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E.K. Kuncoro, T. Lehtonen, J. Roussy, Guibal Eric. Mercury removal by polymer-enhanced ultrafiltration using chitosan as the macroligand. 15th International Biohydrometallurgy Symposium (IBS 2003), Sep 2003, Athènes, Greece. hal-04755793

HAL Id: hal-04755793

<https://imt-mines-ales.hal.science/hal-04755793v1>

Submitted on 31 Oct 2024

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Mercury removal by polymer-enhanced ultrafiltration using chitosan as the macroligand

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Chitosan is an aminopolysaccharide produced from crustacean shells. This biopolymer is very efficient at sorbing metal ions through different mechanisms including (a) chelation on its amine group in near-neutral solutions or (b) ion exchange in acidic solutions (protonated amine groups interact with metal anions). Alternatively, dissolved chitosan can be used for the recovery of metal ions using Polymer-Enhanced Ultrafiltration (PEUF) technique. The process makes profit of the ability of the macromolecules to bind metal ions and to be retained by membranes of selected cut-off. The process has been tested in the case of mercury using an Amicon ultrafiltration system. The efficiency of the process has been investigated using membranes of different cut-off (10 kDa, 50 kDa, 100 kDa). The influence of pH, metal concentration, chitosan concentration and pressure has been studied on permeation flux and the retention of both the polymer and the metal. The coupling of metal binding and ultrafiltration allows reaching retention efficiency greater than 95 % under appropriate experimental conditions. For mercury, metal recovery occurs by chelation and the optimum pH is close to pH 5-6. The mercury/chitosan binding constant has been determined close to $10^{7.3}$.

Keywords: chitosan, ultrafiltration, mercury, chelation, retention efficiency, pressure drop.

1. INTRODUCTION

The need for efficient and economical recovery of metals from dilute effluents is motivated by the drastic development of environmental regulations. To face up the problem of the removal of toxic or valuable metals from dilute effluents, biosorption processes have been developed for the last twenty years. Many biosorbents have been tested for the recovery of a broad range of metals, especially bacteria, fungi, algae [1]. More recently a great attention has been paid to the use of agricultural waste materials, or wastes from food industry [2]. An increasing interest has focused on the use of biopolymers extracted from marine materials: alginate (from algae), chitin and chitosan (from crustaceans). The presence of chelating functions on these biopolymers (carboxylic functions for alginate, amine groups for chitosan) may explain the growing interest in checking their ability to recover metal ions [3-5].

[#] E.K.K. thanks the French Ministry of Foreign Affairs for his Ph.D fellowship.

* E.G. The authors thank the European Community for financial support under Growth Program (3SPM project, Contract G1RD-CT2000-00300) for attending the IBS'03 conference.

Chitosan is an amino-polysaccharide that is produced by an alkaline deacetylation from chitin, the most abundant biopolymer in nature after cellulose. The presence of amine groups may explain its high efficiency for the chelation of metal cations in near-neutral solutions [6-7]. However, due to its cationic behavior [8], in acidic solutions the protonation of amine groups leads to interesting ion exchange properties [9-11]. Metal anions are efficiently sorbed by electrostatic attraction. However, chitosan is soluble in most mineral and organic acids (with the exception of sulfuric acid); it is thus necessary to crosslink the polymer to prevent its dissolving in acid media for an easy recovery of loaded material. Alternatively, the biopolymer can be used in its dissolved form providing a suitable filtration system is used for the recovery of loaded macromolecules. This property can be used in polymer enhanced ultrafiltration processes (PEUF) [11-12]. The main element of any membrane separation process is the semipermeable membrane. Certain solution components will pass through the membrane forming the permeate, whereas others will be retained by the membrane forming the retentate or the concentrate. The retention of the component depends on many parameters [13], including solution type, solution composition, pH, temperature, membrane material, pore size, hydrodynamics etc... In many cases, however, the size of the dissolved component is the crucial factor for the retention. In order to improve separation, the metal ions can be bound to macromolecules, thus enlarging the molecular dimensions of the components to be separated [14-18].

