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Mercury recovery from aqueous solutions by polymer-enhanced ultrafiltration using a sulfate derivative of chitosan

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Abstract. The sulfatation of chitosan, by reaction with chlorosulfonic acid under controlled conditions, allowed increasing the pH range of chitosan solubility. The biopolymer was characterized using FTIR and ^{13}C-NMR spectroscopy, elemental analysis and titration analysis and it was tested for mercury recovery by polymer enhanced ultrafiltration (PEUF). In slightly alkaline conditions (*i.e.*, pH 8) mercury recovery was possible and at saturation of the polymer the molar ratio $-NH_2/Hg(II)$ tended to 2.6. Polymer recycling was possible changing the pH to 2 and the polymer was reused for 3 cycles maintaining high metal recovery. The presence of chloride ions influences metal speciation and affinity for the polymer and "playing" with metal speciation allowed using the PEUF process for mercury separation from cadmium; at pH 11 the formation of hydroxo-complexes of Hg(II) limits it retention. Cake formation reveals the predominant controlling step for permeation flux.

Keywords: recovery; mercury; cadmium; polymer enhanced ultrafiltration; PEUF; chitosan; sulfated chitosan.

1. Introduction

The discharge of heavy metal ions to the environment is strictly controlled due to their potential for bioaccumulation. Mercury is one of the most emblematic of these metals. The dramatic events that occurred during the Minamata contamination illustrated the possible impact of the discharge of these metals on public health. For these reasons, the regulations concerning mercury discharge, among other metals, became more and more stringent. Though the current trend is to substitute as much as possible other process to those that used mercury, some industrial units are still using mercury-based processes. For example, plants manufacturing electronic devices and chloro-alkali processes are large-scale units that can generate mercury-containing effluents. The processes commonly used for the treatment of mercury containing effluents consists in cementation (Ku *et al.* 2002), precipitation (using sulfur compounds for example) (Tonini *et al.* 2003), sorption including

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resins (Rivas *et al*. 2002, Samczynski 2006, Neagu *et al*. 2007), activated carbon (Goel *et al*. 2004, Inbaraj and Sulochana 2006, Kadirvelu *et al*. 2008), or biosorbents (Baba *et al*. 1998, Donia *et al*. 2008a, Donia *et al*. 2008b), liquid/liquid extraction (Fabrega and Mansur 2007), extractants (including ionic liquids) encapsulated materials (Guibal *et al*. 2008). Membrane processes have also retained a great attention for the last decade (Uludag *et al*. 1997, Muslehiddinoglu *et al*. 1998, Barron-Zambrano *et al*. 2002, Rodríguez Pastor *et al*. 2003, Barron-Zambrano *et al*. 2004, Zeng *et al*. 2009). Ultrafiltration processes have been used associated with complexation: the complexation of the metal ions with a complexing macromolecules opens the possibility to retain small-size metal ions on ultrafiltration membranes: this is the basis of the so-called polymer enhanced ultrafiltration process (PEUF). Synthetic polymers such as polyethyleneimine (PEI) (Uludag *et al*. 1997, Muslehiddinoglu *et al*. 1998, Barron-Zambrano *et al*. 2004), or polyacrylic acid sodium (PAA) can be used (Zeng *et al*. 2009); however, natural polymers bearing reactive groups have been also widely investigated (Taha *et al*. 1995, Juang and Chiou 2000, Juang and Chiou 2001, Kuncoro *et al*. 2003, Llorens *et al*. 2004, Kuncoro *et al*. 2005, Aroua *et al*. 2007). For example, chitosan, an aminopolysaccharide obtained from the treatment of crustacean shells, is very efficient for metal sorption (Guibal 2004), including mercury recovery (Baba and Hirakawa 1992, Argüelles-Monal and Peniche-Covas 1993, Kawamura *et al*. 1997, Jeon and Holl 2003, Vieira *et al*. 2007). Mercury can be sorbed on chitosan through complexation on amine groups at near-neutral pH or by ion exchange due to electrostatic attraction on protonated amine groups when mercury ions form anionic chlorocomplexes in HCl solutions. The protonation of amine groups in acidic solutions leads to polymer dissolving, except in sulfuric acid media. The pk_a of amine groups depends on the degree of acetylation of the biopolymer and the neutralization degree of amine functions. However, for conventional chitosan samples, not completely deacetylated, the apparent pk_a is in the range 6.4-6.7 (Sorlier *et al*. 2001). In most acid solutions, the polymer dissolves and can be used for coagulation-flocculation (Roussy *et al*. 2004, Guibal *et al*. 2005, Roussy *et al*. 2005), or PEUF (Taha *et al*. 1995, Juang and Chiou 2000, Juang and Chiou 2001, Kuncoro *et al*. 2003, Llorens *et al*. 2004, Kuncoro *et al*. 2005, Aroua *et al*. 2007). In the case of dye recovery using chitosan with both sorption and coagulation-flocculation (Guibal *et al*. 2005), as well as in the case of mercury recovery by sorption and PEUF (Guibal *et al*. 2005, Kuncoro *et al*. 2005), it appeared that the binding capacity was greater for the use of the polymer in the dissolved state compared to the sorption process using the polymer in the solid-state. The dissolving of the polymer allows opening the structure of the biopolymer, which in turns makes more available and more accessible the reactive groups of the biopolymer (*i.e*., amine groups). Using the polymer in the dissolved-state allows a better rational use of amine groups explaining the higher molar ratio Hg (or dye)/-NH_2 in PEUF and coagulation-flocculation processes compared to sorption processes. The major drawback of chitosan for the recovery of mercury from neutral or alkaline solutions in PEUF is the precipitation of the biopolymer. The challenge is thus modifying the biopolymer to increase the pH range for its application in PEUF while maintaining the reactivity of chitosan. This means that the modification of the biopolymer should leave the amine groups free for interacting with metal ions.

The grafting of sulfate on chitosan has been developed for increasing the solubility of the biopolymer in alkaline media, for enhancing its antimicrobial effect (Huang *et al*. 2004, Jayakumar *et al*. 2007), its blood anticoagulant effect (Vongchan *et al*. 2002, Vikhoreva *et al*. 2005), and its antioxidant effect (Xing *et al*. 2005). Sulfated chitosan has been prepared by different methods and it has been shown that the sulfation conditions of chitosan essentially affect the position and degree of substitution with sulfate in derivatives of chitosan (Gamzazade *et al*. 1997, Hayashi 1993);

however, the grafting of the polymer should be stereo-selective, preserving amine groups (Baumann and Faust 2000).

The present work investigates the potential of a sulfate derivative of chitosan for the binding of mercury in slightly alkaline solutions. Prior the investigation of PEUF performance, the modified biopolymer was characterized by titrimetric analysis, elemental analysis, Fourier-Transformed Infra-Red spectrometry (FTIR) and ^{13}C Nuclear Magnetic Resonance spectrometry (^{13}C NMR). In the first step of process analysis, the impact of pH on mercury PEUF was carried out comparing raw chitosan and sulfated chitosan (SC). In a second step the experimental conditions have been varied (changing polymer/metal ratio) in order to evaluate the "binding isotherm". In a third step the impact of environmental parameters on mercury retention was investigated. More specifically, the impact of the presence of anions and competitor metal ions has been studied. The recycling of the biopolymer is also investigated considering the possibility to remove the metal from macromolecule and to re-use the biopolymer for 3 successive complexation/dissociation cycles. Finally, the mechanism involved in the control of permeation properties is identified considering standard, complete and intermediary blocking models and cake filtration model.

