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Mercury Recovery by Polymer-Enhanced Ultrafiltration: Comparison of Chitosan and Poly(Ethylenimine) Used as Macroligand

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Abstract: Chitosan is an aminopolysaccharide that has been widely studied for metal ion recovery. In most cases it is used as a sorbent in solid form, but the polymer can also be used in a dissolved form in the so-called Polymer-Enhanced UltraFiltration (PEUF) process. The present work focuses on the use of dissolved chitosan for the removal of mercury from dilute solutions using an Amicon ultrafiltration unit. Recovery performance is compared to that obtained with poly(ethylenimine) (PEI), a synthetic amine-bearing polymer. The pH, metal concentration, and polymer concentration are the principal parameters to be taken into account in evaluating the recovery process. The impact of these parameters was tested with respect to metal and polymer retention and the filtration flow rate. In the case of chitosan, the comparison of molar metal/amine group ratios at saturation of the polymer in its solid state (adsorption process) and dissolved state (PEUF process) shows that dissolving the polymer improves the accessibility of sorption sites and enhances the sorption capacity. Although the addition of chloride strongly decreased mercury retention, it hardly influenced PEUF performances when using PEI; this indicates a different binding mechanism or, at least, different contributions on the part of electrostatic attraction and chelating mechanisms at different pHs for these different polymers: linear polymer (chitosan) and branched polymer (PEI).

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INTRODUCTION

The need for efficient and economical recovery of metals from dilute effluents is motivated by the dramatic development of environmental regulations. To tackle the problem of removing toxic or valuable metals from dilute effluents, biosorption processes have been developed over the last 20 yrs. Many biosorbents, especially of bacterial, fungal, or algal origin (1), have been tested for the recovery of a broad range of metals. More recently, considerable attention has been paid to the use of agricultural waste materials or of waste from the food industry (2). Increasing interest has also been focused on the use of biopolymers extracted from marine materials: alginate (from algae) and chitin and chitosan (from crustaceans). The presence of chelating functions on these biopolymers (carboxylic functions for alginate, amine groups for chitosan) explains the growing interest in testing their ability to recover metal ions (3–5).

Chitosan is an aminopolysaccharide that is produced, by alkaline deacetylation, from chitin, the most abundant polysaccharide in nature after cellulose. The presence of amine groups explains 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 to ensure 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) (12–14). 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 (15), including solution type, solution composition, pH, temperature, membrane material, pore size, and hydrodynamics. 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 out (15–19).

Although there is abundant literature on the use of chitosan for metal sorption, only a few studies have focused on the use of chitosan for PEUF (20–22). This study focuses on the use of chitosan dissolved in HCl solutions for the binding of mercury and the subsequent separation of loaded macromolecules by an Amicon ultrafiltration unit. Alternatively, poly(ethylenimine) (PEI) was used. This is an amine-bearing polyelectrolyte that has also been tested for the recovery of metal cations (23–28). Polymers can be characterized by different parameters such as their molecular weight; the fraction of primary, secondary, and tertiary amine groups; and the type of structure (linear or branched polymer). In this study, a high-molecular-weight–branched polymer was used. The efficiency of the process was investigated using membranes of different cut-off (10, 50, 100 kDa). The influence of pH, metal concentration, chitosan concentration and pressure on the flux, and retention of both polymer and metal was studied. Ultrafiltration performances can be correlated to the sorption behavior of the biopolymer, and it is, thus, possible to predict the uptake performance of the dissolved biopolymer and anticipate the chemical modifications required to increase its efficiency.

MATERIAL AND METHODS

Material

Chitosan was supplied by Aber Technologies (Plouvien, France). The characteristics of the samples had previously been determined (9). 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. PEI was supplied by Fluka AG (Switzerland); its molecular weight was 600,000–1,000,000 g mol^{-1}. It is important to comment that the polymer was used as supplied and was not treated by ultrafiltration before being used. Pretreatment would have removed small polymer chains that could permeate through the membrane, and would increase retention efficiency. Mercury nitrate was also purchased from Fluka AG. Other common reagents were supplied by Carlo Erba (Italy).

Ultrafiltration Module

Ultrafiltration experiments were performed using an Amicon 8400 ultrafiltration module 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 by means of a local pressurized air network using suitable manometers. Experiments were performed under transmembrane pressure differences, ΔP (bars), ranging from 0.5 to 2.5 bars. In the text, the transmembrane pressure difference will be written as pressure applied to the system. The membranes were cleaned and checked between successive experimental series. The check was carried out by determining the water permeation rate under fixed conditions (pressure: 1 bar). The cleaning of the membrane was stopped when variation in the permeation rate was less than 5% of the permeation rate of the reference material (first use of the membranes).

Ultrafiltration Experiments

Chitosan was dissolved in a suitably concentrated HCl solution, and the solution was mixed with metal solution at fixed concentrations. PEI was directly diluted in water. The mixture was agitated under pH control for 2 h prior to 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 (at least 5) successive fractions of 25 or 50 mL was monitored. The flux (J, $\mathrm{L\,m^{-2}\,h^{-1}}$) 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 were taken from these fractions to determine both metal and polymer content. Blank experiments were performed using mercury-containing solutions (without addition of polymer) in order to determine the amount of metal that could be retained by sorption on the experimental equipment (glassware, ultrafiltration membrane). The amount of mercury that was "passively" retained did not exceed 3%, which can be neglected. Polymer concentration was determined using a Shimadzu TOC-5000 TOC-meter (Japan) and a calibration curve prepared from pure chitosan solutions (or PEI solutions). Metal concentration was determined using an Inductively Coupled Plasma Atomic Emission spectrometer (JOBIN-YVON JY 2000, Longjumeau, France).

RESULTS AND DISCUSSION

Characterization of the Permeability Properties of Ultrafiltration Membranes

Since the formation of a filtration cake at the surface of the membrane during the ultrafiltration of the polymer-containing solutions is a controlling parameter in the efficiency of the process (flow-rate control), it is necessary to determine water permeability rates without any polymer. Figure 1 shows the profiles of flow rates for the three membranes (M10, M50, and M100) at different pressures. Flux varied linearly with the pressure. Moreover, it was empirically observed that 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).

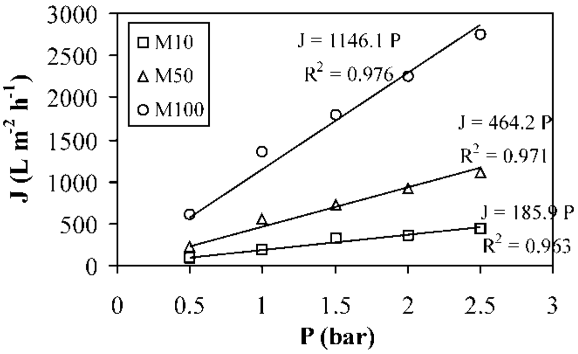

Figure 1. Permeability properties of Amicon membranes for water.

