Novel Metal-Complexing Membrane Containing Poly(4-vinylpyridine) for Removal of Hg(II) from Aqueous Solution

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A novel poly(vinyl alcohol)/poly(4-vinylpyridine) (PVA/P$_4$VP) complexing membrane for removal of Hg(II) ions from aqueous solutions represents a significant improvement over a previously reported PVA/ poly(ethylenimine) (PEI) membrane. This membrane was prepared by the semi-interpenetrating polymer network technique, and its cross-linking by three different agents was studied. The best results were obtained with gaseous 1,2-dibromoethane at 140 °C for 1 h that gave a membrane with a swelling ratio of 0.66. The sorption reaction of Hg(II) followed a first-order rate law, and the rate-limiting step was shown to be the association of Hg(II) ions with the complexing sites of P$_4$VP. Sorption experiments at pH 2.5 showed that the retention ratio could reach 100% under optimized conditions for the initial concentration of Hg(II) and mass of membrane, $c_0 = 100$ mg L^{-1} and $m_D = 100$ mg, respectively. The retention ratio was remarkably insensitive to water hardness or the presence of NaCl, suggesting possible use for the purification of real wastewaters. The retention capacity of the membrane was 450 mg g^{-1} compared to 311 mg g^{-1} reported for the PVA/PEI membrane. Sorption isotherms were determined at various temperatures, according to the Langmuir model, for the determination of the thermodynamical parameters. When T increased, mercury uptake at equilibrium did not change, whereas the sorption coefficient b decreased and the change in free energy $\Delta G°$ decreased. This result is probably due to a large favorable entropic effect, ascribed to the displacement of protons from the protonated sites of P$_4$VP while they bind with Hg(II) ions. The membrane could be regenerated by 0.5 M nitric acid with less than 3% loss of efficiency. The membrane was used for filtration experiments. The elimination ratio was 99.9% or more for filtration of Hg(II) solutions in the $c_0 = 16.6-89.1$ mg L^{-1} range.

Introduction

The development of industrial activities throughout the world results in an increasing release of chemicals and heavy metals in the environment. Consequently, the health risks due to the accumulation of heavy metals in the human body become a matter of growing concern. Among heavy metals, a serious threat is represented by mercury, due to its toxicity at low levels and its widespread presence in the aquatic environment.[1−6] This element exists in three major forms: elemental (metallic) mercury, inorganic mercury compounds, and organic mercury.[3] Although some natural sources release little elemental mercury to the environment, anthropogenic emissions from coal-fired electric power generation facilities, chlor-alkali production, waste incineration, and other industrial activities represent the main current sources of mercury.[1−10] However, it is now widely recognized that chronic exposure to all forms of mercury can harm the central nervous system and the renal system.[6,11,12] This has led to regulatory actions to reduce the exposure of humans to mercury on many fronts. According to the Agency for Toxic Substances and Disease Registry (ATSDR), it is necessary to alleviate this metal from aquatic systems.[12]

As for other heavy metals, many methods are available for the removal of mercury from wastewaters.[7−13] All heavy metals can be removed by nonspecific adsorption on solid matrixes, such as activated carbon, metal oxides, and ion-exchange materials, or by specific adsorption on suitable sorbents. A specific sorbent consists of a ligand (e.g., a complexing or chelating agent) that interacts with a metal ion specifically, and a support matrix, which may be an inorganic material (e.g, aluminum oxide, silica or glass) or an organic material (e.g, poly(methyl methacrylate), polystyrene, cellulose). Specific sorption can take place with a resin (often in beads form) or with a membrane, the latter having the advantage of shorter filtration time. An interesting membrane technique for the removal of heavy metal ions is polymer-enhanced ultrafiltration (PEUF).[9,14] This technique is based on the complexation of the metal ions by water-soluble complexing polymers, in order to form complexes of large size that are retained in subsequent ultrafiltration (UF). In PEUF, frequently used complexing polymers are synthetic poly(acrylic acid), poly(ethylenimine) (PEI), and their derivatives,[7,9] or natural ligands, such as alginate and chitosan.[8]

During the past decade, several metal-retaining membranes, containing a variety of complexing or chelating ligands, have been reported to efficiently remove heavy metals.[15−20] The research field of our team is the design of UF membranes in which the complexing water-soluble polymer is integrated, in order to group the complexation and filtration steps in a single operation.[20−22] Thus, these complexing membranes will retain the metal ions during the filtration. This principle slightly differs from that of PEUF, in which the complexed metal ions are rejected in the retentate. The first advantage of such complexing

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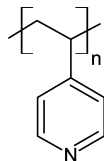
Figure 1. Formula of poly(4-vinylpyridine), P_4VP.

membranes is that the amount of polymer used is much lower than in PEUF. A second advantage is that the method possesses the same selectivity as PEUF, when provision is made for the appropriate choice of the complexing polymer. Like PEUF, such membranes cannot be operated continuously, because the membrane accumulates metal ions and must be periodically regenerated. Because the complexing polymer is water soluble, its incorporation must be followed by immobilization in the membrane. This may be achieved by grafting a complexing polymer on an inert polymer matrix such as low-density polyethylene (LDPE).[23] A simpler way for immobilizing the complexing polymer in the matrix is the semi-interpenetrating polymer network (s-IPN) technique. In this case, chains of a complexing polymer are immobilized, without chemical bonding, within the matrix network of a cross-linked polymer. We have previously established that poly(vinyl alcohol) (PVA) was particularly suitable for the matrix, because of its excellent film-forming properties and high density of hydroxyl groups that provides numerous sites for cross-linking.[20−22] Several reagents, such as gaseous 1,2-dibromoethane (DBE), glutaraldehyde (GL), and hydrochloric acid (HCl), have been reported as cross-linkers for the PVA matrix.[20−22,24−26]

A PVA/PEI membrane of this type was recently reported to be efficient for the removal from aqueous solutions of Pb(II), Cd(II), and Cu(II)[22] or Hg(II).[27] However, whereas excellent retention of the metal ions was observed, this membrane was not really reusable, because regeneration in 0.5 M HNO_3 was accompanied by extensive degradation, whereas regeneration in 0.05 M HCl or HNO_3 was not quantitative. These results prompted the study of membranes containing ligands with a better resistance to oxidizing desorption agents. Poly(vinylpyridine) seemed a likely candidate, because the presence of an aromatic ring results in increased stability of the polymer. Moreover, poly(vinylpyridines) and their copolymers are commercial compounds commonly used as ion exchangers.[28−30]

The subject of this work was the design of a novel complexing membrane containing poly(4-vinylpyridine) (P_4VP, Figure 1) as an efficient ligand for mercury. P_4VP is known to be a ligand for heavy metals,[28,29,31−35] and was used as a sorbent for precious and noble metals.[36] P_4VP cannot be expected to be a specific sorbent for Hg(II), because the electron donor is nitrogen, as for PEI, and therefore P_4VP is a soft ligand that will complex soft metal ions such as Cd(II) and Pb(II). Hence, these metal ions are likely competitors for mercury. The case of borderline metals such as Cu and Fe is not so clear. It was shown that Cu(II) was quite well retained by a PVA/PEI membrane,[22] and this unexpected result was attributed to additional complexation by the PVA matrix. The case of Fe is also of interest, because this metal is present in large concentrations in many hydrometallurgical waste streams. In principle, P_4VP should not present a high affinity for the hard Fe(III) ion, whereas the hard PVA matrix could show some affinity; the borderline Fe(II) ion is expected to show less affinity than Cu(II) for the ligand, as is known for the Irving−Williams series.[37] In fact, the complete study of the interferences in mercury removal should be specifically made for each real projected application.