2. Experimental section

2.1 Materials

Chitosan was supplied by ABER-Technology (Plouvien, France). The biopolymer was previously characterized by FTIR analysis and by Size Exclusion Chromatography coupled with Light Diffraction for the determination of the degree of deacetylation and molecular weight, respectively. The degree of deacetylation was found close to 87% and the molecular weight MWn was close to 125,000 g mol^{-1}.

The reagents used for the synthesis of sulfated chitosan were of analytical grade (Fisher): acetic acid (HAc), methanol, sodium hydroxide, hydrochloric acid. Dimethylformamide (DMF), and chlorosulfonic acid ($HClSO_3$) were supplied by Sigma-Aldrich. Mercury chloride ($HgCl_2$) and cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) were supplied by Fluka and stock solutions (1 g metal L^{-1}) were prepared adding HCl or HNO_3 in order to avoid metal hydroxide precipitation. Other salts (sodium sulfate, sodium chloride, potassium chloride, calcium chloride) were supplied by Carlo Erba.

2.2 Synthesis of sulfate chitosan (SC)

The sulfatation of chitosan may be controlled by the accessibility of reagents to reactive groups, especially for internal groups. Using chitosan as a solid (which is characterized by a poor porosity) would lead to poorly efficient modification and heterogeneous material. For this reason, the chitosan samples were pre-treated preparing chitosan gels: One gram of chitosan (dried for 4 h at 40-45 ^{o}C) was dissolved in 50 mL of HAc (1 % w/w), before being precipitated as a gel by addition of 50 mL of NaOH (0.25 M). The gel was washed up of NaOH with demineralized water until neutral pH. The gel was removed by filtration on paper membranes and the excess of water was removed by smooth pressure (between paper sheets). The gels was then submitted to a series of soaking steps in methanol for 24 h for solvent exchange and for enhancing the precipitation of fine particles. In the next step of the process, DMF was used for two successive solvent exchange steps. The chitosan

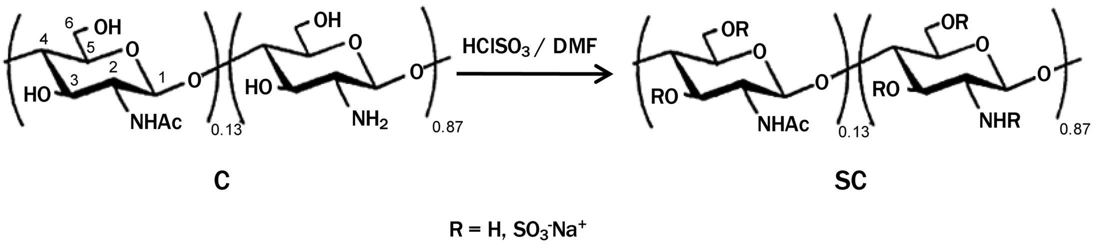

Fig. 1 Sulfate-grafting reaction

gel impregnated with DMF was thus used for reaction with chlorosulfonic acid (Fig. 1).

Sixty mL of DMF were introduced in a tri-opening flask (under 200 rpm agitation) disposed in an ice-bath. Two mL of $HClSO_3$ were added drop to drop to DMF. Addition should be progressive since the reaction of DMF and $HClSO_3$ is strongly exothermic. This procedure was followed for the preparation of the "standard" sulfated chitosan. Alternative samples were prepared using higher amounts of chlorosulfonic acid (*i.e.*, 4, 6 and 9 mL). The mixture is maintained under agitation for 4 h in order to prepare the sulfating reagent, with a temperature that was increased to 35-40 °C. The DMF-impregnated chitosan gel was then introduced in the flask and maintained under agitation for 12 h. The gel was dissolved obtaining a brown viscous solution containing the synthesized SC. In the last step, the solution obtained at the previous step was reacted with 10 M NaOH solution till pH 12, obtaining a solution with a beige solid in suspension. The solid was filtrated and rinsed with methanol before being dried at room temperature. The dry solid was dissolved in water before being purified by ultrafiltration using a polyestersulfone membrane (Alfa Laval, cut-off: 10 kDa), in order to remove salts and depolymerized chains of low molecular weight. The retentate was dried at 40-45 °C to obtain films of SC, which were crushed for storage.

2.3 Polymer characterization

FTIR spectra were obtained using a Perkin-Elmer Spectrum One, after inclusion of the polymer powder into a KBr disc. The solid-state ^{13}C NMR spectra were obtained using a Varian Gemini 2000 NMR spectrometer (300 MHz). The elemental analysis was obtained using an Elemental Analyzer Fisions EA 1108. Titrimetric analysis was operated using a Metrohm Titrino DMS 716 with a glass electrode and Ag/AgCl electrode as reference: the polymer was dissolved in an excess of HCl (0.1 M) at pH 2 and 0.1 M NaOH solution was added as the titrating agent. The solubility of the polymer samples was tested over a large pH range (*i.e.*, 2-12): the samples were dissolved in water at the concentration 300 mg L^{-1}, giving a final pH close to 9. Salts (*i.e.*, Na_2SO_4, $CaCl_2$, KCl, NaCl) at concentration 0.1 M were added to the solution before controlling the pH at target value using 0.1 or 1 M HCl or NaOH solutions.

2.4 PEUF experiments

Ultrafiltration experiments were performed in an Amicon cell (8400) using an ultrafiltration membrane (Alfa Laval, DSS-GR81PP, polysulphone/polyethersulphone on polypropylene, MWCO: 10 kDa). A new membrane was used for each experiment, the membrane was pre-conditioned with a series of 3 washing steps at 55°C for 10 min in a Branson 2210 ultrasonic bath: (a) water, (b) NaOH solution at pH 10.5-11, and (c) water. The filtration flux was systematically determined for verifying the correct operative conditions of the membranes.

The polyelectrolytes used in PEUF experiments were only the chitosan (C) and the 'standard' sulfate derivate of chitosan (synthesized using 2 mL of chlorosulfonic acid for 1 g of chitosan).

The polyelectrolyte stock solutions (*i.e.*, 5 g L^{-1}) were prepared in demineralized water for SC or acidic solutions (0.1 M HCl or HNO_3) for chitosan in order to achieve complete dissolving of the polymer. The solutions (50-1000 mg L^{-1}) for PEUF experiments were prepared by dilution of stock solution with demineralized water. Metal concentration was set in the range: 10-180 mg L^{-1} by dilution of the stock solutions with demineralized water. The pH was systematically adjusted (with HCl, HNO_3 or NaOH) at fixed values before ultrafiltration of the mixed polymer-metal solutions. The ultrafiltration was operated by applying the appropriate pressure (3.4 bars) only after two hours of reaction in order to allow the complexation of the metal by the polyelectrolyte. The temperature was 21 ± 0.5 °C, while the agitation was maintained at 250 rpm. The volume of feed solution used for these experiments was 90 mL and the ultrafiltration was operated till obtaining 50 mL of permeate and 40 mL of retentate. Metal concentration in aqueous solutions was determined by ICP-AES Jobin Yvon JY 2000 (Longjumeau, France).

