Chemical Engineering Journal 164 (2010) 37–48

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Mercury removal from wastewater using a poly(vinylalcohol)/poly(vinylimidazole) complexing membrane

H. Bessbousse [a,b], T. Rhlalou [b,1], J.-F. Verchère [a], L. Lebrun [a,*]

[a] *UMR 6270 CNRS-Université de Rouen, FR 3038, 76821 Mont-Saint-Aignan Cedex, France*
[b] *Université Hassan I^{er}, FST de Settat, BP 577, Settat, Morocco*

ARTICLE INFO

Article history:
Received 11 March 2010
Received in revised form 24 June 2010
Accepted 3 August 2010

Keywords:
Mercury
Poly(vinylimidazole)
Poly(vinylalcohol)
Chelating membrane
Sorption
Wastewater treatment

ABSTRACT

Removal of Hg(II) ions from aqueous solutions by a novel complexing membrane was investigated by performing sorption and filtration experiments. The membrane, prepared by the technique of semi-interpenetrated polymer networks, consists in a matrix of poly(vinylalcohol), crosslinked by gaseous dibromoethane, that immobilizes chains of poly(vinylimidazole), a complexing polymer synthesised for this purpose. The morphology of the membrane was observed by scanning electron microscopy, showing an homogeneous structure, but surface unevenness. The dissolution of the membrane in water was slow and limited to 8% in 2 months, showing the efficiency of the crosslinking process. Efficient retention of Hg(II) was observed at pH 2.5. The kinetics of sorption were studied. The sorption equilibrium was satisfactorily represented by the Langmuir model. Isotherms performed at different temperatures allowed the calculation of the thermodynamical parameters. The sorption of mercury was endothermic, with a large positive entropy change that was ascribed to proton release. The effects of parameters such as water hardness, and the presence of complexing chloride anions were investigated, showing little influence on the retention ratio. Fast and efficient regeneration of the membrane was performed with a 0.5 M HNO_3 solution. The maximum capacity of the membrane was 120 mg Hg g^{-1}, whereas the theoretical exchange capacity was 853 mg Hg g^{-1}, showing that most internal complexing sites of the membrane were not accessible to mercury ions in sorption experiments. When used in the filtration mode, the elimination ratio of Hg(II) was ≥99.4% for solutions containing 91.6 or 17.5 mg Hg L^{-1}.

1. Introduction

The presence of increasing amounts of toxic heavy metals in aqueous water streams, resulting from rapid industrialisation advances, is a worldwide environmental problem. Treatment of contaminated water to remove these soluble pollutants has been and continues to be a technical challenge, due to very low concentration levels laid down by current regulations. Stringent national and international regulations on water pollution make it essential to develop better and more efficient techniques for separating these contaminants from effluent water. Among heavy metals, mercury is in most widespread concern to human health [1–3]. The prescribed limit of 0.001 ppm for mercury [4,5] is the lowest among all those for heavy metal ions. Mercury in any form attacks the central nervous system, causing mental and motor dysfunction such as paralysis, blindness, and chromosome breakage [1–6]. Elevated levels of Hg(II) in water may come from a variety of sources, such as effluents from manufacturing of chlorine, switch gear/batteries, fertilizers, pharmaceuticals, combustion of fossil fuels, textile industries, pulp and paper industry, and agricultural chemicals. There are several methods for removing heavy metals from aqueous solutions, such as chemical precipitation, membrane filtration, biological treatment, ion exchange, and adsorption. Several types of adsorbents have been considered in the literature. The use of adsorbents containing natural polymers such as chitosan is currently growing [7,8], especially in the form beads or microspheres [9,10]. Low cost adsorbents, often derived from biomass, have received growing attention in the recent past [11,12] at the expense of synthetic adsorbents, because they are inexpensive, while showing remarkable and sometimes specific efficiency in reducing the concentration of heavy metal ions to very low levels [13]. Many metals ions have been studied in this respect, including Hg(II) [14,15].

Membrane processes are probably the most attractive and efficient methods for removing heavy metals [10,16–25]. One of the most promising methods is the use of chelating adsorbing membranes. Many articles that cover a vast number of different chelating membrane were reported [16,18–20,26–28]. Immobilized chelation process for the removal of soluble metals has become an

---

[*] Corresponding author. Tel.: +33 2 35 14 67 02; fax: +33 2 35 14 67 04.
E-mail address: laurent.lebrun@univ-rouen.fr (L. Lebrun).

[1] Sadly, Prof. Rhlalou passed away during writing of the manuscript.