In this paper, we report the preparation and characterization of a novel PVA/P_4VP membrane. The performances of this membrane for removal of Hg(II) from aquatic systems under a wide range of conditions were investigated. The sorption properties of the membrane were determined by considering many experimental factors, such as pH, contact time, initial metal ion concentration, ionic strength, water hardness, and temperature, that have a large variability in real wastewaters. Throughout this paper, the binding of Hg(II) ions with the membrane will be referred to as sorption rather than adsorption, because there is no proof that binding takes place only at the membrane surface, and experimental data suggest that at least part of the complexing sites present within the membrane are involved in metal removal. Sorption of Hg(II) ions from aqueous solutions by the membrane was investigated by static and dynamic experiments. Sorption isotherms and kinetic models were used with isotherm modeling to study the sorption behavior. The effect of the temperature on mercury complexation was accounted for by calculating the relevant thermodynamical data.

Experimental Methods

Chemicals and Materials. PVA (99% hydrolyzed, $\bar{M}_w = 124\,000−186\,000$ g mol^{-1}) and P_4VP ($\bar{M}_w = 160\,000$ g mol^{-1}) were provided by Sigma-Aldrich.

Commercial GL 25% (v/v) (Merck-Schuchardt), magnesium chloride hexahydrate (Sigma-Aldrich), DBE (99%) (Sigma-Aldrich), aqueous solutions (Sigma-Aldrich) of acetic acid (1 mol L^{-1}), nitric acid (65%), and hydrochloric acid (37%) were used without further purification.

The solutions of Hg(II) ions were prepared by dissolving weighed amounts of mercury nitrate (Aldrich) in purified water (Milli-Q). The pH was measured with a Tacussel LPH-230T pH-meter fitted with a combined glass electrode.

Commercial salts, sodium chloride, and calcium nitrate were commercial coumpounds (Sigma-Aldrich) of the highest available grade.

During the sorption experiments, aliquots of aqueous solutions containing Hg(II) were withdrawn for analysis. The determination of the concentration of mercury in these samples was performed by atomic absorption spectroscopy (AAS), using a Spectra AA 10/20 flame atomic spectrometer from Varian, Mulgrave, Australia. Mercury standard solutions (1 wt %/v in HNO_3) from Sigma-Aldrich were used for the calibration of the spectrophotometer. All AAS measurements were duplicated and were reproducible within 0.4% accuracy. The wavelength value for mercury measurements was 253.5 nm.

Preparation of the Membranes. The PVA/P_4VP membranes in the appropriate (60/40) mass ratio were prepared in the same manner as described elsewhere,[20−22] except that P_4VP was introduced in the form of a 10 g L^{-1} aqueous acetic acid solution. The membranes were eventually obtained by casting and evaporating the solution in a Petri box, except in the case of GL cross-linking.

For cross-linking by GL, various GL/PVA ratios were tested ($n_{GL}/n_{PVA} = (0.25, 0.5, 1, 2, 4)$, where n_{PVA} is the amount of PVA repetition units in the membrane) and a few milligrams of magnesium chloride catalyst[20,24,25] were added to the PVA/P_4VP solution; this solution was stirred overnight, casted into a Petri box, and evaporated to yield the membrane. The membranes were finally annealed for 6 h in an oven at 80 °C in order to ensure completion of the cross-linking reaction.

Gaseous DBE cross-linking was performed at 140 °C on the membranes for various cross-linking times t, using a previously described experimental setup.[20,21]

The membranes to be cross-linked by HCl were suspended into a hermetically sealed Teflon reactor (volume = 1000 cm³) containing 0.6 cm³ of commercial 37% HCl solution.[20,26] The reactor was placed in an oven at 110 °C for various cross-linking times t (from 60 to 240 min) to perform the cross-linking.

After cross-linking, the membranes underwent successive washings in baths of water in order to eliminate the traces of residual GL or HCl, or HBr formed from DBE.

Membrane Swelling. The swelling ratio S_w of each membrane was determined by dipping strips of dry membrane (weight, m_D) in Milli-Q water at room temperature. After 24 h, the membrane samples were taken out from the water, carefully wiped using a filter paper, and weighed (m_S). The swelling ratio was calculated using eq 1:

$$S_w = (m_S - m_D)/m_D \qquad (1)$$

Infrared Spectroscopy. The efficiency of the cross-linking reaction was checked by FTIR measurements in transmission mode (ATR) using the Nicolet Avatar 360 FTIR. The spectra of the membrane samples were compared before and after the cross-linking treatments.

Sorption−Desorption Experiments. Membrane samples, initially weighed (m_D) when dry, were placed into aqueous solutions of Hg(II) (volume V, initial concentration c_0) previously brought to the desired pH (±0.1 units) by adding either NaOH or HNO₃. For kinetic studies ($V = 230$ cm³), samples of 5 cm³ of solution were withdrawn at known times. For static experiments ($V = 50$ cm³), samples of 5 cm³ of solution were withdrawn before introduction of the membrane and at equilibrium. The Hg concentrations in the samples were determined by AAS. All experiments were performed in duplicate at room temperature ($T = 21 \pm 3$ °C).

The mass q of mercury absorbed at equilibrium per g of membrane (mg g⁻¹) was obtained as follows:

$$q = \frac{(c_0 - c_{eq})V}{m_D} \qquad (2)$$

where c_0 and c_{eq} are the initial and equilibrium concentrations of Hg(II) ions in the solution (mg L⁻¹), respectively. V is the volume of solution (L) and m_D is the mass of dry membrane (g).

The metal ion retention ratio R of the membrane (%) is defined as

$$R = \frac{(c_0 - c_{eq})}{c_0} \cdot 100 \qquad (3)$$

The metal ion retention efficiency ratio f of the membrane (%) is defined as

$$f = \frac{n_r}{n_{VP}} \cdot 100 \qquad (4)$$

where n_r is the quantity (mol) of Hg(II) retained in the membrane, and n_{VP} is the quantity (mol) of 4-vinylpyridine repetition (VP) units in the membrane. n_r and n_{VP} are calculated by eqs 5 and 6, respectively:

$$n_r = \frac{(c_0 - c_{eq})V}{200.7 \times 10^3} \qquad (5)$$

$$n_{VP} = \frac{0.4m_D}{105} \qquad (6)$$

where 200.7 g mol⁻¹ is the molar mass of Hg, 105 g mol⁻¹ is the molar mass of VP; the factor 10^3 is introduced because c_0 is in mg L⁻¹ instead of g L⁻¹; the factor 0.4 is introduced because the membrane contains 40% (w/w) P₄VP.

Desorption of Hg(II) ions was achieved by using 0.5 M HNO₃ as the desorbing medium. For static experiments, at room temperature, the membrane was loaded with Hg(II) ions at the desired pH by immersion during 24 h in a Hg(II) solution ($c_0 = 100$ mg L⁻¹). Then, the membrane was placed in 50 cm³ of 0.5 M HNO₃ and stirred at a stirring rate of 10.4 rad s⁻¹ up to 24 h. For kinetic experiments, the membrane was loaded with Hg(II) ions at the desired pH and room temperature, by immersion in a Hg(II) solution ($c_0 = 250$ mg L⁻¹) during 24 h. Then, the membrane was placed in 100 cm³ of 0.5 M HNO₃ and stirred at a stirring rate of 10.4 rad s⁻¹ up to 24 h. Samples (3 cm³) were withdrawn at known times. The concentrations of Hg(II) ions in the withdrawn samples were determined by AAS. The desorption ratio D was calculated using eq 7:

$$D = \frac{n_d}{n_r} \cdot 100 \qquad (7)$$

were n_d is the quantity of desorbed Hg(II).

For the study of the effect of water hardness, duplicate experiments were carried out on samples of the same membrane ($m_D \approx 100$ mg) immersed in stirred solutions of Hg(II) at pH 2.5 ($V = 50$ cm³, $c_0 = 100$ mg L⁻¹) containing Ca(II) ions at four different concentrations (0−200 mg L⁻¹). After 24 h, the solutions at equilibrium were analyzed for Hg(II) by AAS.