This study focuses on the use of chitosan dissolved in HCl solutions for the binding of mercury and the further separation of loaded macromolecules by an AMICON ultrafiltration unit. The efficiency of the process has been investigated using membranes of different cut-off (10 kDa, 50 kDa, 100 kDa). The influence of pH, metal concentration, chitosan concentration and pressure has been studied on both flux and retention of polymer and metal. Ultrafiltration performance can be correlated to the sorption behavior of the biopolymer and it is thus possible to predict the uptake performance of dissolved biopolymer, and to anticipate on the chemical modifications that can be required to increase its efficiency.

2. MATERIAL AND METHODS

2.1. Materials

Chitosan was supplied by Aber Technologies (Plouvien, France). The characteristics of the samples have been previously determined. The deacetylation degree was found to be 87 %, using FTIR spectrometry measurements, and the molecular weight was 125,000 g mol⁻¹, using SEC measurements. Mercury nitrate was purchased from Fluka AG (Switzerland). Other common reagents were supplied by Carlo Erba (Italy).

2.2. Ultrafiltration module

Ultrafiltration experiments have been performed using an AMICON ultrafiltration module, AMICON 8400, with the following characteristics: membrane diameter 76 mm, volume of solution 200 mL, maximum pressure 75 psi (5.3 bars). The membranes used for these experiments were Amicon membranes (M10, M50 and M100) made of polyethersulfone with different molecular weight cut-off (MWCO): 10,000, 50,000 and 100,000 Da, respectively. Pressure was obtained from local pressurized air network using suitable manometers. Experiments were performed under pressures ranging between 0 and 2.5 bars.

2.3. Ultrafiltration experiments

Chitosan was dissolved in HCl solutions at suitable concentration and the solution was mixed with metal solution at fixed concentrations. The mixture was agitated under pH control for at least 2 hours prior being placed in the ultrafiltration module. For the measurement of flux, the first 10-mL fraction was removed and then the time necessary to filtrate successive (at least 5) fractions of 25 or 50 mL were monitored. The flux (J , $L m^{-2} h^{-1}$) was calculated as the mean value of these 5 time-fractions taking into account the volume passed through the membrane during the nominal times and the surface of the membrane. Samples have been collected from these fractions for the determination of both metal and polymer content. Polymer concentration was determined using a TOC-meter Shimadzu TOC-5000 (Japan) and a calibration curve prepared from pure chitosan solutions. Metal concentration was determined using an Inductively Coupled Plasma spectrometer (JOBIN-YVON JY 2000, France).

3. RESULTS AND DISCUSSION

3.1. Characterization of permeation properties of ultrafiltration membranes

The permeation properties of the membranes have been determined using Milli-Q demineralized water. The fluxes have been measured (Figure 1, left panel)). Flux linearly varied with the pressure. Moreover, the slope of the curves, s , may be correlated to the cut-off, CO (Da), of the membranes according to the equation: $s = 0.0111 CO$ (R^2 : 0.969). This equation may be used to predict the permeate flux for a given pressure and a given membrane (fixed cut-off): $J = 0.0111 CO * P$. The right panel in Figure 1 compares experimental data with calculated values.

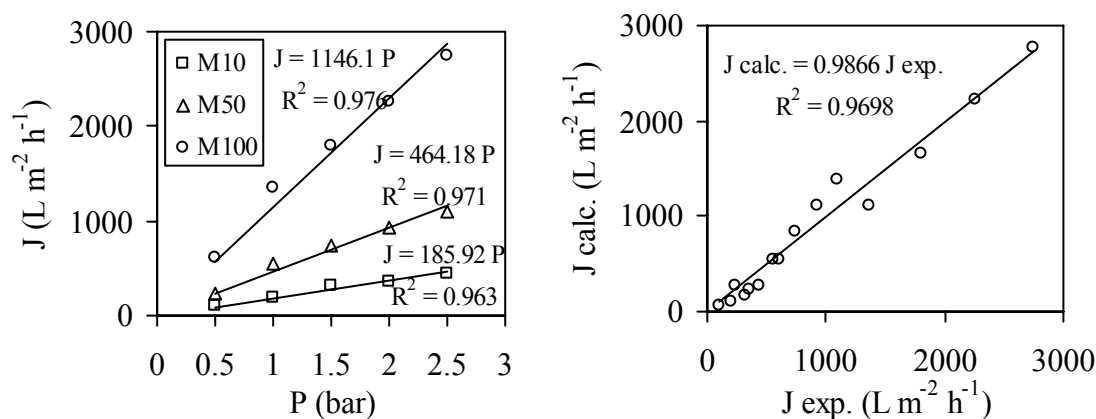


Fig. 1. Flux characteristics of ultrafiltration membranes.