The total organic carbon (TOC) was measured using a Total Organic Carbon analyser Shimadzu TOC-5000 A, in order to verify polyelectrolyte retention. The results showed that the biopolymer was systematically retained: the loss did not exceed 3%. This means that the preliminary ultrafiltration of the polyelectrolyte during the preparation of SC was efficient at removing the low-molecular weight fractions and that the polymer was not degraded during PEUF operations.

All experiments were performed in triplicate. The results showed a standard deviation less than 3%. The efficiency of the process was measured through the determination of 4 parameters:

(a) Determination of the permeation flux, J_V (L/m^2 h)

$$J_V = \frac{\Delta V}{S * \Delta\tau} \tag{1}$$

where ΔV is the filtrate volume (L), S is the surface of the membrane (m^2) and Δτ is the filtration time (h).

(b) Metal permeation, % P

$$\%P = \frac{C_p}{C_f} * 100 \tag{2}$$

where C_p and C_f are the metal concentration in the permeate and in the feed solution (mg L^{-1}).

(c) Metal retention, % R

$$\%\,R = 100 - \%\,P \tag{3}$$

(d) Metal recovery, % r

$$\%r = \left[\frac{(V_c C_c + V_p C_p)}{V_f C_f}\right] * 100 \tag{4}$$

where % r is the ratio between the amount of metal present in the permeate and the retentate divided by the amount of metal in the feed. This parameter allows evaluating the possible retention of the metal on the membrane. This parameter was systematically higher than 95%. This means that the amount of metal adsorbed or precipitated on the membrane was negligible.

The effect of environmental characteristics such as the presence of salts: Na_2SO_4, KCl, $CaCl_2$, NaCl or competitor metal Cd(II) was studied following the same procedure with just a change in the composition of the feed solution.

The possibility to recycle the polymer is a key step in the evaluation of the potential interest of the process. This requires verifying the possibility to destabilize the complex by pH change. Three cycles were operated, each cycle consisting in three steps:

(a) First step – Metal retention: Three hundred mL of a solution (at pH 8) containing both Hg(II) and SC at concentrations of 40 mg L^{-1} and 300 mg L^{-1}, respectively, was ultrafiltrated until the retentate volume reached 40 mL (260 mL of permeate);

(b) Second step – Complex destabilization: the retentate volume was completed with water up to 300 mL adjusting the pH to 2 with HCl. The solution was then ultrafiltrated till obtaining a volume of permeate of 40 mL.

(c) Thirst step – Preparation of the next retention step: the retentate was completed with water at pH 8, adding the appropriate amount of mercury to reach the target metal concentration (*i.e.*, 40 mg L^{-1}).

This operating sequence was repeated for three cycles; samples in the feed, retentate and permeate were collected and analyzed at each stage for mass balance on mercury.

3. Results and discussion

3.1 Polymer characterization

3.1.1 Solubility

The solubility of the "standard" sulfate derivative of chitosan (SC) was tested in the pH range 2-12. Actually, the derivative of chitosan was totally soluble in water (without salt addition) in the whole pH range when using 300 mg L^{-1} polyelectrolyte concentrations. Different media were also used for testing the solubility of the different compounds (*i.e.*, 0.1 M Na_2SO_4, $CaCl_2$, KCl, and NaCl). The results are summarized in Table 1. At low chlorosulfonic acid concentration (*i.e.*, for 2 mL and 4 mL volume addition), the polymers were totally soluble in the whole pH range, regardless of the type of electrolyte added to the solution. The results are substantially different at high chlorosulfonic

Table 1 Polymer solubility as a function of the composition of the solution and the amount of sulfonic acid introduced in the reactive media

Derivative (volume of $HClSO_3$)	pH	Without salt addition	Na_2SO_4 (0.1 M)	$CaCl_2$ (0.1 M)	KCl (0.1 M)	NaCl (0.1 M)
SC-2 mL	2-12	Soluble	Soluble	Soluble	Soluble	Soluble
SC-4 mL	2-12	Soluble	Soluble	Soluble	Soluble	Soluble
SC-6 mL	2-7	Soluble	Soluble	Insoluble	Insoluble	Insoluble
	7-12	Soluble	Soluble	Soluble	Soluble	Soluble
SC-9 mL	2-7	Soluble	Soluble	Insoluble	Insoluble	Insoluble
	7-12	Soluble	Soluble	Soluble	Soluble	Soluble

Soluble: totally soluble; Insoluble: partially insoluble. ([SC]: 300 mg L^{-1})

acid concentration: in sodium sulfate solutions the polymers remained totally soluble in the entire pH range (2-12), while for calcium chloride, potassium chloride and sodium chloride solutions, the polymer maintained its solubility solely in the alkaline region (*i.e.*, pH 7-12). The ionic strength of the solution may interfere with the behavior of the polymer in solution due to charge screening effects on protonated groups and change in the conformation of the polymer (charge repulsion, etc).

3.1.2 FTIR characterization

Fig. 2 shows the FTIR spectra of raw chitosan (A) and sulfated chitosan samples (B-E). The strict comparison is made difficult by the differences in the resolution of the spectra. However, comparing the raw chitosan (A) with the "standard" sulfated chitosan (B), three major differences can be observed with the appearance of two new bands at 804 cm^{-1} and 1240 cm^{-1} and the changes in the band in the 1550-1700 cm^{-1}. The first band (*i.e.*, at 804 cm^{-1}) is representative of the C-O-S bond stretching, while the second band (*i.e.*, at 1240 cm^{-1}) shows the asymmetric S = O bond stretching. These two strong peaks are characteristics of the grafting of sulfate groups (Vongchan *et al.* 2002, Huang *et al.* 2004, Vikhoreva *et al.* 2005, Xing *et al.* 2005). On chitosan spectrum, two peaks are appearing around 1600 cm^{-1} (at 1655 and 1590 cm^{-1}) these bands representative of amide I band (combination of C = O and C-N stretching bonds) and amine groups, respectively (Kasaai 2008). After chemical modification the two bands were modified and a single and broad band appeared at 1630 cm^{-1}. This change shows that the amine groups were not completely protected and that at least a small fraction of these groups was probably involved in sulfate grafting.