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.08.004

Nomenclature

Abbreviations

AAS	atomic absorption spectroscopy
AIBN	2,2′-azo-bis-isobutyronitrile
DBE	1,2-dibromoethane
EDTA	ethylenediaminetetraacetic acid
PAUF	polymer-assisted ultrafiltration
PVA	poly(vinyl alcohol)
PVI	poly(vinylimidazole)
SEM	scanning electron microscopy
s-IPN	semi-interpenetrating polymer network
TGA	thermogravimetric analysis
TOC	total organic carbon
UF	ultrafiltration
1-VI	1-vinylimidazole

Symbols

b	sorption coefficient in Langmuir isotherm ($\mathrm{L\,mg^{-1}}$)
c	concentration ($\mathrm{mol\,L^{-1}}$ or $\mathrm{mg\,L^{-1}}$)
c_{eq}	equilibrium concentration ($\mathrm{mg\,L^{-1}}$)
c_{F}	filtrate concentration ($\mathrm{mg\,L^{-1}}$)
C_p	apparent exchange capacity of the membrane ($\mathrm{mmol\,g^{-1}}$)
c_{t}	concentration at time t ($\mathrm{mg\,L^{-1}}$)
C_{th}	theoretical exchange capacity of the membrane ($\mathrm{mmol\,g^{-1}}$)
c_0	initial concentration ($\mathrm{mg\,L^{-1}}$)
D	desorption ratio (%)
E	elimination ratio (%)
f	retention efficiency ratio (%)
k	rate constant ($\mathrm{s^{-1}}$)
m	mass of the dry membrane (g or mg)
m_{PVI}	mass of PVI in the membrane (mg)
m_{w}	mass of the wet membrane (g or mg)
$\overline{M_w}$	molecular weight of the polymer ($\mathrm{g\,mol^{-1}}$)
N	number of nitrogen atoms in a complexing site
n_{a}	quantity of sorbed Hg in the membrane (mol)
n_{d}	quantity of desorbed Hg (mol)
n_{N}	quantity of nitrogen atoms in the membrane ($\mathrm{mmol\,g^{-1}}$)
n_{r}	quantity of Hg retained in the membrane (mol)
$n_{\mathrm{1\text{-}VI}}$	quantity of 1-vinylimidazole monomer units in the membrane ($\mathrm{mmol\,g^{-1}}$)
$n_1 - n_2$	number of equivalents exchanged (mmol)
q	quantity or mass of Hg retained at equilibrium per g of membrane ($\mathrm{mmol\,g^{-1}}$ or $\mathrm{mg\,g^{-1}}$)
q_{lim}	experimental quantity or mass of Hg retained per g of membrane ($\mathrm{mmol\,g^{-1}}$ or $\mathrm{mg\,g^{-1}}$) from sorption isotherm
q_{max}	maximum quantity or mass of Hg retained per g of membrane ($\mathrm{mmol\,g^{-1}}$ or $\mathrm{mg\,g^{-1}}$) calculated from Langmuir isotherm
q_{th}	theoretical quantity or mass of Hg retained per g of membrane ($\mathrm{mmol\,g^{-1}}$ or $\mathrm{mg\,g^{-1}}$)
R	retention ratio at equilibrium (%)
R_{L}	equilibrium parameter from Langmuir isotherm
r^2	correlation coefficient of a linear regression
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 or s)
V	volume of solution (L or $\mathrm{cm^3}$)
V_{calc}	calculated volume of filtrate at saturation of the membrane (L or $\mathrm{cm^3}$)
V_{F}	volume of filtrate (L or $\mathrm{cm^3}$)

important option in the integrated approach to aqueous waste treatment. A wide range of chelating agents has been used for removing heavy metals from wastewaters and has been reviewed by Rivas [29]. Another related technique for the removal of metal ions, named polymer-assisted ultrafiltration (PAUF), consists in the addition of water-soluble metal-binding polymers prior to ultrafiltration. The filtration is made easier because the addition of complexing polymers creates large complex entities that increase the size of the solute to be retained.

The subject of this work was the design of UF membranes in which a complexing water-soluble polymer was integrated, in order to group the complexation and filtration steps of PAUF in a single operation. Thus, the membranes would retain the metal ions during the filtration. The advantages of complexing membranes are: (i) the amount of polymer used is much lower than in PAUF, (ii) the method should retain the selectivity of PAUF, if provision is made for the appropriate choice of the complexing polymer, and (iii) the number of procedural steps is reduced.

Because the complexing polymer is water-soluble, it must be immobilised in the membrane for application to aqueous solutions. For this goal, the semi-interpenetrating polymer network (s-IPN) technique was employed. In this technique, chains of the complexing polymer are entrapped in a crosslinked polymeric matrix. Considering previous work performed in the laboratory [24], we selected the use of a poly(vinylalcohol) (PVA) matrix crosslinked by a treatment with gaseous 1,2-dibromoethane (DBE).