3.2. Ultrafiltration of chitosan solutions

The permeation characteristics of chitosan have been determined on M10 (cut-off: 10,000 Da) membranes at a polymer concentration of $200 mg L^{-1}$. Results are presented on Figure 2. As expected, increasing the pressure increased the permeation flux: it was doubled from 0.5 to 2.5 bars, while the retention rate only slightly varied (around 99 %).

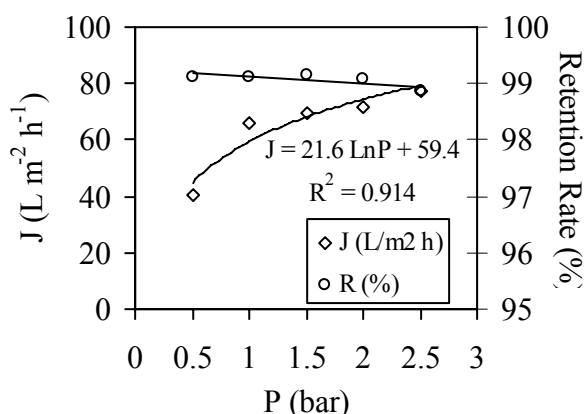


Fig. 2. Influence of pressure on permeation flux (J) and polymer retention rate (R) (membrane cut-off: 10.000 Da; chitosan concentration: 200 mg L⁻¹).

Table 1 shows the influence of chitosan concentration on the flux and retention rate at pressures (P) 1 and 2 bars for membranes M10, M50 and M100. In most cases, the retention rate exceeded 92 %. With the M100 membranes, at low chitosan concentration the retention was lower, in the range 86-89 %, whatever the pressure applied to the membrane. Increasing polymer concentration partially restored retention efficiency (above 93 %). In the best cases, the retention of the polymer reached 97 %, but it was not possible to recover the entire amount of the polymer. This may be explained by the presence of small polymer chains (partially hydrolyzed) that cannot be retained by the membranes, even with the smallest cut-off (M10). This polymer loss could be avoided by a preliminary ultrafiltration of the polymer solution to remove small size polymer chains.

Table 1

Permeation fluxes (L.m⁻².h⁻¹) and retention rates (into brackets, %) for chitosan ultrafiltration in function of polymer concentration, pressure and membrane type.

P (bar)	1				2				
	C (mg/L)	0	50	100	200	0	50	100	200
M10	0	196.0	154.5	142.3	131.5	362.2	185.4	170.5	158.2
	200		(96.2)	(96.2)	(96.4)		(94.8)	(96.2)	(97.0)
M50	0	554.0	231.7	172.2	147.8	926.7	273.9	217.0	173.4
	200		(96.5)	(93.3)	(96.9)		(95.1)	(92.4)	(97.2)
M100	0	1358.4	233.9	194.1	136.0	2253.7	280.9	272.8	161.0
	200		(86.5)	(93.2)	(96.8)		(89.3)	(92.8)	(95.5)

Table 1 also shows the permeation fluxes for selected experimental conditions. These fluxes can be compared to those obtained with pure water filtration. The presence of chitosan strongly decreased the permeation fluxes, especially for large cut-off membranes and for large pressures. Indeed, in the case of M10 membranes at P: 1 bar, the decrease of the permeation flux was between 21 and 33 %, but when the pressure increased to P: 2 bars, the decrease reached 49-56 %. With the M100 membranes the influence of chitosan on permeation fluxes was much more drastic: at the highest polymer concentration the decrease in permeation

fluxes raised to 90-93 %. Similar decrease in permeate fluxes have been observed by Tangvijitsri et al. in the case of PEUF of chromate, sulfate and nitrate [15]. This decrease in the flux may be explained by the accumulation of polyelectrolyte near the membrane surface (hydrodynamic boundary layer), though the agitation was maintained in the ultrafiltration cell.