The FTIR analysis of the different chitosan derivatives showed that the amount of sulfate functions decreased when increasing the amount of chlorosulfonic acid (Fig. 2 B-E). This result is consistent with the trend followed by solubility properties: the amount of chlorosulfonic acid in the

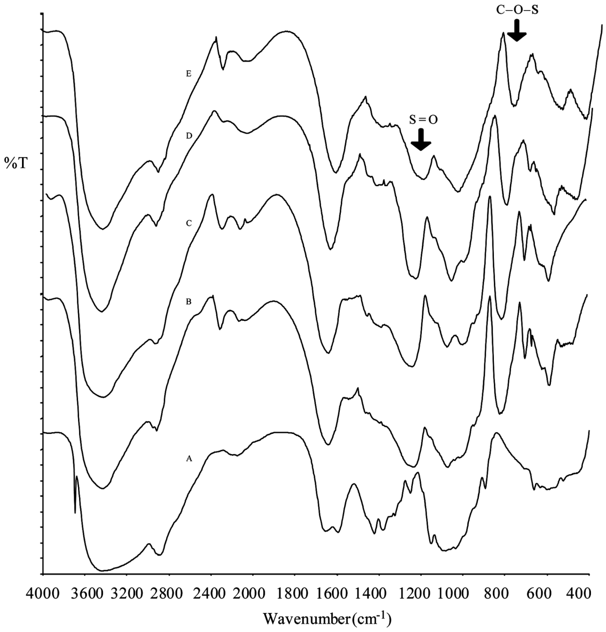

Fig. 2 FTIR spectra of chitosan (A) and different sulfated chitosan samples (B: SC-2 mL; C: SC-4 mL; D: SC-6 mL; E: SC-9 mL)

reactive media controls the amount of sulfate groups grafted on chitosan backbone, which, in turn, influences the chemical behavior of the polymer in solution.

3.1.3 ^{13}C NMR analysis

The different samples were analyzed by ^{13}C NMR spectroscopy; the spectra are shown in Fig. 3. Table 2 summarizes the assignation of the different C signals for the different SC derivatives. Some signals were poorly affected by chemical modification: C_1, C_2 and C_3 signals were shifted by less than 1 ppm in most cases, except for C_3 at the highest chlorosulfonic concentration. This means that the grafting of sulfate compounds probably occurred preferentially on C_6 with a limited impact on C_5. Significant differences were also observed between the different SC: at high chlorosulfonic acid content C_1, C_2, C_3, C_5 and C_6 signals were increased after sulfate grafting, while for low chlorosulfonic acid concentrations the variations were less significant for C_1, C_2 and C_3 signals and

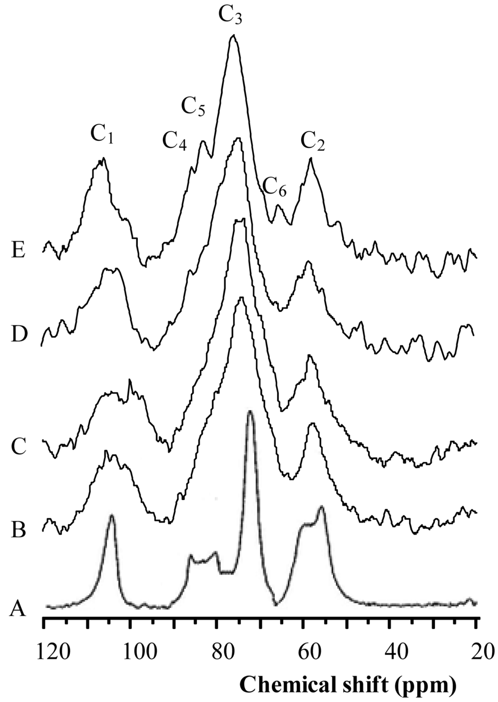

Fig. 3 ^{13}C-NMR analysis of chitosan (A) and different sulfated chitosan samples (B: SC-2 mL; C: SC-4 mL; D: SC-6 mL; E: SC-9 mL)

Table 2 ^{13}C NMR analysis of polymer samples

Polymer	C_1	C_2	C_3	C_4	C_5	C_6
Chitosan	105	56	73	87	81	60
SC-2 mL	105	57	73.5	-	-	-
SC-4 mL	103.9	57.4	72.9	-	-	-
SC-6 mL	105.5	57.3	74	89.5	84	64
SC-9 mL	106.1	57.7	75.6	84	83	65

the signals C_4, C_5 and C_6 almost disappeared (the shoulders were masked by the surrounding peaks). Sulfate grafting is probably occurring on the C_6 group and the environment of the C_2 group (bearing the amine function) is not strongly affected by sulfate grafting. This confirms that the grafting procedure was partially regio-selective so that only few amine groups were involved in sulfate grafting. At high chlorosulfonic acid concentration the changes in the NMR spectra were less marked than for low reagent dose; this is consistent with previous observations: an excess of reagent causes a decrease in the grafting yield.

3.1.4 Titrimetric analysis

Chitosan and derivatives were dissolved in an excess of HCL, and NaOH was added as titrating agent. The pontentiometric titration curves show two equivalent points corresponding to neutralization of HCl excess and $-NH_3^+$ groups. The proportion of protonable amine groups obtained for chitosan (86%) is consistent with the deacetylation degree (87%). The values obtained for the sulfate derivatives were similar to those of chitosan. This confirms that only few amine groups were involved in sulfate grafting.

Using the Henderson-Hasselbach equation it was possible determining the pk_a of amine functions. The results are summarized in Table 3. The pk_a of amine groups in raw chitosan was close to 6.2; the grafting of sulfate compounds shifted the pk_a to higher values: however the change strongly depended on the amount of chlorosulfonic acid used for polymer modification. At low $HClSO_3$ content, the pk_a varied between 8.0 and 8.1; on the opposite hand, in the case of large excess of $HClSO_3$, the increase of the pk_a (around 7.5) was less than that observed at low chlorosulfonic acid content.

3.1.5 Elemental analysis

The elemental analysis focused on the distribution of N and S elements in the different polymers in order to evaluate the substitution degree. Table 4 reports the main results obtained after elemental analysis. As the amount of chlorosulfonic acid increases the amount of sulfur element grafted on the polymer progressively decreases, especially for volumes higher than 4 mL of chlorosulfonic acid; the S/N mass ratio and the substitution degree (atomic ratio) followed the same decreasing trend. However, the substitution degree greater than 1 indicates that the grafting of chitosan occurs through a rather complex mechanism: additionally to the grafting of sulfate functions on the C_6, sulfate groups have been also grafted on other reactive sites of the biopolymer. Previous observations on titrimetric analysis have shown that the substitution did not occur on amine groups. The only other possibility for sulfate grafting, taking into account the steric hindrance of other hydroxyl groups is the substitution on the –OH groups hold by C_3 carbon. On the ^{13}C-NMR spectra (Fig. 3), the width of the C_1 band (appearing around 105 ppm) significantly increased (especially for SC-4 mL),

Table 3 pk_a of amine groups for chitosan and SC-derivatives

Polymer	pk_a
Chitosan	6.2
SC-2 mL	8.1
SC-4 mL	8.0
SC-6 mL	7.5
SC-9 mL	7.6

Table 4 Elemental analysis (S/N, mass ratio), substitution degree (S/N atomic ratio) and distribution of mono- and di-substituted forms

Compound	S/N	Subst. degree	Mono-substituted (%)	Di-substituted (%)
Chitosan	-	-	-	-
SC-2 mL	3.8	1.68	32	68
SC-4 mL	3.6	1.58	42	58
SC-6 mL	2.6	1.15	85	15
SC-9 mL	2.4	1.03	97	3

possibly as the result of the shift of C_3 band (for those groups that were substituted with sulfate groups). This secondary band is decreasing when increasing $HClSO_3$ amount. At low chlorosulfonic acid concentration the substitution process leads to the formation of di-substituted SC (hydroxyl groups on C_3 and C_6 carbons), while an excess of reagent limits the substitution of hydroxyl groups hold on C_3 carbon.