Ultrafiltration of Polymer Solutions

Table 1 gives the ultrafiltration properties of pure solutions of chitosan (at pH 5.5) and PEI (at pH 9.3) (i.e., retention rate and permeation fluxes). There were some noticeable differences in the ultrafiltration of these polymers, regarding the effect of experimental parameters (polymer

Table 1. Comparison of polymer retention and permeation fluxes at different pressures on M50 and M100 membranes for chitosan and PEI solutions (Polymer concentrations: 50, 100, and 200 mg L^{-1}, pH 5.5 for chitosan and pH 9.3 for PEI)

		Chitosan			PEI		
		Polymer conc. (mg L^{-1})					
Membr.	P (bar)	50	100	200	50	100	200
Retention rate (R_P, %)							
50	1	96	93	97	82	88	94
50	2	95	92	97	93	96	98
100	1	87	93	97	87	93	99
100	2	89	93	95	95	96	98
Permeation flux (J, L m^{-2} h^{-1})							
50	1 (1358)[a]	232	172	148	196	157	144
50	2 (2254)[a]	274	217	173	260	250	169
100	1 (554)[a]	234	194	136	265	199	180
100	2 (927)[a]	281	273	161	318	239	215

[a] Permeation fluxes for water.

concentration, pressure, and membrane cut-off). For example, the concentration of PEI had a limited effect on PEI retention while increasing the concentration of the polymer increased chitosan retention (especially for the membrane M100). The concentration of the polymer (whether chitosan or PEI) affected permeation fluxes: an increase in polymer concentration significantly decreased flux (especially for PEI and the M50 membrane). Generally, at low polymer concentration, the retention was significantly higher for PEI than for chitosan, while retention rates were comparable at higher concentrations.

Pressure had a limited effect on polymer retention and permeation fluxes (in the pressure range investigated). In the case of chitosan, additional experiments (not shown) were performed on a M10 membrane at a greater number of different pressures (between 0.5 and 2.5 bars) with a fixed polymer concentration of 200 mg L^{-1}, and the retention rate decreased slightly with increasing pressure but the retention rate remained very high (greater than 98.8%). Logically, the permeation flux increased with increasing pressure, but above a pressure of 1 bar the improvement in permeation was very low (from 65–78 $L\,m^{-2}\,h^{-1}$). Therefore, it is not necessary to increase the operation pressure above 1 bar.

As expected, the type of membrane (its cut-off) influenced the retention rate of both polymers: increasing the cut-off resulted in a greater loss of polymer. In the case of chitosan, this effect was more marked with low polymer concentrations. Logically, higher membrane cut-off increased permeation fluxes in the case of PEI, while it had a limited influence on chitosan solutions.

These differences may be explained by several factors related to differences in (a) polymer weight, (b) molar concentrations (relative to equivalent monomer units), and (c) viscosity of the solution and possible chain/chain interactions (critical entanglement concentration). The molecular weights of the polymer were significantly different: 125,000 g mol^{-1} for chitosan, compared with 600,000 to 1,000,000 g mol^{-1} for PEI. This marked difference may explain the higher retention of PEI. The molecular weights of the equivalent monomer units were 166 g mol^{-1} and 43 g mol^{-1} for chitosan and PEI, respectively. Therefore, the molar concentrations (based on the molecular weight of the equivalent monomer units) were significantly higher for PEI than for chitosan. A key parameter in the control of permeation rates is the formation of a filtration cake at the surface of the membrane. The agitation of the solution at the surface of the membrane is expected to limit the formation of this diffusion-limiting layer. However, this is not sufficient to totally prevent the accumulation of polymer chains or aggregates in the neighborhood of membrane pores. The shape and size of the polymer chains, which in turn controls their retention, may be influenced by coiling phenomena and by the formation of hydrogen bonds between the chains. The ionic strength of the solution, the concentration (below or above the critical concentration of entanglement, C*) control these phenomena. C* is the reciprocal of the limit viscosity of the polymer. Increasing the molecular weight of the polymer increases the limit viscosity of the solution and therefore diminishes C*. Increasing polymer concentration reinforces the interactions between the chains of the polymer and its retention. This has a more marked effect on chitosan than on PEI because even a low PEI polymer concentration (i.e., $50\,\mathrm{mg\,L^{-1}}$) is high enough to make hydrogen bonds between polymer chains. The permeation fluxes were significantly higher for chitosan compared to PEI. At pH 5.5, chitosan is partly protonated; therefore, chains repel each other, and this phenomenon prevents coiling and aggregation. Aggregation may cause the accumulation of large molecules at the surface of the membrane and partial blockage of membrane pores, leading to a dramatic decrease in permeation rates.

Influence of pH on Polymer Retention and Permeation Flux

As pointed out previously, pH is a key parameter in the control of polymer retention. It may cause aggregation phenomena or, conversely, repulsion of polymer chains. However, the pH may also cause precipitation of the polymer. For example, in the case of chitosan, the intrinsic pK_a, which depends on the deacetylation degree and neutralization of charges, is close to 6.5. When the protonated amine groups are neutralized at alkaline pH, the polymer precipitates. This is not the case of PEI in the pH range investigated. Figure 2 shows the effect of pH on polymer retention (top figure) and permeation flux (bottom figure) for both chitosan and PEI. In the case of chitosan, a very narrow pH range was observed for the optimum retention of chitosan (close to 97–98%), at pH close to 4–4.5. Outside this pH range, chitosan retention significantly decreased. However, in the pH range 2–6, polymer recovery exceeded 90%. At very low pH, partial depolymerization of chitosan may occur, which explains why small polymer fractions may pass through the ultrafiltration membrane, while at high pH the decrease in polymer retention may be explained by a change in its conformation. Generally, polymers have a flexible structure, and under certain hydrodynamic conditions the shape of such molecules can change from a sphere to an ellipse or a slim cylinder, enabling them to pass through the membrane even though their mass is less than the nominal cut-off of the membranes used (12). With increasing pH, protonation of amine groups decreases and therefore interchain repulsion decreases; hydrogen bonds between the chains lead to possible modifications of the conformation of the polymer. In the case of PEI, the influence of pH was significantly lower. Actually, the efficiency for polymer retention remained higher than 95 over a broad pH range (ca. pH 2–9). Juang and Chen (23) also observed a very efficient retention of PEI in a