Figure 3 shows the influence of pH on the ultrafiltration of chitosan (initial concentration: 200 mg L⁻¹) with M50 and M100 membranes under a pressure of 2 bars. The permeation flux shows an optimum at pH 4 that appears to be independent of the membrane type. The permeate flux can be fitted by a quadratic equation. The retention rate varied between 90 and 98 %, with a maximum retention obtained at pH 4. Generally, polymers have flexible structure and under certain hydrodynamic conditions the shape of such molecules can change from a sphere to an ellipse or to a slim cylinder so that they will pass through the membrane even though their mass is less than the nominal cut-off of the membranes used. This effect is emphasized by the pH of the solution that changes the conformation of the polymer (hydrogen bonding, electrostatic repulsion) [14]. The presence of metals ions partially neutralizes their charge, which in turn influences the conformation of polymer chains and their overall size.

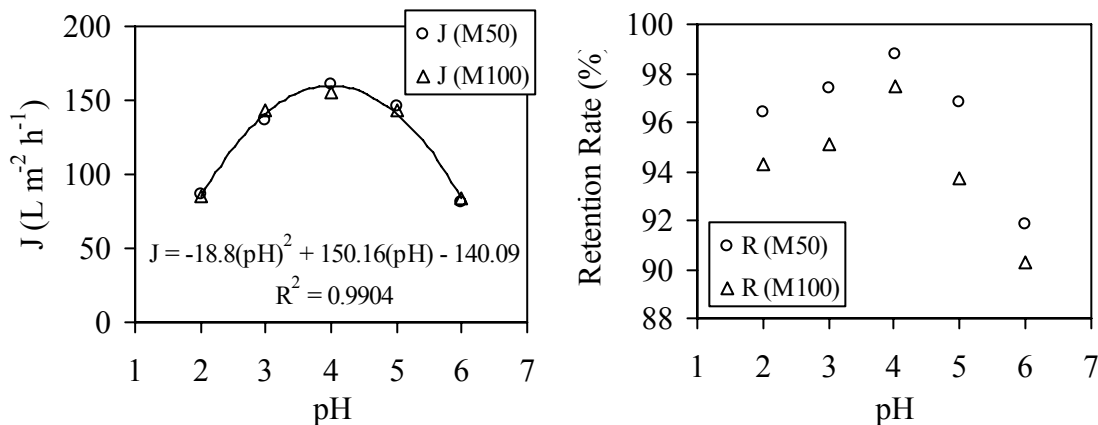


Fig. 3. Influence of pH on permeation flux and retention rate for chitosan solutions (conc.: 200 mg L⁻¹; P: 2 bars; and membranes M50 and M100).

3.3. Influence of pH on mercury removal by PEUF

Figure 4 shows the permeation properties (flux, retention rates for mercury and polymer) in function of the pH of the mixed (Hg/chitosan) solutions. The maximum permeation flux (around 150 L m⁻² h⁻¹) was obtained between pH 3 and pH 4. The flux was halved at changing the pH to pH 2 or pH 5-6. These values are comparable to those obtained with chitosan solutions in absence of mercury. For polymer recovery, the maximum retention rates (around 97-98 %) were obtained at pH 2.5-3.5: again, these values are comparable to those obtained without mercury. The retention rate decreased to 94-96 % when the pH was increased to values 5-6. It is slightly higher than the levels of chitosan recovery in pure polymer solutions, especially at pH 6. This increase in retention efficiency may be explained by the linking effect of metal-polymer interaction that can increase the size of the polymer chains and allows the complementary retention of small size chains, since mercury is supposed to interact with different polymer chains. Indeed, different studies on mercury or copper (in presence of EDTA) recovery by PEI-(polyethyleneimine) binding/ultrafiltration have pointed out the change in the stoichiometry between metal ions and amine/imine groups [12,18-20]. These studies have shown the possibility for different chains to contributing to metal ion binding.

