a surface area close to  $71 \text{ m}^2 \text{ g}^{-1}$  while raw chitosan has a surface area lower than  $5 \text{ m}^2 \text{ g}^{-1}$ . A solution for improving kinetics would probably consist in immobilizing the sulfur groups on chitosan beads; indeed, the preparation of chitosan beads allows increasing the surface area up to  $250 \text{ m}^2 \text{ g}^{-1}$  [31].

The pseudo second-order rate constant  $k_2$  was of the same order of magnitude than the value cited by Zhou et al. [78], i.e.,  $5.55 \times 10^{-5} \text{ g mg}^{-1} \text{ min}^{-1}$ , using thiourea modified magnetic chitosan microspheres. In the same study, Zhou et al. [78] obtained much higher (2 orders of magnitude) rate constants for Cu(II), Ni(II) with the same sorbent. Wan Ngah and Fatinathan [79] tested chitosan gel beads (raw and modified) for the sorption of Cu(II); they found very high rate constants ( $1.5\text{--}4.6 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ ). The conditioning of the biopolymer under the form of gels beads allowed increasing substantially the sorption kinetics, probably due to the enhancement of diffusion properties.

### 3.6. Desorption study

A series of eluents have been tested for mercury recovery from loaded resins. The selection of these eluents was based on acid-base properties (HCl,  $\text{H}_2\text{SO}_4$ ) or complexation reactions (KSCN, thiourea, KI) [16,63,80]. Table 5 reports the results obtained with both S2 and SC2 sorbents. The trends were the same: (a) acidic media were not sufficient for reaching high desorption efficiency (maximum 20%); (b) KSCN (alone or in acidic media) did not significantly desorb Hg(II) (less than 16%); (c) with KI desorption reached 58%; (d) thiourea revealed the most efficient eluent and its efficiency was increased with the presence of HCl. It is noteworthy that the color of the sorbents turned to strong black during desorption in the presence of sulfur ligands (KSCN and thiourea), with the exception of thiourea prepared in 2 M HCl solution. The change in color means

**Table 5**  
Screening of Hg(II) desorption.

Eluent	Desorption efficiency (%)		Color change
	Resin S2	Resin SC2	
HCl 4 M	20.0	17.7	
KSCN 2 M	7.0	7.7	Black
KSCN 1 M/HCl 0.5 M	15.2	15.7	Black
Thiourea 0.1 M/HCl 0.5 M	68.3	66.0	Almost all black
Thiourea 0.1 M/HCl 2 M	70.7	76.6	
Thiourea 0.25 M	47.9	47.7	Black
H <sub>2</sub> SO <sub>4</sub> 4 M	1.9	1.7	
KI 0.5 M	58.7	54.7	

Experimental conditions for (a) sorption: SD: 0.2 g L<sup>-1</sup>; C<sub>0</sub>: 70 mg L<sup>-1</sup>, pH 2 controlled with sulfuric acid; (b) desorption: SD: 0.2 g L<sup>-1</sup>; contact time 2 h.

a significant degradation of the sorbent during the desorption. It is possible to suggest that a desulfurization of thiourea occurred: ~NHCSNH<sub>2</sub> being converted to ~NHCONH<sub>2</sub> while mercury reacts with sulfur to form HgS (black-colored metacinnabarite). Optimum desorption was obtained with 0.1 M thiourea solution prepared in 2 M HCl solutions: desorption efficiency ranged between 70 and 77%. This is probably not sufficient for an efficient recycling of the sorbent: the number of sorption/desorption cycles will be probably not sufficient for justifying resin reuse. Further optimization seems necessary (varying for example the temperature) for enhancing the recycling of the sorbent before transferring the process to industrial scale. The efficiency in the desorption of mercury from thio-bearing resins strongly depends on experimental conditions (type of resin and characteristics of the eluents) has pointed out by the great variability in the elution yields cited in the literature (from 50 to 95%) [16,63,80].

#### 4. Conclusion

Chitosan is known to sorb mercury by chelation on amine groups in near neutral solutions. The grafting of sulfur groups on chitosan (thiocarbamoylation) allowed extending significantly the pH range for its application in mercury recovery. Sorption capacity as high as 450 mg Hg g<sup>-1</sup> (i.e., 2.3 mmol Hg g<sup>-1</sup>) can be reached at pH 2, while Hg(II) sorption with raw chitosan was negligible at this pH. The presence of competitor metal ions (such as Cu(II), Ni(II), Zn(II), Cd(II) or Pb(II)) at the concentration of 50 mg metal L<sup>-1</sup> hardly influenced Hg(II) binding. The presence of competitor anions such as chloride or sulfate anions strongly decreased sorption capacity (down to 1 mmol Hg g<sup>-1</sup> at 0.8 M of competitor anion), while nitrate anions only had a limited impact. Thiourea (in 2 M HCl solutions) allowed a partial desorption of mercury (about 75%). Kinetics are controlled by a combination of reaction rate (pseudo second-order equation) and resistance to intraparticle diffusion.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.10.005.

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