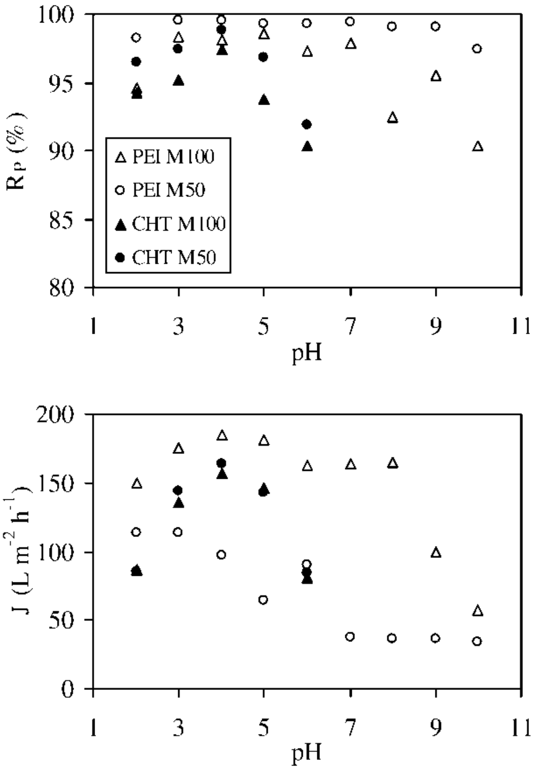

Figure 2. Influence of pH on polymer retention and permeability flux (membranes M50 and M100; polymer concentration, 200 mg L^{-1}).

wide pH range (ca. between pH 3 and pH 7). There are several reasons to explain this difference, the first being that the higher polymer weight of PEI improves retention efficiency. Another explanation may be related to the difference in the structure of the polymers. While chitosan bears primary amine groups as side groups on linear chains, PEI holds primary, secondary, and tertiary amine groups [in the proportion 1 : 2 : 1, respectively (29)], with different acid-base properties for amine groups on branched chains located on the main chains or for side groups. As a consequence, the protonation of amine functions (and the repulsive effect they can cause) remains active over a larger pH range. Kobayashi et al. (30) observed that the pK_a of PEI depends on the structure and, more specifically, the degree of polymerization (varying between 8.5 and 9.15, with decreasing DP) and that less than 75% of total amine groups can be protonated at saturation (i.e., close to pH 2). They compared the chelating properties of linear and branched PEI (in the presence of KCl electrolyte) and also observed that the specific viscosity of branched PEI was significantly lower than that of linear PEI and independent of the pH of the solution, while that of linear PEI reached a minimum between pH 5 and pH 6. It is interesting to observe that branched PEI was significantly more efficient than linear PEI for complexing several metal ions (such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} but not UO_2^{2+}). The conformation of the polymer is a key parameter. Branched PEI can be considered as a spherical polyion (29), while chitosan may be assimilated to a linear polyion. The pH strongly influences the conformation of the polymer: the higher the pH, the lower the amount of protonated positively charged groups, thus making them comparatively more flexible, which can penetrate into the membrane pore more easily than the more rigid ones.

The same trends were observed in the experimental study of permeation flux. A sharp optimum pH range was observed in the case of chitosan, while for PEI the optimum pH range was much broader. The most significant difference was observed with the permeation rates obtained using the M50 membrane. While membrane cut-off hardly influenced permeation rate for chitosan ultrafiltration, the permeation flux dramatically decreased using the M50 membrane in the medium acidic to neutral pH range.

Influence of pH on Mercury Binding on Polymers—Mercury and Polymer Retention, Permeate Flux

The pH was varied in order to measure the binding efficacy of the different systems and determine the optimum pH for metal recovery. To avoid any precipitation problems (metal, polymer), pH variation was limited to pH 6. There were significant differences in the profiles of both mercury retention and polymer retention on chitosan and PEI (Fig. 3). For chitosan, an optimum pH was observed for chitosan recovery at pH close to 3 (in the range 2.5–3.5); however, polymer retention was systematically greater than 94%, independently of the pH. This is slightly higher than the levels reached in the ultrafiltration of pure chitosan solutions. This was completely different in the case of PEI; the retention rate increased continuously from 80 to 96% with increasing pH. This is significantly lower than the levels reached in the ultrafiltration of pure PEI solutions at comparable pHs. In the case of chitosan, the formation of chemical bonds between polymer chains and mercury may cause a kind of cross-linking that improves polymer retention. In the case of PEI, no explanation was found for this decrease in polymer retention.

The profiles for mercury retention are much more interesting. With PEI, metal retention increased with pH. Increasing the pH resulted in a partial neutralization of protonated amine groups and therefore a greater reactivity of

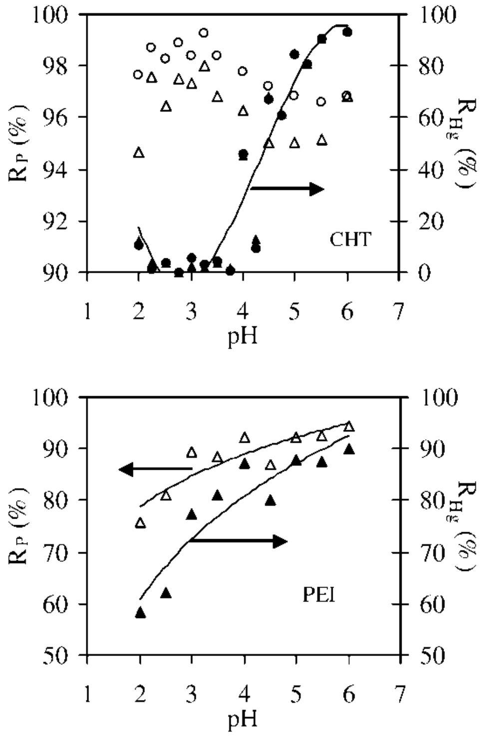

Figure 3. Influence of pH on mercury and polymer retention (membranes, M50 (△/▲) and M100 (○/●) for chitosan (left panel); and M100 for PEI (right panel); polymer concentration: 200 mg L^{-1}; mercury concentration: 25 mg Hg L^{-1}).

amine functions for mercury chelation. However, it is interesting to observe that, even at pH 2–3, mercury retention exceeded 60–75%. In this pH range, though PEI holds different amine functions, the acidic conditions are relatively strong and poorly favorable for the chelation mechanism. The pH of the solution was controlled with hydrochloric acid. Dissociation of the acid adds chloride ions to the solution, which can form chloro complexes with mercury (31). These chloro complexes are anionic ($HgCl_3^-$, $HgCl_4^{2-}$) and can be electrostatically attracted by protonated amine groups of the polymer. A similar pattern was observed at low pH in the case of chitosan. Mercury retention was close to zero in the medium acidic region and increased with increasing pH (chelation favored by the decrease of protonation of amine groups); but at low pH (close to pH 2), there was a small but significant increase in retention efficiency. Similar changes in the uptake mechanism have been observed using chitosan as a sorbent (32–35) under the effect of the presence of ligands (chloride ions, chelating agents). In the case of chitosan, the contribution of electrostatic attraction remained weak compared to what happened with PEI. The sharp increase in the retention profile for chitosan (compared to PEI) may be explained by the fact that the polymer is a simple primary amine compound, while PEI, bearing primary, secondary, and tertiary amines, can contribute to metal chelation in different pH ranges, due to the different acid-base properties of these amine groups. It is interesting to observe that, under the selected experimental conditions, the optimum retention of mercury was slightly higher than that obtained at using PEI.