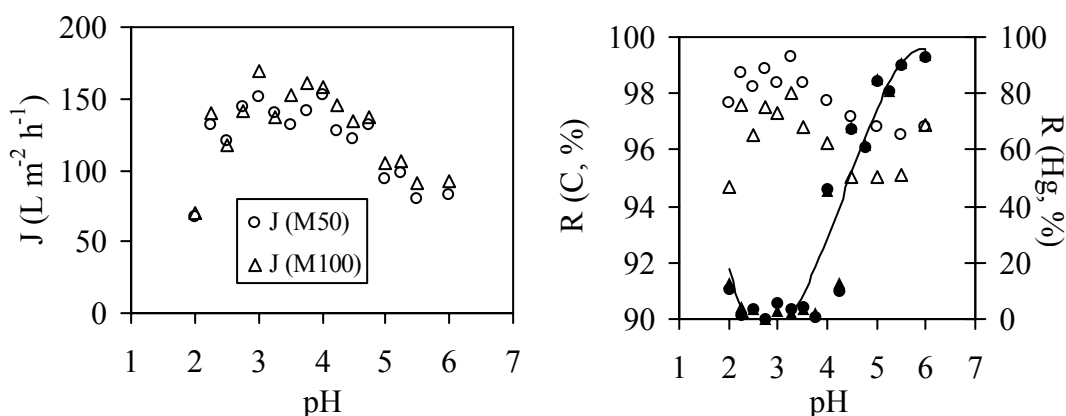


Fig. 4. Influence of pH on permeation fluxes (left panel); and polymer (open symbols) and mercury (closed symbols) retention rates (right panel) (M50 and M100 membranes; P: 2 bars; Chitosan concentration: 200 mg L⁻¹).

More interesting are the retention curves for mercury. A sigmoid trend was observed at increasing the pH. From pH 2 to pH 3 the retention rate decreased from 15 to 4 % and then increased drastically up to pH 6 with a maximum mercury retention that exceeded 95 % at pH 6. Blank experiments have been performed with pure mercury solutions (i.e. without chitosan) and mercury retention was less than 4 % below pH 4, and progressively increased to 10-14 % when the pH was raised to 6. This mercury retention may be explained by a partial adsorption of mercury on the membrane rather than to precipitation of mercury under selected experimental conditions. So, chitosan significantly improved the efficiency of mercury recovery. Optimum pH conditions for mercury recovery appear to be close to pH 6, though the permeation flux is significantly reduced at these pH values. The non-null recovery of mercury at very low pH (around pH 2-2.5) may be explained by a different interaction mechanism. Indeed, at low pH, controlled with hydrochloric acid, the concentration of chloride is high enough to influence the speciation of mercury and to displace the distribution of its species toward the formation of anionic chloro-complexes. Under these acidic conditions amine functions of chitosan are fully protonated and then available for the ionic attraction of anionic species. This interpretation is consistent with mechanisms cited for mercury removal in acidic solutions on cross-linked materials [4].

It is interesting to note that the preliminary ultrafiltration of the polymer solution (prior to contact with metal ion solution) would increase metal retention. Indeed, metal ions can bind to small size chains of the polymer, which are not retained by the membrane. It induces a loss of both metal ions and polymer.

According to Rumeau et al., the logarithm of the apparent complex formation constant should vary with the pH of the solution (far from the pK_a of the polymer) and the slope of the curve should be n , the number of ligand molecules per metal ligand complex [21]. Similar equation has been established by Juang and Chen in the case of poly(ethylenimine) with several simplifying hypotheses [22]. More specifically, the equation was demonstrated considering that metal ion is only present in the solution in the free form. Obviously, the solution of the problem would be more complex taking into account the speciation of metal ions. Different values of n have been tested (n : 1, 2, 3 and 4) using the following equation for the calculation of the apparent complex formation constant (β'_n) [21]:

$$\frac{1}{\beta'_n} = \frac{1}{R} \left[(1-R)(L)^n \left(1 - n \left(\frac{M}{L} \right) R \right)^n \right] \quad (1)$$

with R retention yield, M and L metal and ligand concentrations, respectively.