The effect of chloride ions was studied by carrying out a series of sorption isotherms on samples of the same membrane ($m_D \approx 100$ mg) immersed in stirred solutions of Hg(II) ($V = 50$ cm³, $c_0 = 100$ mg L⁻¹) containing 0.005, 0.05, 0.5, and 10 g L⁻¹ NaCl concentrations.

For studying the effect of the temperature, batch sorption experiments were carried out in duplicate at various T (288, 298, 308, 318, 328, and 338 K). The temperature was controlled (±1 K) by a thermostatted Friocell closet (Fisher Bioblock Scientific). Samples of the same membrane ($m_D \approx 100$ mg) were equilibrated during 24 h in Hg(II) solutions at pH 2.5 ($V = 50$ cm³, $c_0 = 100−2000$ mg L⁻¹).

Regeneration Experiments. Different membrane samples ($m_D \approx 100$ mg) were loaded with Hg(II) before being placed in 50 cm³ of a desorption medium, consisting of an aqueous solution of HNO₃ of variable concentration (0.5−0.01 M). The sorption steps were performed during 24 h in a stirred solution of Hg(II) at pH 2.5 ($V = 50$ cm³, $c_0 = 100$ mg L⁻¹). The membrane loaded with Hg(II) ions was placed in the desorption medium and stirred at 100 rpm for 24 h at room temperature. The amounts of Hg(II) liberated during each desorption step in the desorption medium were determined by AAS.

For a study of the membrane stability through several regeneration steps, consecutive sorption−desorption cycles were

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TABLE 1: Optimization of the Cross-Linking Conditions of the PVA/P$_4$VP Membrane: Influence on the Swelling Ratio S_w of the GL/PVA Ratio and of the Cross-Linking Time t for DBE or HCl

cross-linking agent	n_{GL}/n_{PVA}	S_w (%)	remarks
GL	0.25	0.36	brittle
GL	0.5	0.32	brittle
GL	1	0.26	brittle
GL	2	0.21	brittle
GL	4	0.19	brittle

| cross-linking agent	t (min)	S_w (%)	remarks
HCl	60	0.67	brittle, burnt
HCl	120	0.65	brittle, burnt
HCl	240	0.66	brittle, burnt
DBE	60	0.66	
DBE	120	0.68	
DBE	180	0.65	

repeated five times by using the same membrane sample ($m_D \approx 100$ mg). The five desorption steps were performed in 0.5 M aqueous HNO$_3$.

Frontal Filtration Experiments. The filtration experiments were performed using the thermostated (25 $\pm$ 0.5 °C) two-chamber cylindrical cell ($V = 450$ cm^3) previously described.[20] The membrane (effective area, 28.3 cm^2) was weighed when dry (m_D) and then swollen for 24 h in water before being placed in the cell. The upstream chamber was filled with 400 cm^3 of aqueous solution containing the Hg(II) ions to be removed ($c_0 = 16.6$ or 89.1 mg L^{-1}). This solution was stirred with a Teflon magnetic rod suspended in the chamber and driven at 200 rpm by a magnetic stirrer placed below the cell. The filtration experiment was started by applying pressure (0.30 $\pm$ 0.01 MPa) to the upstream chamber. The filtrate that ran through the downstream chamber was continuously evacuated. Aliquots of the filtrate were removed every 24 h and analyzed by AAS. The concentration in the upstream chamber was determined at the beginning and at the end of the experiments.

Results and Discussion

Characterization of the PVA/P$_4$VP Membranes. *Swelling as a Criterion for Cross-Linking.* Cross-linking of the membrane PVA matrix is necessary because this water-soluble polymer would dissolve in aqueous solutions. When cross-linked, the matrix interaction with water is limited to swelling. The swelling ratio S_w is an indicator of the efficiency of the cross-linking reactions. Swelling must be limited ($S_w < 0.7$) in order to retain the mechanical properties of the membrane. The smaller S_w, the better the cross-linking. However, most commercial ion-exchange membranes are limited to $S_w > 0.2$, because below this value the membranes generally are rigid and show insufficient flow rates.

Table 1 presents the calculated average values of S_w. The membranes cross-linked by GL showed decreasing swelling when the GL/PVA ratio (n_{GL}/n_{PVA}) increased, but appeared too brittle for any n_{GL}. Membranes prepared with $n_{GL}/n_{PVA} < 0.25$ showed insufficient mechanical properties. For HCl cross-linking, the membranes became burnt and brittle for any t. For gaseous DBE cross-linking, the reaction times t were optimized in order to prepare membranes with S_w values between 0.2 and 0.7. The optimized cross-linking time t was defined when no further noticeable reduction of S_w could be observed. Thus, only the membranes cross-linked by a treatment with gaseous DBE at 140 °C for 60 min were used for the Hg(II) removal experiments.
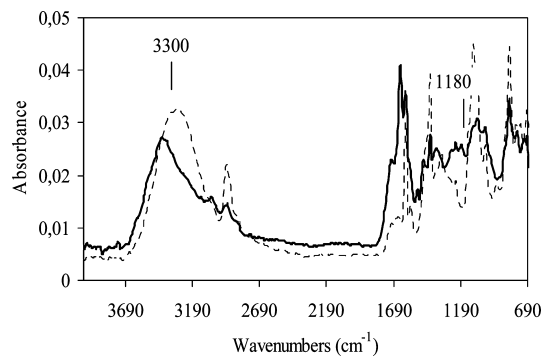
Figure 2. FTIR spectra of PVA/P$_4$VP films before (---) and after (—) DBE cross-linking (1 h, 140 °C).

TABLE 2: Effect of pH on the Retention Ratio of Hg(II) by the Membrane[a]

pH	R (%)	solubility limit of Hg(II) (mg L^{-1})
1.02	41.4	2×10^6
2.04	58.4	2×10^4
2.97	99.2	2×10^2

[a] Room temperature; $m_D = 100$ mg; $c_0 = 100$ mg L^{-1}; $V = 50$ cm^3.

FTIR Evidence for Efficiency of the DBE Cross-Linking. FTIR spectra of the 60/40 PVA/P$_4$VP blend, before and after DBE cross-linking (Figure 2), show that cross-linking causes (i) a decrease in the intensity of the bands located at ≈ 3300 and 2900 cm^{-1}, attributed to the stretching vibrations of the hydroxyl groups of PVA, and (ii) the appearance of a new band centered at ≈ 1180 cm^{-1}, attributed to the presence of OCH$_2$ groups. These spectral changes agree with the formation of ether links from HO groups of the PVA chains,[38] and prove effective cross-linking of the PVA chains.

Static Sorption Experiments. *Effect of the pH.* The pH of the Hg(II) solution affects the extent of sorption because it strongly influences the metal speciation and precipitation, and the protonation degree of the P$_4$VP ligand. For an aqueous solution of Hg(II) ions ($c_0 = 100$ mg L^{-1}), the effect of pH on the retention ratio R is reported in Table 2.

Because the pH of the solution modified the solubility of Hg(II) ions, the conditions of pH and Hg(II) concentration were chosen so that no precipitation could occur during the experiments. At pH 2.5, Hg(II) ions would not precipitate if their concentration is $< 2 \times 10^3$ mg L^{-1}. This limit was calculated using the value of the solubility product (p$K_s = 25.0$) reported for Hg(OH)$_2$.[39] Moreover, since precipitation was not instantaneous, experiments could be performed at pH 2.5 even at $c_0 = 4 \times 10^3$ mg L^{-1}.