The mean permeate flux was measured at different pHs for the ultrafiltration of mercury in the presence of chitosan and PEI (Fig. 4), and these curves were compared to those obtained in the absence of polymers. The binding of mercury to chitosan (or PEI) did not significantly change the permeation flux nor affect the influence of pH on the permeation of polymer solutions. Changing the cut-off of the membrane did not change the profile of permeate flux, as was observed in the absence of mercury binding. At maximum permeation (around pH 3) permeate flux was comparable for chitosan and PEI. Since mercury does not bind to chitosan at this pH, it was predictable to find comparable permeation fluxes when mercury is present in the solution.

Matlock et al. (36) have shown that the pH had a very weak effect on the precipitation of mercury using a new ligand 1,3-benzenediamidoethanethiol ($BDETH_2$). Increasing the pH from 4 to 6 resulted in a variation of precipitation efficiency lower than 1%. With this precipitation process, the influence of pH is significantly decreased compared to the PEUF process using chitosan and remained comparable to the behavior of PEUF process with PEI.

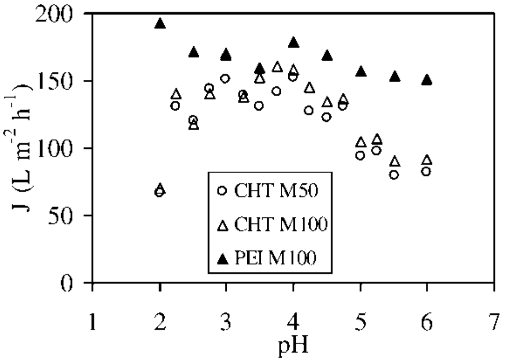

Figure 4. Influence of pH on permeation flux (membranes, M50 and M100; polymer concentration, 200 mg L^{-1}; mercury concentration, 25 mg Hg L^{-1}).

Influence of Initial Ligand/Metal Ratio on Polymer and Metal Retention

The ligand to metal (L/M) molar ratio (initial ratio) was varied in order to determine the effect of polymer excess on metal retention. Figure 5 shows mercury (and polymer) retention rates obtained at pH 5.5 for chitosan and pH 6 for PEI. As expected, increasing the excess of ligand improved mercury retention. However, above a 10-fold excess of ligand (5-fold in the case of PEI), metal retention did not significantly increase. Uludag et al. (24) used a continuous system for the study of mercury PEUF retention with PEI at different L/M ratio and observed that retention stayed close to 99%, while the ratio remained lower than 1 (above this limit, mercury retention drastically decreased). It is important to observe that PEI reached higher retention efficiency than chitosan: under optimum experimental

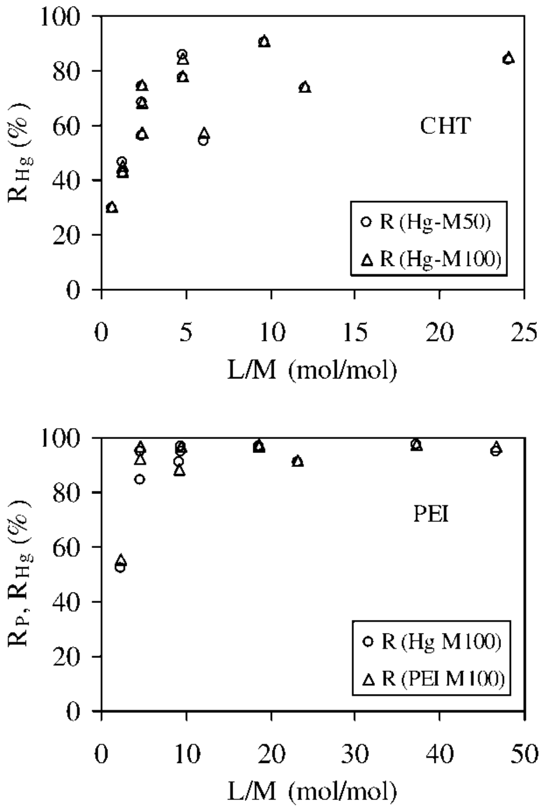

Figure 5. Influence of initial ligand/metal (L/M) molar ratio on metal and polymer retention (pH 5.5 for chitosan; pH 6 for PEI; membranes, M50 and M100).

conditions mercury retention exceeded 95% with PEI, while with chitosan it reached 82–85% (and a maximum at 90%). These experiments were performed by contacting polymer solutions at concentrations of 50, 100, and 200 mg L^{-1} with mercury-containing solutions at concentrations of 10, 25, 50, and 100 mg Hg L^{-1}. In most cases, changing the concentration for a given L/M molar ratio did not significantly change the retention rate; however, with chitosan in the case of low mercury and low polymer concentrations, the retention rate was significantly (and repeatedly) lower than the expected trend. This indicates that it is not only the L/M ratio that should be taken into account but at low concentrations there was a decrease in the efficiency of the system.

Influence of Initial Ligand/Metal Ratio on Permeation Flux

Permeation fluxes were systematically measured, and their mean values were plotted vs. the initial L/M molar ratio (Fig. 6). The curves were completely different for the chitosan and PEI systems. While, in the case of PEI, permeate flux was hardly influenced by the excess of ligand with a permeate flux that remained almost constant and close to 100 L m^{-2} h^{-1}, for chitosan, increasing the excess of polymer dramatically reduced permeation flux. The curves were plotted with reference to polymer concentration: for a given L/M ratio, the permeation rate strongly decreased with increasing chitosan concentration. The excess of polymer, not involved in mercury sequestration, contributed to limiting the permeation rate by accumulation at the surface of the membrane. The differences between the different chitosan concentrations tended to level off when the L/M ratio increased; and the asymptotic trend overlapped with the curves obtained using PEI as the macroligand. At low L/M ratio, the mercury present in the solution contributed to linkages between the polymer chains and limited the accumulation of free polymer chains at the entrance to membrane pores. These results are confirmed by plotting permeation flux vs. initial mercury concentration (bottom panel of Fig. 6) for different polymer concentrations. Except at very high mercury and low PEI concentrations, the permeation flux was independent of mercury concentration, whatever the concentration of PEI. On the other hand, the permeation flux increased drastically when mercury concentration increased, especially at low relative polymer concentration. The interactions of mercury ions with amine groups of chitosan contribute to a kind of cross-linking of the polymer that may (a) improve the permeation by reducing the agglomeration of polymer chains or the accumulation of free polymer chains on the surface of the membrane and (b) prevent the formation of a filtration cake. Similar interactions of chitosan in a dissolved state with metal ions have been cited for the coagulation of chitosan (37, 38).