In this work, our attention was focused on the development of a membrane containing poly(vinylimidazole) as a complexing polymer for removal of mercury. Poly(vinylimidazole), hereafter called PVI, was selected because its imidazole groups readily form complexes with divalent metallic ions such as Co(II), Cu(II), Ru(II) and uranyl [30–35] and it is relatively simple to synthesize and purify to produce a reasonably sharp molecular weight distribution.

The sorption of Hg(II) ions from aqueous solutions by a PVA/PVI membrane was studied. The term sorption is preferred to adsorption, because the binding of Hg(II) takes place within the membrane and not only at its surface. In view of application to the treatment of real wastewaters that may have very different compositions, the sorbing capacity of the membrane for Hg(II) ions was investigated under different operating conditions, namely: initial mercury concentration, initial solution pH, mass of membrane, sorption time, ionic strength, water hardness and solution temperature. Sorption isotherms were determined at various temperatures, and the rates and thermodynamical parameters of the sorption process were calculated. Finally, the membrane was used in frontal filtration experiments.

2. Experimental

2.1. Chemicals

PVA (99% hydrolysed, $\overline{\mathrm{M_w}} = 124{,}000–186{,}000\ \mathrm{g\,mol^{-1}}$) was provided by Sigma-Aldrich (38297 Saint Quentin Fallavier, France). Toluene, 1-vinylimidazole (99%) (1-VI), and DBE (99%) were also supplied by Sigma-Aldrich and were used without further purification. 2,2′-Azo-bis-isobutyronitrile (98%) (AIBN) was purchased from Acros Organics (Fisher Scientific, 67403 Illkirch, France). Ethylenediaminetetraacetic acid (EDTA) (99%) was provided by

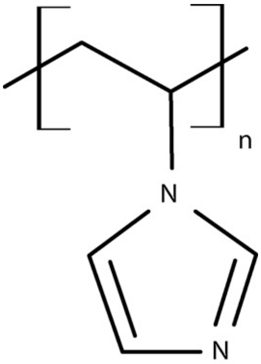

Fig. 1. The chemical structure of poly(vinylimidazole) (PVI).

Labosi. (Fisher Scientific). Nitric acid (65%) and hydrochloric acid (37%) were supplied by Sigma-Aldrich. Mercury nitrate and the mercury standard (1% wt/v in HNO_3) used for the calibration of the atomic absorption spectroscopy (AAS) were also supplied by Sigma-Aldrich.

2.2. Equipments and methods

The PVI polymer was synthesised, following a reported method [23], by free-radical polymerisation of distilled 1-VI (10 g) in anhydrous toluene (100 cm^3) using AIBN (1.64 g) as an initiator, during 6 h at 75 °C. After filtration on sintered glass, PVI was purified by washing with toluene and dried in an oven (70 °C, 48 h). The average molecular weight $\overline{M_w}$ of PVI was determined by the static light scattering technique using the Sematech (06200 Nice, France) SEM-Classical photogoniometer (laser He-Ne 3 mW, $\lambda_0 = 632.8$ nm) using the classical Zimm's plot graphic representation. The light scattering intensities were measured for various PVI concentrations (2.5, 5, 7.5 and 10 g L^{-1}) in 0.1 mol L^{-1} NaCl at various angles (from 20° to 150°). Before light scattering experiments, samples were clarified by filtration under vacuum (Millex units from Millipore; 0.45 μm pore size). The refractive index increment (dn/dC) of the polymer in solution was measured using a Shimadzu (77420 Champs-sur-Marne, France) RID-6A refractive index detector associated to a peristaltic pump delivery system. The chemical structure of PVI is shown in Fig. 1.

The preparation of the PVA/PVI membrane was carried out as described elsewhere for related polymers [24,26,36]. A mixture of PVA and PVI in the appropriate (60/40) mass ratio was made in aqueous solution. The solvent was evaporated in a Petri dish (diameter 13.7 cm) at room temperature for 5 days, until obtaining a film (mass ≈1.7 g; area ≈140 cm^2; thickness ≈70 μm). The thickness of the membranes was measured with a Palmer, using dry samples maintained for 24 h in a desiccator over phosphorus pentoxide. Several measurements were made at nine different locations on the membrane area. The results were averaged with a ±5 μm uncertainty.

In order to make a membrane that would be insoluble in water, this film was crosslinked by reaction with gaseous DBE at 140 °C during 4 h, using a set-up previously described [24].

The temperature behavior of the film was studied by the thermogravimetric analysis technique (TGA). TGA measurements were performed, in a nitrogen atmosphere, on small samples of polymer film (about 8–15 mg) that were heated (30–140 °C during 11 min), then maintained at 140 °C for 240 min. The TGA curves were drawn with a TGA 7 thermogravimetric analyzer from Perkin-Elmer (91945 Courtaboeuf, France). coupled with a PC computer. The samples had undergone no-drying or other preliminary treatment.