The retention ratio increased between pH 1−3, and reached a maximum value (99%) at pH 3. These results are consistent with protonation of the nitrogen atoms of P$_4$VP at pH < 3 that reduced the number of available binding sites for Hg(II) ions. They agree with the qualitative data of Oyama and Anson[40] showing that P$_4$VP is strongly protonated at pH < 3, and with the values of the pK_a of the ligand. Satoh et al. determined the apparent acidity constants of P$_4$VP and 4-ethylpyridine, a model of its repetition unit, by potentiometric titrations in 0.1 M aqueous NaCl at 25 °C. [41] The polymer (p$K_a = 5.0 \pm 0.3$) is more acidic than 4-ethylpyridine (p$K_a = 6.14 \pm 0.05$), as expected because the surroundings of the pyridine residues of the polymer have a lower dielectric constant than water.

The comparison with the pH effect on sorption of Hg(II) ions by a PVA/PEI membrane[27] shows that the values of R are larger
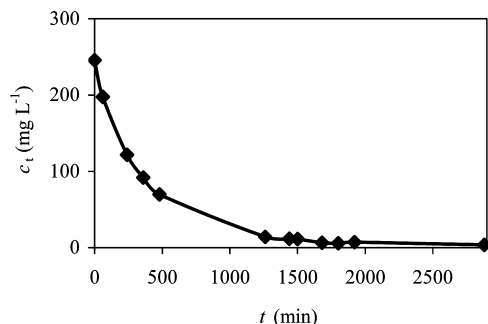
Figure 3. Kinetics of sorption of Hg(II) by the membrane. Concentration c_t of Hg(II) vs time t.

for P$_4$VP than for PEI at any pH, and the maximum value is 99% instead of 85% for PEI. Besides, 50% retention was observed at pH $\approx$ 2 for P$_4$VP and pH $\approx$ 1.5 for PEI. This result was unexpected, because P$_4$VP is more acidic than PEI, the apparent pK_a's of which were reported to be 7.7 and 9.7.[22] A partial explanation would be that the true acidity difference between P$_4$VP and PEI in the membranes is modified because the pK_a values for free polyelectrolytes are likely to change when they are inserted into the polymeric PVA network. However, the important fact is that retention of mercury is almost quantitative at pH > 3 for the P$_4$VP membrane.

Finally, the working range for sorption of Hg(II) by the P$_4$VP membrane was set at pH 2.5. It must be noticed that for the treatment of aqueous waste streams that are nearly neutral, the addition of acid is necessary, but this may be not practicable with highly buffered media.

Sorption Kinetics. The kinetic study of the sorption of Hg(II) by a membrane sample (m_D = 301.6 mg) was performed in a solution (c_0 = 245.7 mg L^{-1}, V = 230 cm^3) at pH 2.5. Figure 3 shows the decreasing concentration of Hg(II) in the solution, c_t, as a function of time t.

The uptake of Hg(II) by the membrane at pH 2.5 was slow. The plateau values were approached after about 1260 min (21 h). These results established the time necessary for the subsequent sorption studies: a shaking period of 24 h was chosen for all sorption experiments.

In order to specify the controlling mechanism of sorption process, the kinetic data were analyzed using the first-order rate expression of Lagergren, which is the most widely used for the sorption of a solute from a solution. The model has the following form:

$$\frac{dq_t}{dt} = k(q_{eq} - q_t) \tag{8}$$

Equation 8 may be linearized as

$$\ln(q_{eq} - q_t) = \ln q_{eq} - kt \tag{9}$$

where k (min^{-1}) is the rate constant of first-order sorption and q_{eq} and q_t (mg g^{-1}) are the masses of mercury sorbed per gram of membrane at equilibrium and at time t, respectively. The values of q were obtained from the values of c by using eq 2. In agreement with a first-order process, the plot of $\ln(q_{eq} - q_t)$ against t is a straight line, the slope of which is $-k$ (Figure 4).

The half-reaction time ($t_{1/2} \approx$ 277 min) reported in Table 3 is consistent with the reaction being complete in $\approx$24 h. The mass of Hg sorbed at equilibrium per gram of membrane,
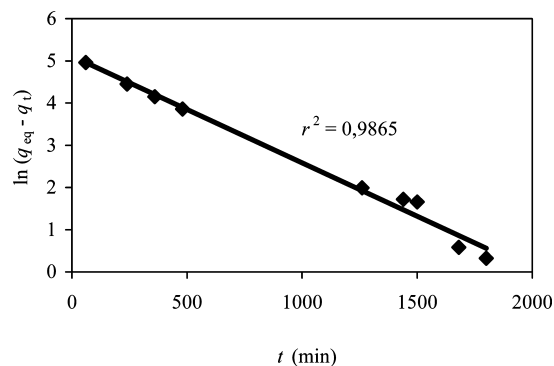
Figure 4. First-order kinetics of sorption of Hg(II) by the membrane.

TABLE 3: Yields and First-Order Kinetics of Sorption: Rate Constant k and Half-Reaction Time $t_{1/2}$[a]

R (%)	f (%)	exptl q_{eq} (mg g^{-1})	k (min^{-1})	$t_{1/2}$ (min)	calcd q_{eq} (mg g^{-1})	r^2
98.5	23.5	178	0.0025	277	166	0.9865

[a] Room temperature; pH 2.5; V = 230 cm^3; m_D = 301.6 mg; accuracy k ± 10%.

calculated from the intercept of Figure 4, was q_{eq} = 166 mg g^{-1}. This calculated value is in the same range as the experimental value after 24 h contact time (q_{eq} = 178 ± 10 mg g^{-1}).

The fact that the kinetic law is of first order is probably due to the large excess of complexation sites of the membrane with respect to the concentration of Hg(II) ions in solution. The data for R and f support this hypothesis, because almost all (98.5%) mercury ions were sorbed at equilibrium, while only 23.5% of the sites were occupied.

However, some reports point that a first-order sorption kinetics may not be due to a rate-limiting complexation process, but to a slower diffusion process between the stirred liquid medium and the sorbent sites.[42] Two mass transfer diffusion models are considered. The first one is the external mass transfer diffusion model, in which the limiting step would be the diffusion of mercury in the boundary layer that surrounds the sorbent surface. This hypothesis was not considered in this work, because the uptake of Hg by the membrane is so slow ($t_{1/2} \approx$ 277 min) that diffusion of Hg(II) ions in solution is likely a much faster process. The second one is the intraparticular mass transfer diffusion model. Adapted to the present system, the rate-limiting step would then be diffusion of Hg(II) ions through the membrane.
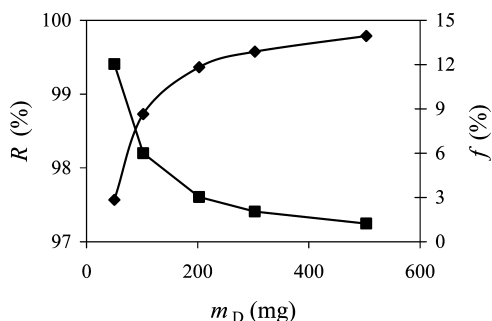
According to the intraparticular mass transfer diffusion model, the mass of mercury sorbed (q_t) should vary with the square root of time ($t^{1/2}$). This relationship is expressed as follows:[42]

$$q_t = k_d t^{1/2} + \alpha \tag{10}$$

where k_d is the intraparticular diffusion rate constant (mg g^{-1} min$^{-1/2}$) and α is the intercept that should normally be nil. This model was tested by plotting the variations of q_t vs $t^{1/2}$. Since the plot (Figure 5) is not linear, the hypothesis that diffusion of Hg(II) through the membrane is the rate-determining step was not supported. We did not attempt to use other models to confirm this point, but we believe that the rate constant reported in Table 3 indeed corresponds to the chemical association between Hg(II) ions and the complexation sites of the membrane.