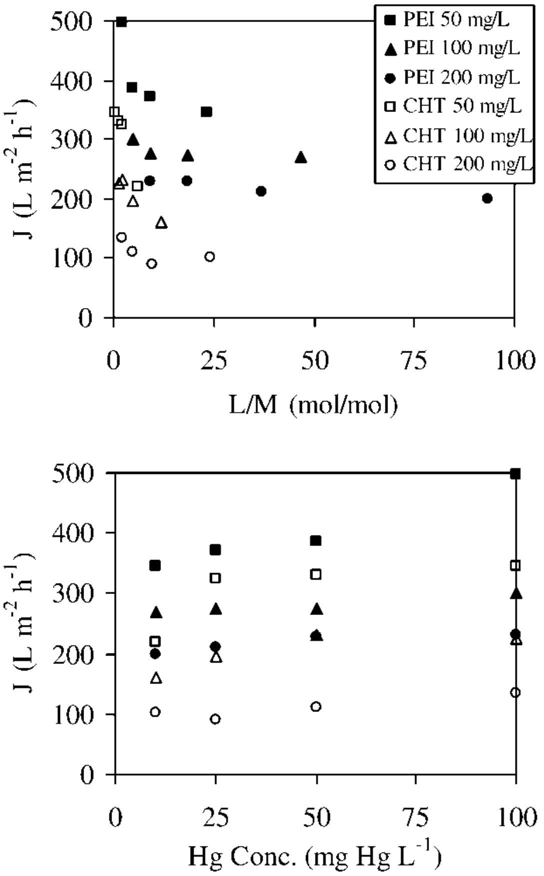

Figure 6. Influence of initial ligand/metal (L/M) molar ratio on permeation flux (pH 5.5 for chitosan; pH 6 for PEI; membranes, M50 and M100).

Influence of Initial Ligand/Metal Ratio on Binding Capacity of Polymers

The mass balance equation was used to calculate the amount of metal that reacted with polymer chains. These amounts were converted to molar units in order to calculate the binding capacity (q, $\mathrm{mmol\,Hg\,mol^{-1}}$ monomer unit). These binding capacities were plotted vs. the initial L/M molar ratio for the different systems (Fig. 7). The binding capacity strongly decreased with increasing L/M ratio. Experimental data fitted a power function. In the case of PEI, the exponent (-0.9) is close to -1. It is also important to observe that at low L/M molar ratios, binding capacities were significantly greater (at least 3 times) for chitosan compared to PEI. At high L/M molar

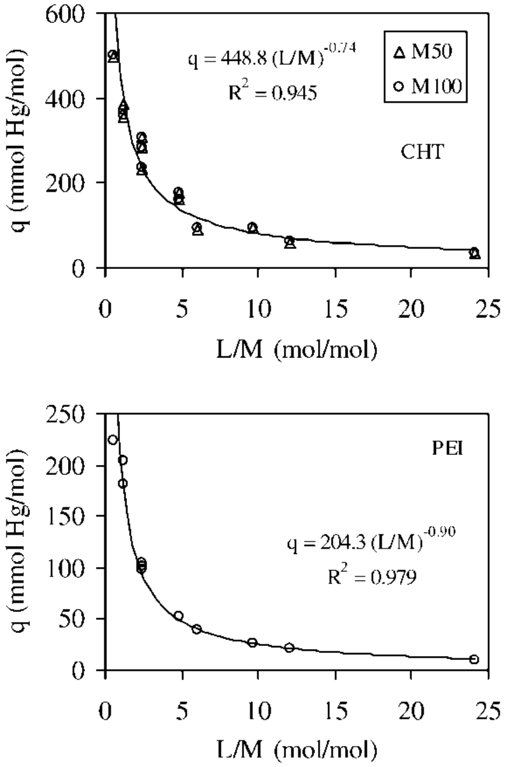

Figure 7. Influence of initial ligand/metal (L/M) molar ratio on molar ratio Hg/mol (monomer unit) (pH 5.5 for chitosan; pH 6 for PEI; membranes, M50 and M100 for chitosan and M100 for PEI).

ratio, the differences tended to level off, but binding capacities for chitosan remained higher (still three times higher for chitosan than for PEI). This indicates that the primary amine functions of chitosan are significantly more reactive than the amine groups of PEI. It is more efficient to use the amine functions in chitosan than those in PEI. Uludag et al. (24), in a continuous PEUF system using PEI for Hg retention, observed a significantly greater binding capacity (at complete recovery of mercury, greater than 99%), corresponding to approximately 1 g of Hg per g of PEI.

Binding Curves

The binding capacity (expressed again in mmol Hg mol^{-1} monomer unit) was plotted vs. the residual metal concentration (concentration in permeate).

Figure 8 shows the results obtained with chitosan and PEI. While the initial slopes of the binding curves were almost identical for the chitosan and PEI systems, the saturation plateau was reached at a lower mercury concentration in the case of the PEI macroligand (compared to chitosan). The maximum binding capacity at saturation was almost doubled for chitosan compared to PEI (480 vs. 220 mmol Hg mol^{-1} monomer unit). There was much better efficiency in the use of amine functions with chitosan than PEI. This may be explained by several reasons: (a) better accessibility of reactive groups due to the hydrophilic properties of chitosan (provided by the $-$OH groups of glucose unit); (b) better availability of amine groups, less involved in hydrogen bonds (lower molar concentrations and effect of critical entanglement concentration); (c) a conformation more favorable for metal chelation (stiffness of chains, aggregation and coiling). It is interesting to observe that mercury sorption capacities on solid-state chitosan (calculated using the same molar system of units, mmol Hg mol^{-1} monomer unit) are lower (by 10–20%) than those obtained in the PEUF system. It is possible to compare the present results with those obtained in the precipitation of mercury by Matlock et al. (32, 39). They obtained with 1,3-benzenediamidoethanethiol and with a new multidentate ligand a 1 : 1 stoichiometric ratio between the metal (mercury) and the ligand. This is higher than the levels reached with chitosan and PEI. The binding capacities are comparable to the sorption capacities obtained with self-assembled monolayers on mesoporous supports (SAMMS) (40, 41).