Figure 5 shows the plots of the apparent formation constant β'_n of the complex Hg/Chitosan versus the pH of the solution using the equation (1) with $n = 1$ and $n = 2$. Though each of the stoichiometric ratios tested gave linear trends in the range pH 3-5, the curve $\text{Log } \beta'_2$ versus pH was the only curve that gave consistent slope (Table 2) (slope close to the theoretical stoichiometric ratio). So, the data have been exploited using the equation (2):

$$\frac{1}{\beta'_2} = \frac{1}{R} \left[(1-R)(L)^2 \left(1 - \left(\frac{M}{L} \right) R \right)^2 \right] \quad (2)$$

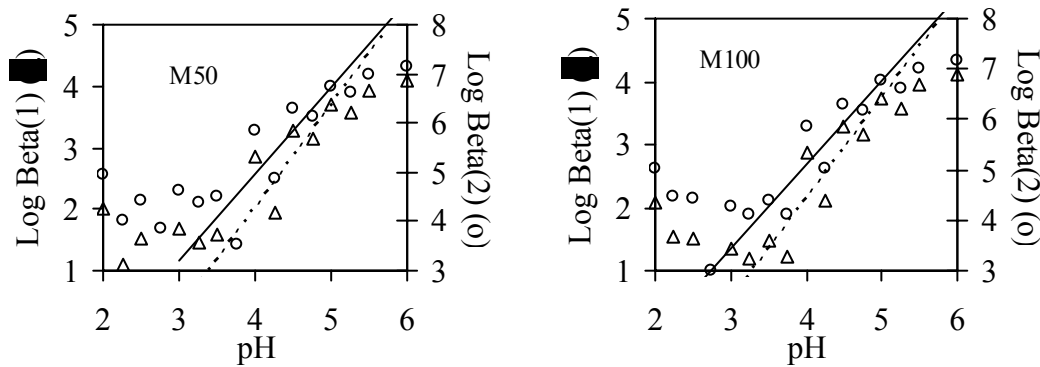


Fig. 5. Plot of $\text{Log } \beta'_i$ as a function of pH for membranes M50 and M100 (M50 and M100 membranes; P: 2 bars; Chitosan concentration: 200 mg L^{-1}).

Table 2

Determination of the stoichiometry of the complex by the equation (1): slope of the curves $\text{Log } \beta'_i$ versus pH.

n	M50	M100
1	1.68	1.58
2	1.76	1.66
3	1.30	1.59
4	1.45	1.75

3.4. Influence of Ligand/Metal (L/M) molar ratio on mercury removal by PEUF

Figure 6 shows the influence of the ligand/metal ratio on the retention efficiency for mercury on membranes M50 and M100 under a pressure of 2 bars. Metal concentration was varied between 10 and 100 mg Hg L^{-1} , while chitosan concentration was varied between 50 and 200 mg L^{-1} . The pH of the solution was controlled to pH 5.5.

When the concentration of mercury increased, a slight increase in the permeation rate was also observed, whatever the concentration of chitosan in the mixture. As expected increasing chitosan concentration decreased the permeate flux. The positive effect of mercury may be related to the formation of polymer/metal aggregates that prevents the blocking of membrane pores during the formation of the polarization layer.

The apparent constant of complexation was calculated using the samples collected with membranes M50 and M100 at pH 5.5 for the different L/M ratios using equation (2). Figure 7 shows the plot of $\text{Log } \beta_2$ for the different L/M ratios. The mean values obtained over 11 values (removing the data obtained at low chitosan concentration with L/M=1 that was not consistent with other experimental points) were $\text{log } \beta'_2 = 7.29 \pm 0.38$ for membranes M 50 and M100.