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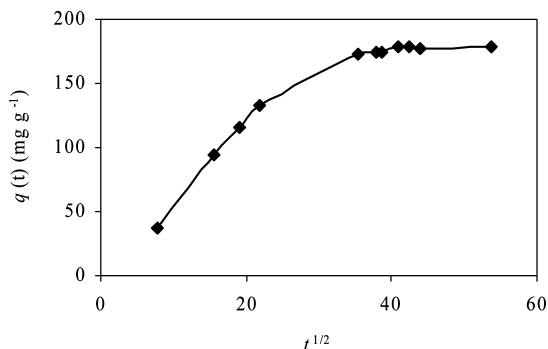
Figure 5. Kinetics of sorption of Hg(II) by the membrane: intraparticular diffusion model.

Figure 6. Influence of the mass of membrane m_D on the sorption of Hg(II); retention ratio R (◆) and efficiency ratio f (■) vs m_D.

TABLE 4: Effect of Presence of Ca(II) Ions on Sorption of Hg(II) by the PVA/P$_4$VP Membrane[a]

concn of Ca(II) (mg L^{-1})	R (%)	q_{eq} (mg g^{-1})
0	99.2	44.0
20	98.4	43.4
40	99.3	43.1
100	97.2	41.1
200	96.7	41.5

[a] Room temperature; pH 2.5; $V = 50$ cm^3; $m_D \approx 100$ mg, $c_0 = 100$ mg L^{-1}. Accuracy $R \pm 3\%$, $q \pm 1.5\%$.

TABLE 5: Effect of NaCl Concentration on the Equilibrium Uptakes and Sorption Yields of Hg(II)[a]

| concn of NaCl (g L^{-1})	R (%)	q_{eq} (mg g^{-1})
0	99.2	44.0
0.005	100.0	44.0
0.05	99.9	43.1
0.5	99.8	43.5
10	98.3	43.4

[a] Room temperature; pH 2.5; $c_0 = 100$ mg L^{-1}; $V = 50$ cm^3; $m_D \approx 100$ mg. Accuracy $R \pm 3\%$, $q \pm 1.5\%$.

Effect of the Mass of Membrane. The effect of the mass of PVA/P$_4$VP membrane on the sorption of Hg(II) at pH 2.5 during 24 h was investigated by varying the membrane mass ($m_D = 50-500$ mg) at a constant Hg(II) ions concentration ($c_0 = 100$ mg L^{-1}). The results are presented in Figure 6 for R and f. Figure 6 shows that, when m_D increased, the retention ratio R slightly increased up to $m_D = 500$ mg and reached a maximum equilibrium value ($R = 99 \pm 2\%$). This result suggests that the relationship between m_D and R was due to the increase in the number of sorption sites, and that all the available metal ions were retained in the membrane at equilibrium. In contrast, Figure 6 shows that the value of f continuously decreased, from 12% to 1%, with increasing m_D. This relationship could be expected, because the same amount of Hg(II) ions reacted with an increasing quantity of sites, resulting in a lower ratio of occupied sites vs the total number of sites.

Since quantitative sorption of Hg(II) was obtained for $m_D > 100$ mg, membranes with $m_D = 100$ mg were used in the following experiments.

Effect of the Hardness of the Water. So-called "hard waters" contain large amount of calcium and magnesium ions, that may interfere with the retention of Hg(II) ions.[27] Since calcium and magnesium are alkaline-earth elements and have similar properties, a single ion, calcium, was selected to investigate the possibility of interference with the formation of the Hg−P$_4$VP complex. Hence, removal by the membrane of Hg(II) ($c_0 = 100$ mg L^{-1}) present in hard waters was investigated at pH 2.5. A set of sorption experiments was performed with stepwise addition of calcium nitrate (0−200 mg L^{-1}). The values of the retention ratio R and the mass q_{eq} of mercury sorbed per gram of membrane at equilibrium are given in Table 4. These data show that the presence of Ca(II) ions at low concentrations (20−40 mg L^{-1}) did not decrease the retention ratio of Hg(II) ($R \approx 99\%$). At larger concentrations of Ca(II) ions (100−200 mg L^{-1}), R decreased only by 2.5%. Such small variations indicated that no competition occurred between the two metal ions, and that effects of ionic strength were negligible. These results are much better than those reported for a PVA/PEI membrane,[27] for which the retention ratio of Hg(II) decreased noticeably, even at low concentrations of calcium nitrate (20−40 mg L^{-1}).

In conclusion, the presence of Ca(II), even in large concentration, had a very small effect on the retention of Hg(II) by the PVA/P$_4$VP membrane that can thus be applied to hard water streams containing mercury ions.

Effect of the Presence of Chloride Ions. Saline wastewaters contain, in addition to toxic heavy metal ions, large quantities of other salts such as sodium chloride. Generally, the sole effect of this presence is a high ionic strength that slightly modifies the values of the equilibrium constants, without introducing new reactions in the system. This is not the case for solutions containing Hg(II) ions, because this element forms very stable complexes with chloride anions.[27] Moreover, it is well-known that the ionic strength affects the binding efficiency of polymeric ligands, due to electrostatic interactions. In the present case, the influence of chloride concentration on the removal of Hg(II) by the PVA/P$_4$VP membrane was studied at pH 2.5 with a solution of Hg(II) ions ($c_0 = 100$ mg L^{-1}) that contained 0.005, 0.05, 0.5, and 10 g L^{-1} of NaCl salts. The variations of the retention ratio and mass of Hg(II) sorbed at equilibrium per gram of membrane with increasing concentration of NaCl are shown in Table 5. It can be seen that the retention ratio of Hg(II) was always >98%, even in the presence of 10 g L^{-1} NaCl. In comparison with the PVA/PEI membrane[27] that suffered an efficiency loss in NaCl medium, the PVA/P$_4$VP is remarkably unsensitive to the presence of NaCl.

This result may be discussed in relation with the known stability constants of the chloride complexes of Hg(II).[39] For the prevailing complex [HgCl$_2$], log $\beta_2 = 13.2$. Hence, the [HgCl$_2$]/[Hg^{2+}] ratio (calculated as β_2[Cl]^2) is 1.14×10^5 for 0.005 g L^{-1} NaCl ($c = 8.5 \times 10^{-5}$ M) and 4.6×10^{11} for 10 g L^{-1} NaCl ($c = 0.17$ M). It shows that all Hg(II) ions were present in complexed form at each chloride concentration and that the concentrations of free Hg^{2+} were always extremely small. Consequently, either the stability constant of the P$_4$VP−Hg(II) complex is very large or the P$_4$VP ligand can bind the HgCl$_2$ complex. Anyway, the variations of the values of R

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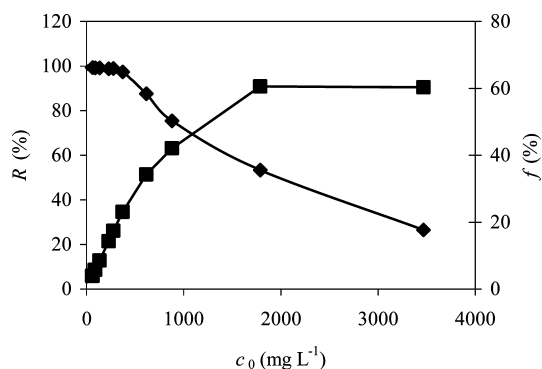
Figure 7. Influence of the initial concentration of Hg(II) c_0 on the sorption of Hg(II); retention ratio R (◆) and efficiency ratio f (■) vs c_0.

Figure 8. Sorption isotherm of Hg(II) by the membrane.

and q_{eq} in Table 5 are so small that calculating a value for the stability constant of the $P_4VP-Hg(II)$ complex would have little meaning.
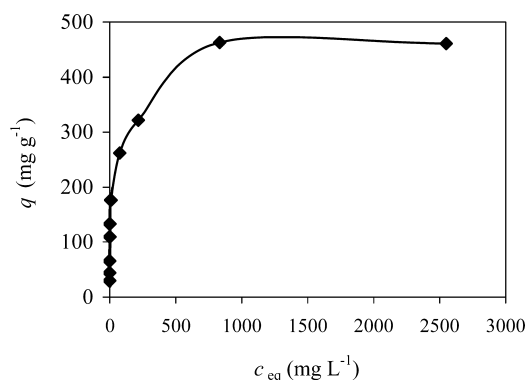
This observation, in relation with the negligible influence of Ca(II) ions on the retention of Hg(II), shows the considerable potential of the PVA/P_4VP for the treatment of waters polluted by mercury. It may be related to a particularly high affinity between Hg(II) and the complexation sites of this membrane.