Another advantage of the PEUF system is related to the kinetics of the process. In the case of the sorption process on chitosan, using similar experimental conditions (pH, metal concentration, sorbent dosage) a 12- to 24 h

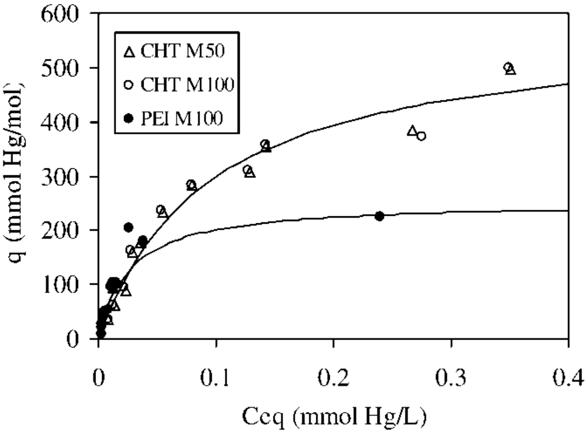

Figure 8. Binding curves (plot of binding capacity in mol Hg mol^{-1} monomer unit vs. residual molar concentration of mercury).

contact time was usually necessary to reach the equilibrium. This contact time sounds very long, but it is necessary to point out that very low sorbent dosages have been used (around 100 mg L^{-1}), compared to other studies (40), in order to identify the limiting diffusion steps. In the case of chitosan used in the dissolved state, the contact time was reduced to the time required for pH control and stabilization (ca. 1–2 h). This may be due to better accessibility to sorption sites. The dissolving of the polymer destroys the residual crystallinity of the material (solid state). The interactions between polymer chains (hydrogen bonds) disappear (except at high concentration of polymer, above critical entanglement concentration), so functional groups remain more available.

The short contact time required in the PEUF process is comparable to the time required by precipitation process using new ligands, though Matlock et al. (32) observed an increase of mercury removal at increasing reaction time. In the case of SAMMS, Mattigod et al. (40) decreased by more than 95% initial mercury concentration within the first 30 min of contact at low mercury concentration (100 mg Hg L^{-1}) and within the first 2 h of contact at higher mercury concentration (about 350 mg Hg L^{-1}), almost independently of the pH (with a high sorbent dosage compared to present experiments, 1.25 g sorbent L^{-1}).

Influence of Chloride Addition on Ultrafiltration Performance

The speciation of mercury is drastically influenced by the composition of the solution, especially the pH and the presence of ligands. For example, in the presence of chloride ions, the distribution of mercury is displaced to the formation of chloro complexes, which may be cationic, neutral, or anionic, depending on chloride concentration and pH. This change in the speciation of mercury may strongly affect the interaction of mercury with polymers. In the case of chitosan, Kawamura et al. (4) have shown that mercury can be adsorbed in acidic solutions when the pH is controlled by HCl, while the metal was not adsorbed when the pH of the solution is adjusted with H_2SO_4. They explained this result by the possibility of protonated chitosan (in acidic solutions) attracting anionic chloro complexes, whereas the absence of chloride ions (in sulfuric acid solutions) did not allow the formation of anionic chloro species so mercury cannot be immobilized on the protonated amine groups on polymer chains. For this reason, the influence of chloride addition on the retention of mercury and more generally on ultrafiltration performances (polymer retention, permeation flux) was considered. Figures 9 and 10 show the effect of the addition of different chloride-containing salts (NaCl, $CaCl_2$, and NH_4Cl), at a concentration of 0.1 M and various pHs, on mercury and polymer retention; and permeation fluxes, respectively. Figure 9 shows that the behaviors of chitosan and PEI due to the effect of chloride were significantly

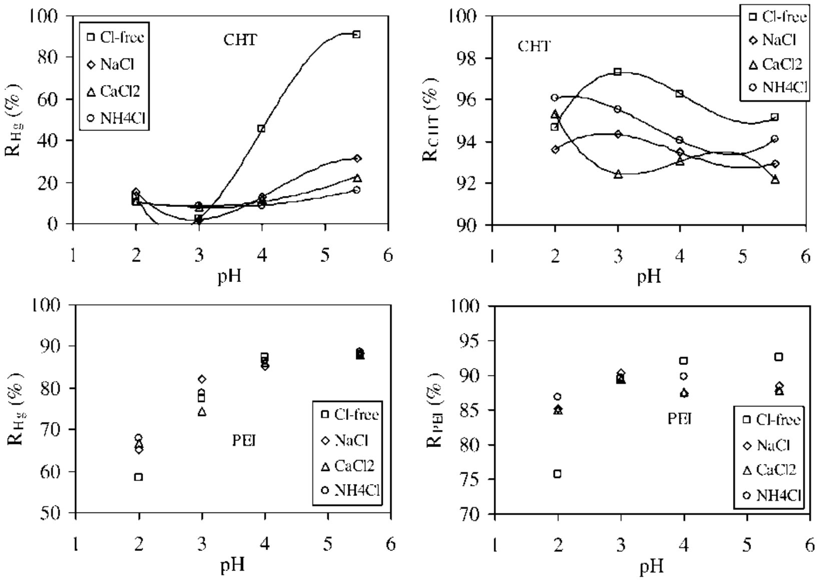

Figure 9. Influence of chloride addition on mercury and polymer retention (polymer concentration, 200 mg L^{-1}; mercury concentration, 25 mg L^{-1}; salt addition, 0.1 M; pH 5.5 for chitosan and pH 6 for PEI; membrane M100).

different. Although the addition of chloride salt did not significantly change mercury retention with PEI, it was sharply diminished in the case of chitosan. Retention did not exceed 32% for the biopolymer at optimum pH (ca. pH 5.5). Retention increased slightly with increasing pH in the case of chitosan but more significantly with PEI (according to the trends observed in the absence of chloride ions). On the other hand, the presence of chloride

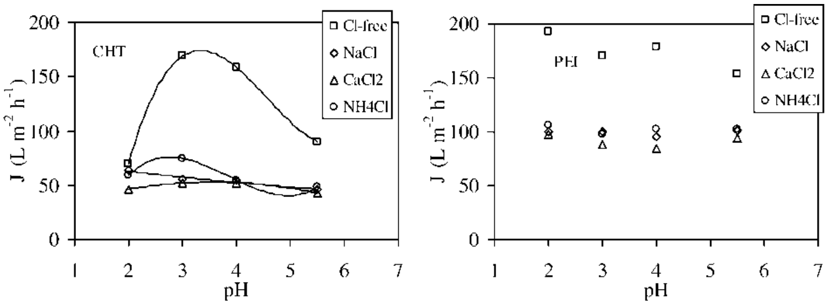

Figure 10. Influence of chloride addition on permeation flux (polymer concentration, 200 mg L^{-1}; mercury concentration, 25 mg L^{-1}; salt addition, 0.1 M; pH 5.5 for chitosan and pH 6 for PEI; membrane M100).