All these characterizations showed that an optimal amount of chlorosulfonic acid should be added to reach the highest degree of substitution: an excess of reagent may cause partial degradation of the polymer including depolymerization among other degradation processes, (Roberts 1992). With the addition of 2 mL of chlorosufonic acid for 1 g of polymer the solubility, the substitution degree (characterized by FTIR, ^{13}C-NMR, potentiometric titration) revealed much better than for higher amounts of reagent, especially above 4 mL. The substitution is roughly regio-selective: sulfate grafting mainly occurs on the C_6 carbon, though under selected conditions a di-substitution may occur by simultaneous substitution of C_3 carbon; additionally few sulfate groups may be grafted on amine groups (change in the bands of amine/amide groups on the FTIR spectra) to a much lesser extent (based on potentiometric titration and ^{13}C-NMR analysis). For these reasons 'standard' sulfated chitosan was the only derivative used in PEUF studies.

3.2 Influence of pH on mercury retention

Fig. 4 compares the impact of pH on the retention of mercury for chitosan (C) and sulfated chitosan (SC). The reference curve corresponding to mercury retention without polyelectrolyte shows that, except at pH 2 (where mercury retention reached up to 6%, probably due to the interaction of chloro-anionic species on the polyestersulfone membrane) mercury retention in the absence of polyelectrolyte was negligible. For chitosan (C), the retention of mercury increased with increasing pH: the pH increase diminished the protonation of amine groups and strongly improved the ability of amine groups to complex mercury ions. Under selected experimental conditions (pH 6) about 90% of total mercury was retained by the PEUF process. It is interesting to observe that when the chitosan solution was prepared in nitric acid (C*, chloride-free solution) the pH edge-curve was steep and parallel to that of HCl-preparation medium (C) but that the curve was shifted toward lower pH. This probably means that the presence of chloride anions decreases the retention yield due to the formation of chloro-complexes that avoid Hg to be efficiently complexed by amine groups. Further experiments varying the amount of chloride will confirm this depreciating effect of chloride anions. Above pH 6, the precipitation of chitosan may cause substantial errors in the understanding of the retention mechanism and the experiments were limited to pH 6 for raw chitosan. The curve representing the retention as a function of pH for sulfated chitosan was shifted

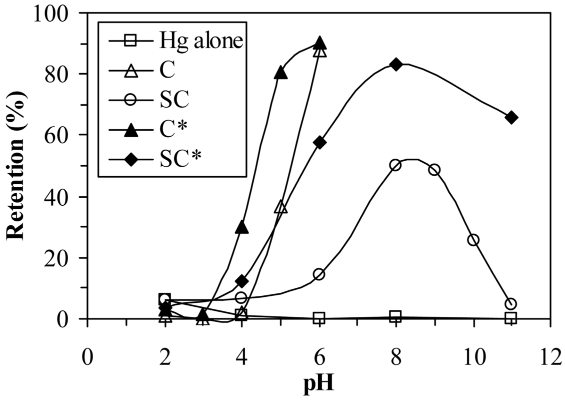

Fig. 4 Influence of pH on Hg retention (Hg alone: Hg solution prepared in water without polyelectrolyte; C: chitosan prepared in HCl solution; C*: chitosan prepared in HNO_3 solution; SC and SC* : sulfated chitosan prepared in water; [Hg]: 10 mg L^{-1}; [polyelectrolyte]: 100 mg L^{-1}, except for SC*: 300 mg L^{-1}

toward higher pH: a 10% retention yield was obtained even in very acidic solutions (*i.e.*, pH 2) and the retention remained at this low value on a broad pH range (up to pH 5). Above pH 5, the efficiency of the process strongly increased up to an optimum value reached close to pH 8. Above pH 8-9 the retention decreased as the result of the formation of soluble hydroxo-complexes (no precipitation was observed) that represents an important competitive reaction. It is interesting to observe that the maximum retention, under comparable conditions (*i.e.*, 100 mg polyelectrolyte L^{-1}), was significantly lower than the value reached with raw chitosan at optimum pH (50% versus 90%). At the same pH (*i.e.*, pH 6) mercury retention did not exceed 15% for SC while it was around 90% for C and C*. The decrease in retention efficiency may be attributed to several reasons: (a) a lower density of reactive groups due to the presence of sulfate groups on the polyelectrolyte (at the same dosage –*i.e.*, 100 mg L^{-1} – the amount of amine groups decreased in proportion); (b) the grafting of sulfate not being totally selective a few amine groups may be occupied by sulfate moieties contributing to slightly reducing the number of amine groups available for interacting with the polyelectrolyte; and (c) amines groups of SC are characterized by a pk_a close to 8 (significantly higher than the pk_a of amine groups on C, *i.e.*, 6.4-6.7), at pH 6 the protonation of SC is much greater than for C, this contributes to reduce the complexation efficiency of amine groups (on SC). The same experiment on SC was carried out at higher polyelectrolyte concentration (*i.e.*, 300 mg L^{-1}), SC*. Similar trends were roughly observed: stable retention at acidic pH (below pH 4) followed by a steep increase in mercury retention up to reach an optimum pH (close to pH 8, with retention close to 83%) and a subsequent decrease in metal retention. Higher polyelectrolyte dosage was required to reach high mercury retention due to a higher pk_a and to the decrease in the density of reactive groups as pointed out above.

3.3 Impact of metal and polyelectrolyte concentration on mercury retention

The concentration ratio between mercury and polyelectrolyte was varied and the retention yield was measured. In a first experiment, the concentration of SC was maintained constant (at 300 mg L^{-1}) and the mercury concentration was varied between 10 and 180 mg L^{-1}. As expected the retention

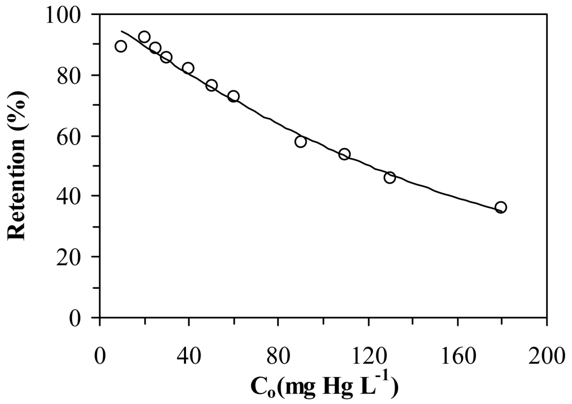

Fig. 5 Influence of initial Hg(II) concentration on mercury retention at pH 8 ([SC]: 300 mg L^{-1})