Equilibrium Sorption Studies: Effect of the Initial Concentration of Hg(II). The experiments were carried out at pH 2.5 on solutions of Hg(II) ions with concentration c_0 ranging between 70 and 3500 mg L^{-1}. The variations of retention ratio R and efficiency ratio f vs c_0 are shown in Figure 7 for several membrane samples of similar size (m_D in the 100.0−103.1 mg range). When c_0 was small, the values of R were close to 100%, indicating complete retention of the few Hg(II) ions present in the solution. This result tallies with the high affinity of the ligand for Hg(II) noticed in the section Effect of the Presence of Chloride Ions. When c_0 increased, the values of R decreased. It can be explained by the saturation of the complexation sites of the membrane, because a given mass of membrane contains a finite number of sorption sites. Once all these sites were bound with mercury, the additional Hg(II) ions could not be retained, because no more sites were available.

On the other hand, the values of f increased, indicating that the available sites of the membrane progressively bound with the increasing amount of Hg(II) in solution (Figure 7). The maximum value, $f \approx 60\%$, is reached for $c_0 \approx 2000$ mg L^{-1}. According to eq 4, f is the ratio between the amount of Hg(II) ions absorbed and the amount of nitrogen atoms in the membrane, because each P_4VP repetition unit contains a single N atom. The observed maximum value $f = 60\%$ corresponds to one Hg(II) ion bound with $1/0.6 = 1.7$ nitrogen atom. This average value means that the prevailing complexes are formed with 1 and mostly 2 N atoms, indicating that most mercury ions bridge two repetition units.

The value $f = 60\%$ shows a noticeable improvement of the PVA/P_4VP complexing membrane efficiency with respect to the previously studied PVA/PEI membrane, which had $f \leq 8\%$ for Pb, Cd, and Cu[22] and $f = 12\%$ for Hg.[27] First, it reflects the higher affinity for Hg(II) of the PVA/P_4VP membrane than the PVA/PEI membrane. Second, the low affinity of the PVA/PEI membrane was explained by the fact that many complexing sites were not available for metal ions;[22] it seems that this drawback was overcome in the PVA/P_4VP membrane.

The uptake of Hg(II) ions by the membrane can also be described in the form of sorption isotherms. Figure 8 shows the mass q of mercury sorbed at equilibrium per gram of membrane (mg g^{-1}) as a function of the equilibrium concentration c_{eq} of Hg(II). The initial concentration c_0 varied in the 20−3500 mg L^{-1} range, at pH 2.5. The values of q increased with increasing c_0, as expected if the sorption equilibrium was displaced by the increasing amount of Hg(II) in solution. The existence of a plateau for $c_{eq} \approx 1000$ mg L^{-1} indicated the final saturation of the membrane. The maximum mass of Hg(II) absorbed at equilibrium per gram of membrane was $q \approx 460$ mg g^{-1}. The theoretical value of q was calculated as follows. For a mass $m_D = 1$ g, the P_4VP content of the membrane is 40%, corresponding to $N = 3.81$ mmol P_4VP units or nitrogen atoms (molar mass of P_4VP is 105 g mol^{-1}). Since an average complexing site contains 1.7 nitrogen atoms, the maximum retained amount of Hg(II) ion should be $N/1.7 = 2.24$ mmol. The mass of Hg that can be retained in 1 g of membrane was finally calculated, knowing the molar mass of Hg(II). This mass is 450 mg g^{-1}, in excellent agreement with the experimental value. For comparison, q_{max} for sorption of Hg(II) by the PVA/PEI membrane at 298 K was twice smaller: 215 mg g^{-1} (experimental) and 217 mg g^{-1} (calculated).[27]

The Langmuir Sorption Isotherm. The sorption equilibrium of mercury by the PVA/P_4VP membrane are classically studied by using the Langmuir, Freundlich, and Dubinin−Radushkevich isotherms. In this study, the two latter models were not obeyed, whereas the Langmuir model gave excellent fitting with the experimental data. The Langmuir model is described by eq 11:

$$q = \frac{q_{max} b c_{eq}}{1 + b c_{eq}} \qquad (11)$$

where q_{max} and b are the maximum sorbed mass at saturation (mg g^{-1}) and the sorption coefficient (L mg^{-1}), respectively. The constants q_{max} and b were determined from the linearized form (eq 12) of eq 11 according to the Hanes−Woolf treatment:

$$\frac{c_{eq}}{q} = \frac{c_{eq}}{q_{max}} + \frac{1}{b q_{max}} \qquad (12)$$

Therefore, a plot of c_{eq}/q vs c_{eq} was a straight line with a slope $1/q_{max}$ and intercept $1/b q_{max}$. The linear Langmuir plot, for $c_0 = 0$−3500 mg L^{-1}, is shown in Figure 9. The isotherm constants q_{max} and b, obtained by fitting the experimental data with eq 12, are given in Table 6. The calculated value of q_{max} was 455 mg g^{-1}, in close agreement with the experimental and theoretical values, 460 and 450 mg g^{-1}, respectively. The good representation of the sorption equilibrium by the Langmuir model supports the hypothesis that sorption of Hg(II) by the
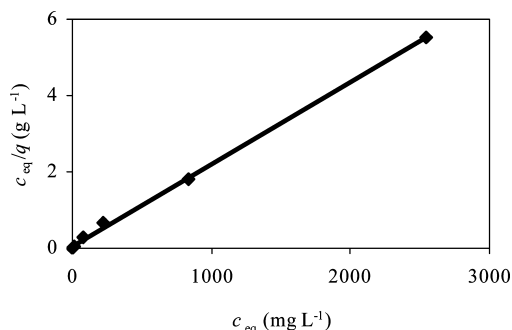
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Figure 9. Langmuir plot for sorption of Hg(II) by the membrane.

TABLE 6: Parameters of the Langmuir Model for the Sorption of Hg(II) by the PVA/P$_4$VP Membrane^a

b (L mg^{-1})	q_{max} (mg g^{-1})	r^2	exptl q (mg g^{-1})
0.04417	455	0.9986	460

^{a} Room temperature; pH 2.5; $m_D \approx 100$ mg; $c_0 = 0-3500$ mg L^{-1}; $V = 50$ cm^3. r^2 is the correlation coefficient of the Langmuir isotherms according to equation (eq 12). Accuracy: $b \pm 5\%$; $q_{max} \pm 5\%$.
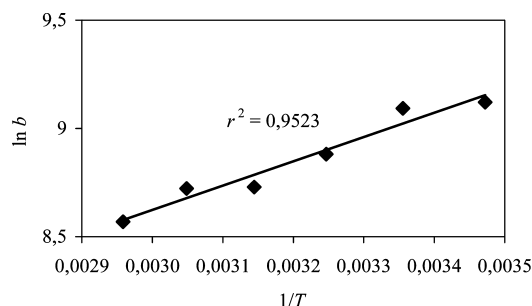

Figure 10. Plot of ln b vs $1/T$ for sorption of Hg(II) by the membrane.

membrane is actually limited by the saturation of the P$_4$VP complexing sites. When these results are compared with those reported[27] for sorption of Hg(II) by the PVA-PEI membrane at 298 K ($b = 0.0162$ L mg^{-1}; $q_{max} = 217$ mg g^{-1}), it is clear that the affinity for mercury of the PVA-P$_4$VP membrane is about twice that of the PVA-PEI membrane.