hardly affected polymer retention. From these observations, it can be concluded that mercury transfer through the membrane cannot be explained by polymer loss (mercury being bound to small polymer chains); and that a better explanation must be the lack of reactivity of the polymer with mercury species. The decrease of mercury retention in the presence of chloride ions in the case of chitosan may result from (a) the competition effect of chloride ions on protonated amine groups and/or (b) the formation of mercury species that cannot be chelated by amine groups at close to neutral pH. In the case of PEI, the branched polymer can be characterized as alternating units of $-CH_2$-CH_2-NH- and $-N$-$(CH_2)_2$-$(CH_2$-$CH_2NH_2)$. Therefore, the polymer bears primary, secondary, and tertiary amine groups, whose acid-base properties are affected by neighboring groups. The change in acid-base properties may affect the protonation of these groups and their reactivity for anionic chloro complexes. Another reason for this lower effect of chloride ions is related to the density of amine groups. It is interesting to observe, in the case of PEUF of Cu–EDTA chelates using PEI, that Juang and Chen (23) noticed a strong effect of salt addition, in contrast with the results of the present study. However, this divergence may be explained by a different mechanism: in the case of Cu–EDTA chelates, the predominant binding mechanism is electrostatic attraction, which is very sensitive to the presence of competitor ions. Taking into account the diversity of monomer units and their structure, it is possible to calculate the molar mass as being 43 g per equivalent monomer unit, as compared to the molar mass of the equivalent unit of chitosan (i.e., 166 g). As a consequence, the sorption density (in amine groups, whether primary, secondary, or tertiary) was more than four times higher for PEI than for chitosan. In the previous section, it was shown that there is greater efficiency in the use of amine groups in the case of chitosan (compared to PEI), whereas in the synthetic polymer the higher density of amine groups contributes to decreasing the impact of competitor anions (Cl^-). The weak competition effect of chloride on mercury retention by PEI may be explained by a stronger binding of mercury on amine groups of PEI compared to the formation constants of mercury with chloride. Usually, chelation mechanisms are little affected by the composition of the solution, compared to the ion exchange mechanism. However, in the present case the change in the speciation of mercury with chloride addition makes the interpretation of the interaction mechanism more complex since the predominant species in the solution changes with experimental conditions. Therefore, the binding mechanism should be considered to be a combination of these mechanisms (i.e., chelation and electrostatic attraction) whose proportions depend on the pH, the relative excess of chloride ions (vs. mercury), and the properties of the polymer (acid-base properties, chelation properties). It is interesting to observe that the effect of chloride was hardly influenced by the type of salt used.

Ionic strength also influences the stability of the metal ions to bind the polymer (19). This is attributed to a change in the value of the dissociation constant during filtration, due to screening effects, changes in the polymer conformation, and competition between monovalent and polyvalent metal ions for binding the polymer.

Figure 10 shows that the presence of chloride ions strongly decreased the permeation rate, especially in the case of chitosan. In the case of the biopolymer, the permeation flux was almost divided by three at the optimum pH (i.e., pH 3–4 for permeation rate); while in the case of PEI, it was decreased by 30–40%. Whatever the polymer, the pH had a very weak effect on permeation properties. The flux remained almost constant between pH 2 and pH 5.5. At pH 2, permeation fluxes were comparable whether in the presence or absence of chloride salts. The type of salt did not significantly affect the effect of chloride addition on permeation flux. This effect of chloride ions on permeation fluxes may result from different mechanisms. The protonation of amine groups at low pH results in electrostatic repulsion of cationic polymer chains, which remain highly dispersed in the solution and thus do not tend to agglomerate and form a layer at the surface of the membrane. With the addition of chloride ions (and their attraction by protonated chains) the cationic chains are at least partially neutralized. The electrostatic repulsion of the chains is assumed to decrease. Therefore, interactions may occur between polymer chains (with hydrogen bonding between monomers of the same or to adjacent chains) leading to coiling and aggregation/entanglement. As a consequence, these agglomerates may accumulate at the surface of the membrane, resulting in a significant decrease in permeation flux.

It was interesting to check whether the concentration of chloride salts affected ultrafiltration performances. The concentration of NaCl was varied between 0 and 0.5 M, and the results are summarized in Fig. 11. This figure confirms the trends observed in previous figures. In the case of PEI, increasing NaCl concentration hardly influenced mercury and polymer retention. The concentration of chloride ions more significantly influenced permeation flux, which was almost halved when the salt concentration was increased to 0.5 M. In the case of chitosan, the concentration of chloride had a non-negligible effect. Though most of the decrease in ultrafiltration performance was observed between 0 and 0.1 M NaCl addition, mercury retention and permeation rate continued to decrease above 0.1 M NaCl concentration. On the other hand, chitosan retention was not significantly affected by the concentration of NaCl (consistently with previous experiments).

Gel Concentrations

The influence of mercury concentration on permeation flux raises questions concerning the effect of interactions between the metal and polymer on the

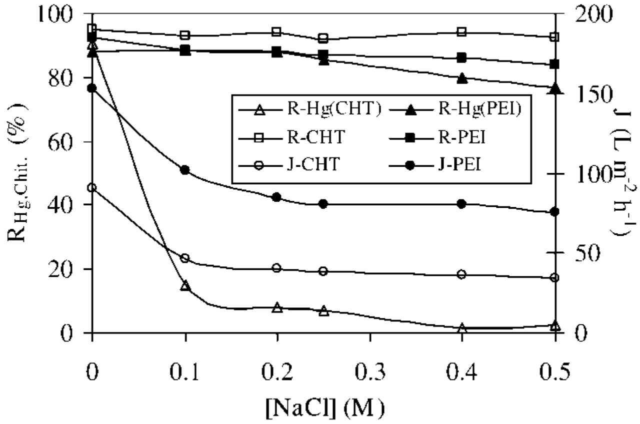

Figure 11. Influence of NaCl concentration on mercury and polymer retention rates and permeation flux (polymer concentration, 200 mg L^{-1}; mercury concentration, 25 mg L^{-1}; salt addition, 0.1 M; pH 5.5 for chitosan and pH 6 for PEI; membrane M100).