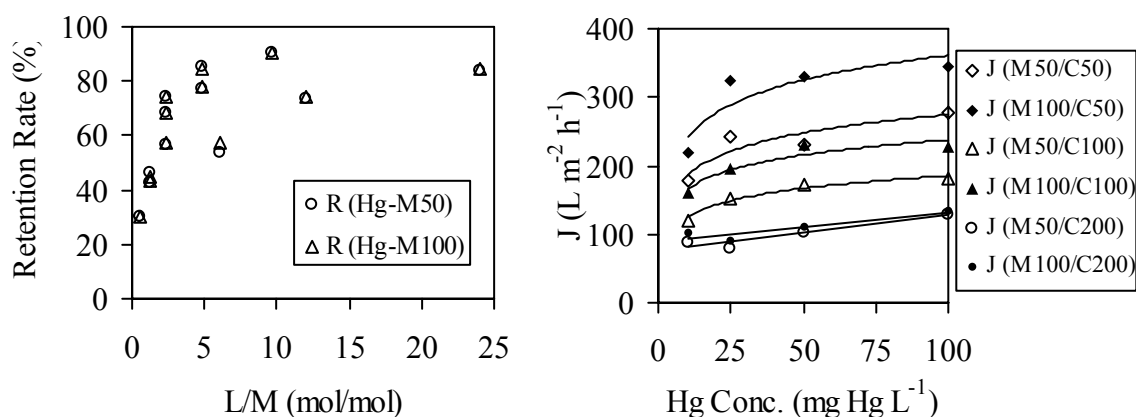


Fig. 6. Influence of ligand/metal ratio on mercury retention (left panel) and permeation flux (right panel) at pH 5.5, with membranes M50 and M100, under P: 2 bars.

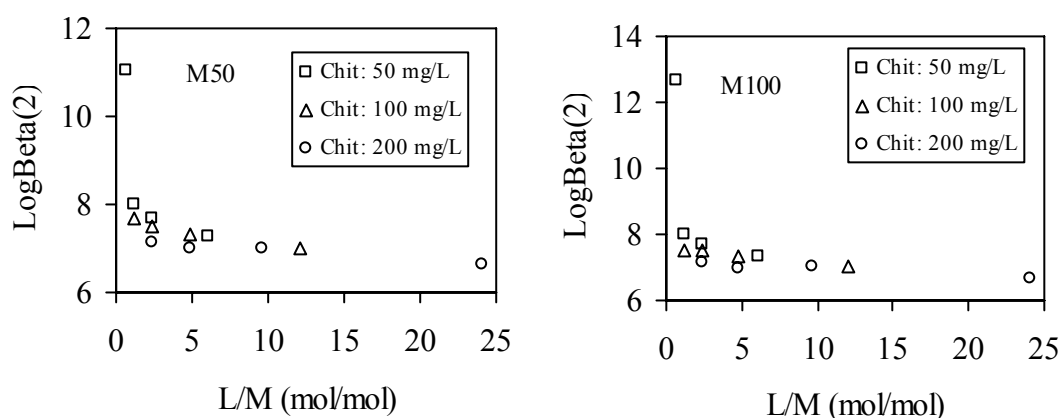


Fig. 7. Influence of ligand/metal ratio on $\text{Log } \beta_2$ at pH 5.5, with membranes M50 and M100, under P: 2 bars.

Figure 8 shows the influence of L/M ratio on mercury uptake capacity (mercury content on retained polymer) and the plot of uptake capacity (q) versus mercury residual concentration (C_{eq}). The uptake capacity (mg or mmol per g of polymer) was converted into a molar unit system (mmol metal per mol of polymer). Indeed, for a chitosan sample with a 87 % deacetylation degree, the molecular weight of the equivalent monomeric unit is 166 g per mol.

The mathematical modeling of experimental data was performed using the Langmuir equation:

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (3)$$

with b ($L \text{ mg}^{-1}$ or $L \text{ mmol}^{-1}$) and q_m (mg g^{-1} or mmol g^{-1}) are Langmuir-model constants.