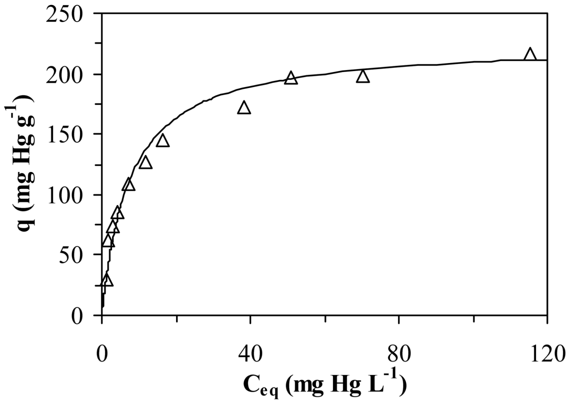

Fig. 6 "Binding isotherm" of mercury on SC at pH 8

continuously decreased (See Fig. 4). These data were used for the determination of a binding capacity by analogy with sorption process. The ultrafiltration of the mixed solution (metal+polyelectrolyte) allows determining free metal concentration. Assuming that metal ions bound to macromolecule were homogeneously distributed on the polymer introduced in the solution, it is possible to evaluate the binding capacity mercury by the mass balance equation. These hypotheses served to establish Fig. 6 that shows the binding capacity q (mg Hg g^{-1} polymer) versus residual mercury concentration (C$_{eq}$, mg Hg L^{-1}, mercury concentration in the permeate, representative of free metal in the mixed solution). By analogy with the analysis of Langmuir sorption isotherms, Fig. 6 was modeled using the following equation (Kuncoro *et al.* 2003, Ghosh and Bhattacharya 2006, Zhang *et al.* 2007)

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{5}$$

where q_m is the maximum binding capacity (mg Hg g^{-1} polymer) and b is the "affinity" coefficient (L mg^{-1}).

Experimental data were well fitted by the equation (the correlation coefficient was 0.996 for 11

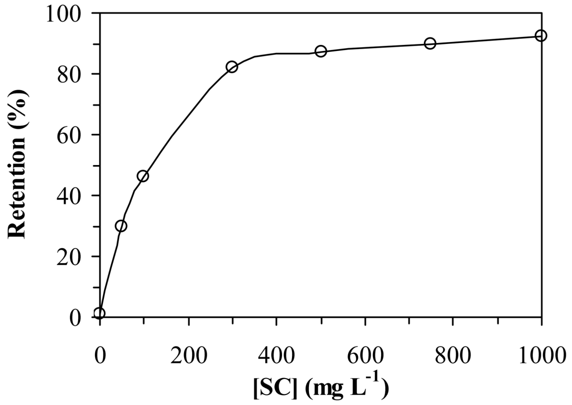

Fig. 7 Influence of SC concentration on Hg(II) retention ([Hg]: 40 mg L^{-1}; pH 8)

values). The maximum binding capacity was 225 mg Hg g^{-1} and the affinity constant was 0.133 L mg^{-1}. This means that the binding capacity was close to 1.12 mmol Hg g^{-1}. Based on a substitution degree (S/N atomic ratio) of 1.68, the equivalent molar weight of the monomeric unit was close to 338 g mol^{-1}. This corresponds to a -NH_2/Hg molar ratio at saturation close to 2.6. The interpretation of this molar ratio requires clarifying some additional points. The pk_a of amine groups on SC being close to 8, a significant fraction of amine groups may be protonated (about 50% at pH 8). This limits the possibility of these protonated amine groups to react with Hg(II).

A second series of experiments was performed at fixed concentration of mercury (*i.e.*, 40 mg Hg L^{-1}) varying SC concentrations (in the range 50-1000 mg L^{-1}). Fig. 7 shows mercury retention with increasing SC concentration. As expected increasing polyelectrolyte concentration allowed increasing mercury retention; however, above a concentration of 400-500 mg L^{-1} further addition of polyelectrolyte did not significantly increase metal retention.

3.4 Influence of environmental parameters on mercury retention

The impact of the composition of the solution is a key parameter for the efficiency of the process and for its possible transfer to industry. The retention of mercury was carried out in the presence of KCl, NaCl, $CaCl_2$ and Na_2SO_4 (at the ionic strength of 0.1 M); as shown on Table 5, the presence of chloride ions strongly reduced the efficiency of the process. This is probably due to the formation of stable chloro-complexes of mercury. These complexes are probably stronger than those formed between mercury and amine groups on the polyelectrolyte. On the other hand, in the presence of sulfate anions the retention of mercury was almost not affected: on Fig. 4 under comparable conditions (without addition of sodium sulfate) mercury retention reached 83%, while it only decreased to 80% in the presence of sodium sulfate. Sulfate anions do not form very stable complexes with mercury and the metal remained free and available for binding to amine groups.

The influence of chloride ions has been investigated in deep. Fig. 8 only shows the 0-0.1 M Cl^- concentration range. Increasing the concentration of chloride ions drastically reduced Hg(II) retention: with a 0.1 M chloride concentration the retention did not exceed 4%. A complementary experiment was performed with a 1 M concentration of chloride ion: mercury retention was also close to 4%. At increasing the concentration of chloride ions the speciation of mercury is displaced to the formation

Table 5 Impact of the presence of salts on mercury retention

Salt	Mercury retention (%)
Without salt	83
Na_2SO_4	80
KCl	8.2
$CaCl_2$	8.9
NaCl	4.2

(pH 8; [Hg]: 25 mg L^{-1}; [SC]: 300 mg L^{-1}; ionic strength: 0.1 M)

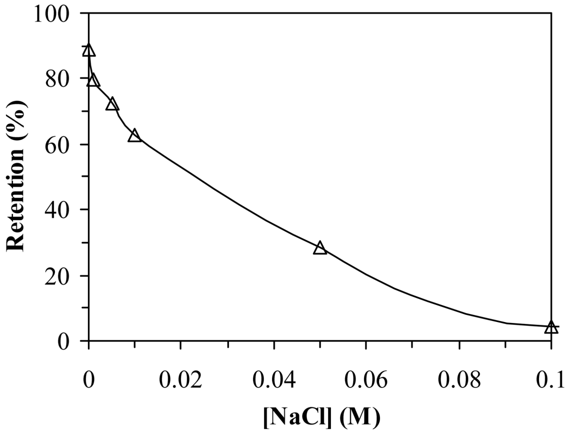

Fig. 8 Influence of chloride concentration on Hg(II) retention (pH 8; [SC]: 300 mg L^{-1}; [Hg]: 25 mg L^{-1})

of chloro-complexes, which are less favorable for interacting with amine groups. For example, when chloride concentration reaches 0.1 M, about 92% of mercury in solution is present under the form of chloro-complexes. The distribution of different chloro-complexes depends on both the pH and the concentration of chloride anions (Baes and Mesmer 1976).