conformation of the polymer. The time necessary for the permeation of given volumes (typically 25 mL) during ultrafiltration experiments was systematically monitored at each step of the process. While the mean value was used to estimate the mean permeation flux, the "individual" values are very important for interpreting the permeation mechanism and identifying the limitations of the process. At each step of the process (after collecting each 25 mL fraction), knowing the retention rate of the polymer, it was possible to calculate the residual concentration of the polymer in the retentate and therefore to plot the relative permeation rate (ratio of experimental permeation rate, J, to the permeation rate of water, J_o, under comparable experimental conditions) in function of residual polymer concentration. Tangvijistri et al. (18) used this method to calculate the "gel concentration" of a polyelectrolyte [poly(diallyldimethyl ammonium chloride), QUAT] for the PEUF of anions (such as sulfate, nitrate, and chromate). They plotted J/J_o vs. the logarithm of polymer concentration and projected the curve to the X-axis; the intercept gives the gel concentration, which depends on experimental conditions and more specifically on the interactions of the polyelectrolyte with the solute (anions). In their experiments, they used high polymer concentrations compared to the present work. The same methodology was used; the concentration of the polymer was calculated using the molar mass of the equivalent monomer unit (i.e., 166 g mol^{-1} for chitosan and 43 g mol^{-1} for PEI). However, due to the range of polymer concentrations used in this study, it was difficult to obtain the X-axis intercept very accurately; and the results presented may be considered only as an indication of the order of magnitude of gel concentrations. Figure 12 summarizes the data obtained in the ultrafiltration of solutions containing 100 mg L^{-1} or 200 mg L^{-1} of polymer and 25 mg Hg L^{-1} (at the optimum pH; i.e., pH 5.5 for chitosan and pH 6 for PEI). In the case of chitosan, it was possible to combine the results obtained with a batch containing either 100 mg L^{-1} or 200 mg L^{-1}, the J/J$_o$ profiles tended to superimpose almost independently of the initial concentration of the polymer and the initial concentration of mercury. Gel concentration in this case varied between 10$^{0.8}$ M and 10$^{0.9}$ M (i.e., 6.3 and 8 mM, or 1–1.3 g chitosan L^{-1}). It was significantly different in the case of PEI, where the J/J$_o$ profiles were significantly influenced by the initial conditions of the system (polymer and metal concentrations). At low initial concentration of PEI (i.e., 100 mg PEI L^{-1}), the gel concentration varied between 10$^{1.2}$ M and 10$^{1.4}$ M (i.e., 15 and 25 mM, or 0.7–1.1-g PEI L^{-1}). At higher initial concentration of PEI (i.e., 200-mg PEI L^{-1}), the gel concentration was higher and increased to 10$^{1.8}$ M (i.e., 25 mM, or 2.7 g L^{-1}) at a mercury

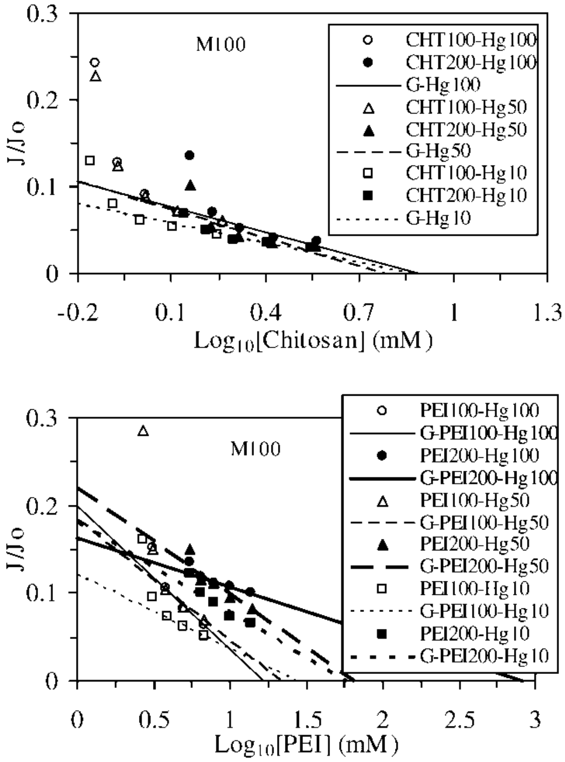

Figure 12. Determination of gelling concentration of polymers in the presence of mercury (pH 5.5 for chitosan and pH 6 for PEI).

concentration of 10–50-mg Hg L^{-1}, while the gel concentration drastically increased to $10^{3.3}$ M (i.e., 0.8 M, or 34 g L^{-1}) when the concentration of mercury increased to 100 mg L^{-1}. The reaction of mercury with polymer chains led to the formation of structured aggregates with enhanced permeability properties. Tangvijitsri et al. (18) observed in the case of anion PEUF with QUAT that a higher [QUAT]/[anion] ratio results in a lower gel concentration. They explained this result by the lower bound counterion/repeating unit polymer unit causing the polymer to be less coiled, forming a more entangled network of polymer chains in the gel layer, which in turn reduces flux.

CONCLUSIONS

Amine-bearing soluble polymers (chitosan and PEI) were shown to be efficient at chelating mercury in dilute solutions. After mercury chelation, loaded polymers can be retained by ultrafiltration membranes in order to recover mercury in a concentrated phase. Comparison of the synthetic and natural polymers showed that the synthetic polymer (with a higher molecular weight) was more efficient than chitosan at removing mercury from 10 to 100 mg Hg L^{-1} solutions. Retention efficiency is usually greater for PEI than for chitosan. Moreover, the permeation fluxes are generally higher for PEI than for chitosan. Because PEI bears primary, secondary. and tertiary amine groups (with different acid-base properties), its retention and metal binding performances are less influenced by pH than those of chitosan. However, considering the maximum binding capacities (mmol Hg mol^{-1} monomer unit) found in this study, it appears that the amine groups on chitosan are used more efficiently than those present on PEI. This may be explained by a lower reactivity of some substituted amine groups. There are also some other significant differences in the behavior of these amine-bearing polymers. While the interaction of PEI with mercury did not significantly affect permeation flux, the reaction of mercury with chitosan significantly improved permeation flux, undoubtedly due to a kind of cross-linking effect that stabilizes the polymer and prevents the deposition of free polymer chains at the surface of the membrane or limits the coiling of the polymer. Increasing the amount of polymer strongly affected permeation flux; however, increasing the L/M ratio above 5 or 10 does not improve metal recovery but increases permeation limitations. Therefore, an optimization process is required to ensure efficient use of the polyelectrolyte and optimum hydrodynamic properties (permeability). Compared to the sorption properties of solid chitosan (under similar experimental conditions) using the biopolymer in a dissolved state (a) reduces the contact time needed to reach equilibrium and (b) increases the efficiency of amine groups (greater molar ratio Hg/$-NH_2$). This is explained by better accessibility of reactive groups (open structure of the polymer in its dissolved state) and better availability (amine functions are not involved in hydrogen bonds with other functional groups in the same chain or from adjacent chains). Surprisingly, the presence of chloride ions strongly influences mercury retention when using chitosan, while it does not influence the binding behavior in the case of PEI. This is an indication of differences in the binding mechanism: Gel concentrations, which depend on the macroligand/metal ratio in the case of PEI, are generally higher than those observed in the case of chitosan. However, the polymer concentrations studied in the present work were relatively low ($50-200\,\mathrm{mg\,L^{-1}}$), and it would be necessary to increase the concentration range to confirm these trends.

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