This equation was used by analogy with metal ion sorption on solid particles, though the physical hypotheses of the sorption model were not satisfied in the present case. The equation served to approximate the theoretical maximum uptake capacity that was found to be $579 \mu\text{mol Hg mol}^{-1}$ chitosan. The maximum experimental uptake capacity was $499.5 \mu\text{mol Hg mol}^{-1}$ chitosan. It means a stoichiometric ratio Hg/Chitosan tending to 1:2, close to the value established above. The maximum theoretical uptake capacity (from Langmuir equation) was close to 698 mg Hg g^{-1} chitosan, slightly higher than the maximum experimental uptake capacity, which is close to 602 mg Hg g^{-1} chitosan. For a residual concentration of 20 mg Hg L^{-1} ($0.1 \text{ mmol Hg L}^{-1}$), the uptake capacity was about $298 \mu\text{mol Hg mmol}^{-1}$ chitosan (i.e. 360 mg Hg g^{-1}). Under comparable conditions (pH 5-6, and residual concentration tending to 20 mg Hg L^{-1} , not shown), the sorption capacity obtained with chitosan flakes was about 240-250 $\mu\text{mol Hg mmol}^{-1}$ chitosan (i.e. 290 mg Hg g^{-1}). This increase in mercury uptake capacity by chitosan using the polymer in PEUF (compared to sorption process) may be explained by a greater accessibility to reactive sites when the polymer is dissolved and highly dispersed in the solution. In the solid form the biopolymer maintain a residual crystallinity that restricts the accessibility to sorption sites [23], moreover some functional groups (amine functions) are involved in hydrogen bonding with water and other amine groups (inter and/or intra-molecular hydrogen bonds): it limits the availability of functional groups for other interactions [24].

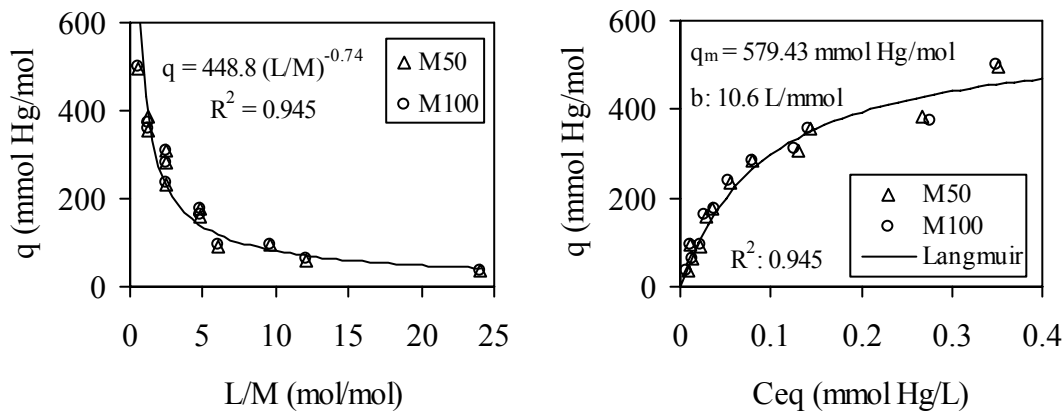


Fig. 8. Influence of ligand/metal ratio on mercury uptake by the polymer (left panel) and uptake isotherm (right panel) at pH 5.5, with membranes M50 and M100, under P: 2 bars.

4. CONCLUSIONS

Polymer enhanced ultrafiltration appears to be a promising technique for the recovery of mercury using chitosan as the chelating agent. The chelation of mercury by chitosan increases with pH. However, due to chitosan precipitation above pH 6, for chitosan-enhanced ultrafiltration processes pH might be set below pH 6. The permeation flux and retention rate are very sensitive to pH (optimum close to pH 4) for chitosan retention. In the presence of

mercury both polymer retention and permeation rates are maintained optimum at a value close to pH 4. The formation constant for the complex Hg-chitosan is found close to $10^{7.3}$. The maximum uptake capacity is close to 600 mg Hg g⁻¹, higher than the levels reached with solid chitosan. This enhancement in sorption capacities may be due to a greater accessibility to sorption sites when chitosan is dissolved. It is also interesting to observe that the dissolving of the polymer allows increasing uptake kinetics. Indeed, a 2-hours contact time prior to ultrafiltration was maintained for the equilibration of the solution (pH stabilization and metal chelation). This contact time was sufficient to achieve a complete uptake of mercury. Under comparable experimental conditions (sorbent dosage and metal concentration), 24 hours of contact were necessary to reach the equilibrium with chitosan in solid form (not shown, in preparation).

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