Effect of Temperature and Thermodynamic Parameters. The thermodynamic parameters (enthalpy $\Delta H°$ and entropy $\Delta S°$) of sorption of Hg(II) were determined by performing batch sorption experiments at six temperatures (i.e., 288, 298, 308, 318, 328, and 338 K). All experiments were performed in duplicate at pH 2.5 ($c_0 = 100-2000$ mg L^{-1}) with twelve different membrane samples ($m_D \approx 100$ mg). A linear Langmuir plot, following eq 12, was drawn for each sorption isotherm. The values of $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (J mol^{-1}), according to eq 13, were determined from the slope and intercept of the plot of ln b vs $1/T$ shown in Figure 10.

$$\ln b = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (13)$$

where R is the ideal gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K).

The change in free energy $\Delta G°$ (kJ mol^{-1}) for the sorption of Hg(II) by the membrane was calculated by eq 14:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (14)$$

TABLE 7: Values of Thermodynamic Parameters for the Sorption of Hg(II) by the PVA/P$_4$VP Membrane^a

T (K)	b (L mol^{-1})	q_{max} (mg g^{-1})	r^2	$\Delta G°$ (kJ mol^{-1})
288	9149.7	456.4	0.9958	−21.86
298	8897.2	454.5	0.9885	−22.55
308	7196.1	416.7	0.9966	−22.76
318	6179.3	384.6	0.9980	−23.09
328	6138.0	400.0	0.9972	−23.80
338	5261.4	416.7	0.9984	−24.10

^{a} pH 2.5; $m_D \approx 100$ mg; $c_0 = 100-2000$ mg L^{-1}; $V = 50$ cm^3. r^2 is the correlation coefficient of the Langmuir isotherms according to eq 12. Accuracy: $b \pm 5\%$; $\Delta G° \pm 1\%$; $q_{max} \pm 9\%$. $\Delta H° = -9.3 \pm 2.0$ kJ mol^{-1}; $\Delta S° = 43.7 \pm 3.0$ J K^{-1} mol^{-1}.

The values of b, q_{max}, $\Delta H°$, $\Delta S°$, and $\Delta G°$ are summarized in Table 7. The sorption constant b decreased with increasing temperature, showing that the sorption reaction is exothermic. However, the sorption reaction was favored with increasing temperature, as shown by the decreasing values of $\Delta G°$. The values of q_{max} were almost constant, in agreement with the fact that the membrane is saturated for high values of c_0.

The negative value of $\Delta H°$ (-9.3 kJ mol^{-1}) is small and does not provide evidence for chemisorption or physisorption of Hg(II) ions by the sites of P$_4$VP. Another aspect to notice is that the value of $\Delta S°$ is positive. A positive $\Delta S°$ value suggests that sorption results in a decrease of order in the system. Since the sorbed Hg(II) are likely more ordered than when free in solution, the overall increase of disorder is probably due to the simultaneous release of protons, which are very mobile counterions, from the complexing sites of the membrane. This is in agreement with the fact that sorption experiments were performed in very acidic medium (pH = 2.5).

For the PVA/PEI membrane,[27] the reported thermodynamic parameters were $\Delta H° = -30.0$ kJ mol^{-1} and $\Delta S° = -29.4$ J mol^{-1}. The comparison shows that, for the PVA/P$_4$VP membrane, sorption of Hg(II) is much less favorable from the enthalpic term, but is strongly favored from the entropic term. In other words, the higher efficiency of the PVA/P$_4$VP membrane is due to a considerable entropic effect, consequent to the release of protons when the sites of complexation bind with Hg(II) ions. Since most P$_4$VP complexes involve one Hg ion bound with two N atoms, two protons may be liberated by fixed Hg ion, explaining the large magnitude of the found entropy effect. In contrast, the negative value of $\Delta S°$ for sorption of Hg(II) by the PEI membrane shows that the release of protons is much smaller.

Regeneration of the PVA/P$_4$VP Membrane. In order to apply sorption by membranes to the treatment of real wastewater, regeneration of the membrane is important for economic reasons. So, in order to determine the reusability of the membrane, desorption experiments with nitric acid were carried out on membrane samples loaded with Hg(II). The sorption steps were performed during 24 h in a solution of Hg(II) ($c_0 = 100$ mg. L^{-1}, $V = 50$ cm^3, pH 2.5). The effect of the concentration of nitric acid (0.5−0.01 M) on the desorption ratio D was studied by placing the membrane samples loaded with Hg(II) ions in the desorption media (50 cm^3 of HNO$_3$ solution) and stirring at 100 rpm for 24 h at room temperature. The desorption ratio D was calculated by eq 7. The results reported in Table 8 show that desorption was quantitative only for 0.5 M HNO$_3$ and that, at lower acidities, the values of D sharply decreased and became nil at pH 2.0. Therefore, the optimal concentration of HNO$_3$, used for the subsequent desorption experiments, was 0.5 M.

For the study of membrane stability through multiple regeneration steps, consecutive sorption−desorption cycles with

TABLE 8: Effet of the Concentration of Nitric Acid on the Desorption of Hg(II)[a]

concn (mol L^{-1})	q (mg g^{-1})	R (%)	D (%)
0.5	46.5	99.8	99.9
0.1	46.4	99.8	44.3
0.05	47.5	99.5	9.6
0.01	46.6	99.2	0.0

[a] Room temperature; $m_D \approx 100$ mg; sorption at pH 2.5; $c_0 = 100$ mg L^{-1}.

TABLE 9: Sorption−Desorption Cycles of Hg(II) with 0.5 M HNO₃[a]

cycle no.	q (mg g^{-1})	R (%)	D (%)
1	46.5	99.8	99.9
2	42.1	90.5	98.4
3	42.5	91.3	98.6
4	43.5	93.5	97.6
5	44.8	96.2	97.4

[a] Room temperature; $m_D \approx 100$ mg; sorption at pH 2.5; $c_0 = 100$ mg L^{-1}.

TABLE 10: Filtration of Aqueous Hg(II) Solutions through PVA/P₄VP Membranes[a]

c_0 (mg L^{-1})	m_D (mg)	flow rate (cm^3 h^{-1})	av c_F (mg L^{-1})	E (%)
89.1	369.6	0.53	0.1	99.9
16.6	369.0	0.56	0[b]	100

[a] $T = 25$ °C; pH 2.5; $V = 400$ cm^3. [b] The limit of detection for Hg(II) was 0.1 mg L^{-1}.

TABLE 11: Theoretical Filtrate Volume for Saturation of the Membranes during Filtration Experiments

c_0 (mg L^{-1})	m_D (mg)	P₄VP (mmol)	Hg retained (mmol)	Hg capacity (mg)	V_{calc} (L)
89.1	369.6	1.408	0.704	166.3	1.866
16.6	369.0	1.406	0.703	166.1	10.006

The performance of the membrane, in terms of quality of the filtrated water, was quantified by the elimination ratio E, defined by eq 15:

$$E = \frac{(c_0 - c_F)}{c_0} \times 100 \qquad (15)$$

An interesting point is that saturation of the complexing capacity of the membrane was not observed for both Hg(II) concentrations, because the c_F concentrations remained very small until the end of each filtration experiment. This finding was rationalized by calculating the theoretical volumes V_{calc} for the saturation of the membranes. Since the theoretical complexing capacity of the membrane, calculated in section 3.2.6, is 450 mg g^{-1}, the values of V_{calc} for both filtration experiments are given in Table 11. In these calculations, the masses of Hg present in the filtrate were neglected. The data show that Hg masses of 166.3 and 166.1 mg correspond to volumes of 1866 and 10 006 cm^3 of filtrate, respectively. Therefore, no saturation of the membranes could occur, as filtration was stopped after recovery of 370 cm^3 of filtrate.