Cadmium is frequently found in mercury-containing effluents. This metal is stable in alkaline solutions: it does not precipitate under the experimental conditions selected in this work. Additionally, cadmium does not form hydroxo-complexes as stable as those formed with mercury. For these reasons it was interesting comparing the retention profile of Cd(II) in function of pH in mono-component solutions and thus to evaluate the retention of both mercury and cadmium from bi component solutions (Fig. 9). The differences observed on the retention of Cd(II) and Hg(II) from single component solutions clearly show the impact of the speciation of the metals on their binding on SC.

The comparison of the stability constants for the formation of soluble mono-metal hydroxo-complexes (Eq. 6-7, Baes and Mesmer 1976) shows that Cd(II) speciation will be less affected by the pH compared to Hg(II) in terms of hydroxo-complexes in the alkaline region selected in this study. It is expectable that Cd(II) more readily binds to amine groups in alkaline regions compared to Hg(II).

$$Cd^{2+} + i\ H_2O \leftrightarrows i\ H^+ + Cd(OH)_i \quad (6)$$

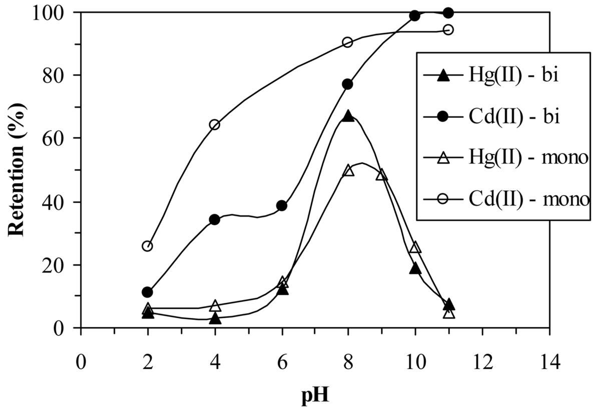

Fig. 9 Influence of pH on Hg(II) and Cd(II) retention from mono- and bi-component solutions ([SC]: 100 mg L^{-1}; [Hg]: 10 mg L^{-1}; [Cd]: 10 mg L^{-1})

with log K_i = –10.1, -20.35, -33.3, -47.35 for i = 1-4

$$Hg^{2+} + i\,H_2O \leftrightarrows i\,H^+ + Hg(OH)_i \tag{7}$$

with log K_i = –3.4, -6.2, -21.1 for i = 1-3

Moreover, the presence of chloride anions contributes to the formation of soluble chloro-complexes that increase metal solubility, especially for Hg(II) that could precipitate at the concentration selected in the study, above pH 4 in the absence of chloride anions. For Cd(II) the formation of hydroxo-complexes begins in alkaline media.

Fig. 9 confirms the importance of metal speciation. At pH 5 Cd(II) was retained while Hg(II) (hydrolyzed form) permeated through the membrane. At pH 8 both Hg(II) and Cd(II) were retained: Cd(II) more efficiently than Hg(II), probably because Cd(II) remained in solutions as Cd^{2+} allowing a greater affinity for amine groups while even in the presence of chloride ions mercury forms soluble hydroxo-complexes. The retention of cadmium remained higher than 90% at pH above 8, while for Hg(II) the formation of soluble hydroxo-complexes reduced the affinity of amine groups for relevant Hg species and the mercury retention decreased.

In bi-component solutions the shape of the retention profiles was not drastically affected by the presence of a competitor metal. For Hg(II) the profiles were almost superimposed: the retention of mercury was increased from 50% to 67% under selected experimental conditions. For Cd(II), the retention efficiency also increased with pH; however, in the presence of Hg(II) the retention was systematically lower than the levels reached in the absence of mercury in the 2-8 pH range. Above pH 8, cadmium was completely removed from the bi-component solution. At pH 8, both Hg(II) and Cd(II) were bound to SC; mercury retention was less influenced by the presence of Cd(II) than the reciprocal. Below pH 8, Hg(II) was almost not retained, contrary to Cd(II).

Based on the HSAB theory (Hard and soft acid-base theory) soft acids such as Hg(II) preferentially react with soft bases (such as S>I>Br>Cl = N>O>F). The softness index for Hg(II) (i.e., 1.27) is more than twice the value for Cd(II) (i.e., 0.58) (Marcus 1997). The polyelectrolyte has probably a greater affinity for Hg(II) than for Cd(II); this may explain that in the presence of Hg(II) the retention of Cd(II) decreased. Above pH 8 in mono-component solutions, Cd(II) retention was almost complete, while Hg(II) retention tended to decrease; this is confirmed with binary solutions. These results confirm the impact of metal speciation, the preference of the polyelectrolyte for Hg(II) and the possibility to separate Hg(II) from Cd(II) from bi-component solutions. At pH 11, Cd(II) recovery was complete, while Hg(II) was almost completely rejected.

3.5 Polyelectrolyte recycling

The recycling is also a key point in the development of the PEUF process. The possibility to recover the metal and to recycle the polyelectrolyte will control the possibility to transfer the process at the industrial scale. The effect of the pH on mercury retention has shown that when the solution is acidic (below pH 3) mercury was not bound to the polymer. This is a first indication on the possibility to reverse the interaction of mercury with the polymer. A series of 3 successive complexation/destabilization steps has been carried out with SC under selected experimental conditions: complexation was operated at pH 8, while complex destabilization was performed at pH 2, adjusting the pH of the solution with HCl. Fig. 10 shows that mercury retention was roughly maintained over the three complexation steps (slight decrease from 88% to 83%), metal recovery during the destabilization step remained very efficient (decreasing from 100% to 98%). This preliminary study gives promising perspectives but would require increasing the number of cycles and a better characterization of the polyelectrolyte after a higher number of cycles.

3.6 Membrane fouling

The efficiency of the PEUF is also controlled by the flow of permeate that can be processed under conventional operating conditions. The flow is generally controlled by the operating time and the progressive fouling of the membrane. The fouling may proceed by blocking and cake filtration (Boerlage *et al.* 2002): several models have been developed for the simulation of flux declines. Boerlage *et al.* remind that the blocking laws (complete, standard and intermediate) are based on constant pressure filtration model and consider that the filter medium can be assimilated to parallel Poiseuille capillary tubes. The complete blocking assumes the tube to be completely obstructed by the particle/colloid. The standard blocking model suggests that the tube is only partially blocked

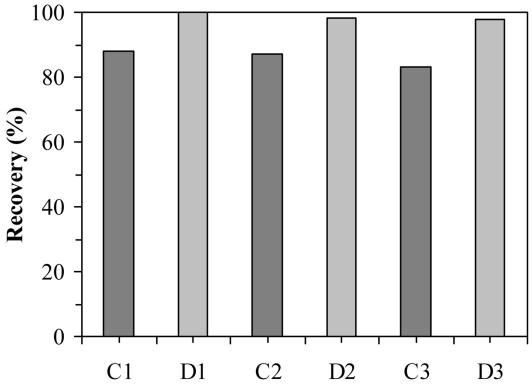

Fig. 10 Polyelectrolyte recycling (complexation: pH 8, [Hg]: 40 mg L^{-1}; SQ: 300 mg L^{-1}; Complex destabilization: pH 2)

(the free tube volume is reduced by the immobilized particle). The intermediate blocking model is a transition between the previous models and the cake filtration model: this is based on the probability of a particle to completely block a tube while inducing further particles to be settled on previously deposited particles to form a cake. The cake filtration assumes all the particles are retained on the membrane by a mechanism of surface deposition. All these models can be approached by a general law

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{8}$$

where k and n are filtration constants, t is the filtration time (h), and V the volume of permeate (L). The values of n define the type of blocking system: 0 for the cake filtration model, 1 corresponds to the intermediate blocking model, 1.5 is used for the standard blocking model, while in the complete blocking model n equals 2.

The general equation was used and integrated for the different models in order to simulate the permeate flux and to identify the controlling blocking phenomenon. Table 6 reports the different plots used for these models. The four models were tested varying the concentration of SC (50-1000 mg L^{-1}). As an example, Fig. 11 shows the linearization of experimental data with the cake filtration model. The plots of the modeling of experimental data with the other equations are not shown. Results for all tested models are summarized in Table 7. The correlation coefficient was systematically higher for the cake filtration model. It is also noteworthy that all the models gave the best correlation coefficient at low SC concentration (*i.e.*, 50 and 100 mg L^{-1}). The curves on Fig. 11 show that the slope increased with SC concentration. The modified fouling index (M.F.I.) can be calculated on the basis of the cake filtration coefficient at constant pressure according to the equation (Boerlage *et al.* 2002)

$$\frac{t}{V} = \frac{\eta R_m}{\Delta PS} + \frac{\eta I}{2\Delta PS^2}V \tag{9}$$

where ΔP is the applied transmembrane pressure (bar), η the water viscosity (N s m^{-2}), S is the membrane surface area (m^2), R_m is the membrane filter resistance (L m^{-1}), I the index for propensity of particles in water to form a layer with hydraulic resistance (L m^{-2}). M.F.I. corresponds to the slope (s m^{-6}) of the plot of t/V versus V (see Table 7). It increased with the concentration of SC between 50 mg L^{-1} and 500 mg L^{-1}; between 500 mg L^{-1} and 700 mg L^{-1} it tended to stabilize, and finally it increased again. These changes may be indicative of different resistances to cake filtration in relation with polyelectrolyte interactions with mercury. These interactions may contribute to a re-organization of the macromolecule by changing the mutual interactions between polymer chains (repulsion/attraction) due to charge neutralization on the biopolymer or to the appearance of new charges. Additionally, increasing the concentration of the polyelectrolyte may

Table 6 Modeling of permeate flux – Determination of blocking phenomenon

General law	$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n$			
Model	Cake filtration (n=0)	Intermediate (n=1)	Standard (n=1.5)	Complete (n=2)
Plot	$\frac{t}{V} = j(V)$	$\frac{dt}{dV} = h(t)$	$\frac{t}{V} = g(t)$	$\frac{dV}{dt} = f(V)$

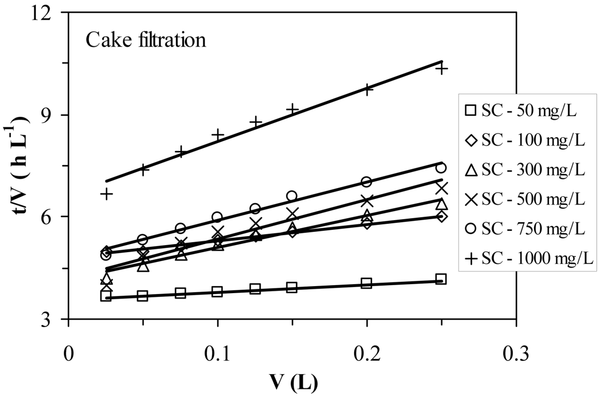

Fig. 11 Modeling of permeate flux with the cake filtration equation – Effect of SC concentration (pH 8, [Hg]: 40 mg L^{-1})

Table 7 Modeling of permeate flux – Effect of SC concentration

Model	[SC] (mg L^{-1})	Slope	Y-axis.I.	R^2	M.F.I. 10^{-9}
Cake filtration model	50	2.27	3.57	0.989	8.16
	100	4.90	4.81	0.991	17.6
	300	9.51	4.15	0.973	34.2
	500	11.4	4.22	0.924	41.2
	750	11.2	4.77	0.983	40.2
	1000	15.7	6.63	0.975	56.7
Intermediate blocking model	50	0.541	3.585	0.991	
	100	0.795	4.859	0.99	
	300	1.408	4.33	0.947	
	500	1.564	4.452	0.89	
	750	1.424	4.987	0.959	
	1000	1.436	6.94	0.947	
Standard blocking model	50	1.011	3.559	0.941	
	100	1.467	4.848	0.963	
	300	2.1833	4.602	0.9	
	500	2.262	4.883	0.833	
	750	2.289	5.273	0.877	
	1000	2.28	7.338	0.918	
Complete blocking model	50	-0.256	0.28	0.935	
	100	-0.264	0.205	0.941	
	300	-0.429	0.222	0.826	
	500	-0.446	0.214	0.689	
	750	-0.384	0.193	0.836	
	1000	-0.275	0.139	0.833	

M.F.I.: Modified fouling index (s m^{-6})

cause entanglement which in turn may affect the size of the macromolecule and its blocking at the entrance of the pores of the membrane. The stiffness of SC is not known however, by analogy with chitosan the rheological properties of SC are affected by polymer concentration and by the ionic strength of the solution (Cho *et al.* 2006).

4. Conclusion

Chitosan is soluble in acidic solutions but begins to precipitate at pH close to neutral media. The modification of the biopolymer with sulfate grafting (through reaction with chlorosulfonic acid) allows increasing the pH range of solubility; however, the amount of reagent should be strictly controlled to prevent polymer degradation and optimum substitution (an excess of reagent causes precipitation of derivative in acidic conditions). The polymer was characterized by FTIR, ^{13}C-NMR analysis, elemental analysis and potentiometric titration before being tested for the recovery of mercury through polymer enhanced ultrafiltration (PEUF). The modification allows mercury recovery on a wider range of pH than raw chitosan (which precipitates at pH above 6) but with lower retention percentages. The mass balance equation was used for establishing a "binding isotherm and evaluating the molar ratio $–NH_2/Hg(II)$ at saturation of the biopolymer, which was close to 2.6 at pH 8: the protonation of amine groups at this pH close to the pk_a limits the number of reactive groups available for metal binding. The presence of chloride ions strongly influences the speciation of the metal, chloroanionic mercury species are formed, which in turn decreases metal affinity for amine groups. In binary solutions (*i.e.*, Cd(II)/Hg(II)) the separation of the two species was possible controlling the pH at 11 for complete recovery of Cd(II), while at this pH the formation of soluble hydroxo-complexes of mercury limited mercury binding. The recycling of the biopolymer after mercury binding was possible decreasing the pH to 2 and the material could be recycled for at least 3 cycles maintaining high metal recovery. The study of permeation fluxes allowed identifying cake filtration mechanism as the limiting step in the filtration process.

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