For both feed solutions, the values of E were close to 100%, showing that the PVA/P₄VP membrane is very efficient for the treatment of wastewaters containing Hg(II) ions.

In conclusion, the PVA/P₄VP membrane shows a very large complexing capacity for Hg(II). A membrane sample of mass 369 mg can treat a volume up to 10.0 L of 16.6 mg L^{-1} solution of Hg(II) before saturation. It means that a membrane with $m_D = 1$ g may be used for the treatment of ≈ 27 L of the same aqueous solution of Hg(II) in a single operation.

0.5 M HNO₃ were repeated five times by using the same membrane sample. For the desorption steps, the membrane loaded with Hg(II) ions was placed in the desorption medium (50 cm^3 of 0.5 M HNO₃ solution) and stirred at 100 rpm for 24 h at room temperature. The results for the retention ratio R (sorption steps) and the desorption ratio D (desorption steps) are shown in Table 9. Values of both R and D were very large (between 90 and 100%) and did not noticeably change (only a 4% change was observed) during the repeated sorption−desorption operations.

The comparison of these data with those reported for regeneration of a PVA/PEI membrane used for the removal of Hg(II) from aqueous solutions at the same pH shows that the PVA/P₄VP membrane has not only higher retention properties but also a much higher resistance to oxidative degradation by 0.5 M nitric acid. In fact, the PVA/PEI membrane was so sensitive to oxidation by 0.5 M nitric acid that dilute nitric acid (0.05 M) had to be used for its regeneration, with limited efficiency.[22] When this membrane was used for Hg removal, a 0.05 M solution of EDTA was used instead of nitric acid.[27] Incidentally, the finding that 0.5 M nitric acid does not attack the PVA/P₄VP membrane shows that the PVA matrix is intrinsically resistant to oxidation by 0.5 M nitric acid and that degradation of the PVA/PEI membrane[22] was due to oxidation of PEI.

Dynamic Experiments: Frontal Filtration. The efficiency of the PVA/P₄VP membrane for filtration of Hg(II) was studied by monitoring the Hg(II) concentration c_F in the filtrate vs time. Two solutions of Hg(II) ($V = 400$ cm^3, $c_0 = 16.6$ or 89.1 mg L^{-1}) were filtrated with two membranes samples ($m_D \approx 369$ mg) and aliquots of the effluents were collected at known intervals. Each experiment lasted several days and was stopped when ≈370 cm^3 of filtrate had been obtained. The reasons are that the membrane should not be allowed to dry up, and keeping a small volume of retentate was necessary for determining the final concentration of mercury. The flow rates were periodically measured, typically 0.53−0.56 cm^3 h^{-1}. Such a low value means that progress should be made in the design of the process (thinner membranes, tubular membranes, etc.) before practical applications to large volumes of waste streams. The very small average values found for c_F in both experiments (Table 10) provide evidence for almost complete removal of Hg(II) by the PVA/P₄VP membrane.

Conclusion

A novel membrane containing P₄VP as a complexing polymer in a PVA matrix showed a high affinity for Hg(II) ions in aqueous solutions. Static sorption experiments established the optimal pH to be 2.5. At equilibrium, the retention ratio R reached 100% when membranes of mass 100 mg were used for 100 mg L^{-1} solutions of Hg(II). The membrane is twice more efficient than a PVA/PEI membrane previously studied, since its complexation capacity was 450 vs 311 mg L^{-1} for the PVA/PEI membrane.

The PVA/P₄VP membrane, prepared by the s-IPN technique, was efficiently cross-linked by gaseous DBE at 140 °C, as shown by FTIR spectroscopy and small values of the swelling ratio.

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A kinetic study showed that the slow sorption reaction followed a first-order rate law and that the rate-limiting step was the association of Hg(II) ions with the complexing sites of P_4VP.

The effects of hardness of water and presence of chloride ions on the retention ratio were investigated in order to assess the membrane potentialities for the treatment of real wastewaters. The membrane showed remarkably little sensitivity to the presence of Ca(II) ions up to 200 mg L^{-1} or NaCl up to 10 g L^{-1}. These findings are in agreement with a high affinity and specificity of the P_4VP ligand for Hg(II) ions.

Equilibrium sorption studies were performed by varying the initial concentration of Hg(II). The efficiency ratio increased and reached a 60% maximum value. It means that statistically each Hg(II) ion is bound with 1.7 N atoms. Data analysis by sorption isotherms showed a good representation by the Langmuir model, that supports the hypothesis that sorption is limited by saturation of the membrane sites.

The thermodynamics of the sorption process were determined by performing sorption isotherms at various temperatures. When T increased, mercury uptake at equilibrium did not change, whereas the sorption coefficient b decreased and $\Delta G°$ decreased. This phenomenon was related to a large entropic effect, which can be explained by the release of protons when Hg(II) ions are sorbed by the protonated sites of the membrane at pH 2.5.

The membrane could be regenerated several times, without noticeable loss of efficiency, by treatment with 0.5 M HNO_3. This considerable improvement with respect to the PVA/PEI membrane, which had to be regenerated with 0.05 M HNO_3 or 0.05 M EDTA with small loss of efficiency, is probably due to the resistance of the P_4VP ligand to oxidation.

The membrane was used in the filtration mode, showing an efficiency ratio E of at least 99.9% for removal of Hg(II) in the 16.6−89.1 mg L^{-1} concentration range. A membrane of mass $m_D = 1$ g has a theoretical sorption capacity of 450 mg of Hg, and hence can be used for treating large volumes of polluted water in a single operation; for instance, 27 L of a solution containing initially 16.6 mg L^{-1} of Hg(II).

Nomenclature

Abbreviations

AAS	atomic absorption spectroscopy
DBE	1,2-dibromoethane
GL	glutaraldehyde
P_4VP	poly(4-vinylpyridine)
PVA	poly(vinyl alcohol)
s-IPN	semi-interpenetrating polymer network

Symbols

α	y-intercept from intraparticular diffusion model
b	sorption coefficient in Langmuir isotherm (L mg^{-1})
c	concentration (mol L^{-1} or mg L^{-1})
c_{eq}	equilibrium (final) concentration (mg L^{-1})
c_F	filtrate concentration (mg L^{-1})
c_0	initial concentration (mg L^{-1})
D	desorption ratio (%)
E	elimination ratio (%)
f	retention efficiency ratio (%)

k	rate constant (s^{-1})
k_d	rate constant of intraparticular diffusion (mg L^{-1} min$^{-1/2}$)
M	molar mass of mercury (g mol^{-1})
m_D	mass of the dry membrane (g or mg)
m_s	mass of the wet membrane (g or mg)
M_w	molecular weight of the polymer (g mol^{-1})
N	quantity of nitrogen atoms in a complexing site
n_d	quantity of desorbed Hg(II) (mol)
n_{eq}	quantity of Hg(II) in the solution at equilibrium (mol)
n_{GL}	amount of the glutaraldehyde solution (mol)
n_{PVA}	amounts of poly(vinyl alcohol) in the membrane (mol)
n_r	quantity of Hg(II) retained in the membrane (mol)
n_0	initial quantity of Hg(II) in the solution (mol)
n_{VP}	quantity of 4-vinylpyridine repetition units in the membrane (mol)
q_t	mass of Hg retained per g of membrane after time t (mg g^{-1})
q_{eq}	mass of Hg retained at equilibrium per g of membrane (mg g^{-1})
q_{max}	maximum mass of Hg retained per g of membrane (mg g^{-1}) from Langmuir isotherm
r^2	correlation coefficient of a linear regression
R	retention ratio (%)
S_W	swelling ratio of the membrane
t	time (h or min)
T	temperature (°C or K)
$t_{1/2}$	half-reaction time of the kinetics of sorption (min)
V	volume of solution (L or cm^3)
V_{calc}	calculated volume of filtrate at saturation of the membrane (L or cm^3)

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