The efficiency of the crosslinking reaction was monitored by determining the swelling ratio S_w for the membrane in water S_w was defined as [16,28]:

$$S_w = \frac{m_w - m}{m} \times 100 \tag{1}$$

where m and m_w are the weights of the dry and wet membrane, respectively.

The efficiency of the crosslinking reaction was also checked by FTIR measurements using the Nicolet (Thermo Scientific, 91963 Courtaboeuf, France) Avatar 360 FTIR. The spectra of the PVA/PVI samples were compared before and after crosslinking treatment.

For structural characterization, the membrane morphology was observed using a Jeol (78290 Croissy-sur-Seine, France) JSM-1200EX II Scanning Electron Microscopy (SEM). All samples were frozen in liquid nitrogen at −196 °C and covered with a gold layer before observation.

The PVA/PVI crosslinked membrane immersed in water may nevertheless disintegrate gradually, releasing chains of PVI or of the PVA matrix. Experiments were made by immersing dry membrane samples ($m \approx 100$ mg) in MilliQ water (Millipore SAS Europe, 67120 Molsheim, France) ($V = 100$ cm^3) for different residence times (1, 4, 7, 14 and 35 days) and determining the dissolved amount of carbon and nitrogen in each of these aqueous solutions. The amounts of organic elements released into water were determined by measuring the levels of total organic carbon and nitrogen with a total organic carbon analyser (TOC), model VCNS, Shimadzu (77420 Champs-sur-Marne, France).

The apparent exchange capacity of the membrane, C_p, is the amount of donating nitrogen atoms per unit mass of membrane (mmol g^{-1}), that was determined by back-titration. The value of C_p was determined after a double alternate conditioning of a membrane sample ($m \approx 100$ mg) in 0.01 M NaOH and 0.01 M HCl for an immersion time of 4 h. Finally, the sample in H^+ form was equilibrated in water for 12 h to remove the free hydrogen ions. After this washing, the membrane was immersed in a known volume (25 cm^3) of 0.01 M NaOH solution. Titration of the initial NaOH solution by 0.01 M HCl gave the initial amount of hydroxide ion (n_1). Titration of the same solution, after immersing the membrane for 4 h, gave the final amount of hydroxide ion (n_2). The apparent exchange capacity (C_p) is defined by Eq. (2):

$$C_p = \frac{n_1 - n_2}{m} \tag{2}$$

where $n_1 - n_2$ is number of equivalents exchanged, and m is a mass of dry membrane (g).

The theoretical exchange capacity of the membrane, C_{th}, is the quantity of monomer units contained in a mass m of dry membrane (mmol g^{-1}). It is given by Eq. (3):

$$C_{th} = \frac{0.4 \times 10^3}{M_{1\text{-VI}}} \tag{3}$$

The 0.4 factor was introduced because the membrane contained 40% (wt/wt) PVI. $M_{1\text{-VI}}$ is the molar mass of vinylimidazole (g mol^{-1}).

A Tacussel Radiometer (Hach Lange France SAS, 69627 Villeurbanne, France) LPH-230T pH-meter fitted with a combined glass electrode was used for all pH measurements.

The concentration of Hg(II) in solution was determined using a Spectra AA 10/20 flame atomic absorption spectroscopy (AAS) from Varian (91941 Les Ulis, France). All AAS measurements were duplicated and were reproducible within 0.4% accuracy.

2.3. Sorption–desorption experiments

The PVA/PVI membrane was tested in static systems for its ability to remove Hg(II) ions, present in aqueous solutions, by sorption.

Static studies were performed to obtain data on the rate and extent of sorption. For sorption isotherms, a series of 50 cm^3 of Hg(II) solutions of varying concentration (in the 20–4000 mg L^{-1} range), were stirred using a mechanical shaker at 100 rpm and studied at the desired pH and temperature. The initial pH was controlled by addition of NaOH or HNO_3. For kinetic studies, samples of 5 cm^3 were withdrawn at known times.

The mass q of mercury sorbed at equilibrium per g of membrane (mg g^{-1}) was calculated using the general definition [16,27,28]:

$$q = \frac{200.7(c_0 - c_{eq})V}{m} \tag{4}$$

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), 200.7 g mol^{-1} is the molar mass of Hg, and m is the mass of membrane (g).

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

$$R = \frac{(c_0 - c_{eq})}{c_0} \times 100 \tag{5}$$

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

$$f = \frac{n_r}{n_{1\text{-VI}}} \times 100 \tag{6}$$

where n_r is the quantity (mol) of Hg(II) retained in the membrane, and $n_{1\text{-VI}}$ is the quantity (mol) of 1-vinylimidazole (1-VI) repetition units in the membrane.

n_r and $n_{1\text{-VI}}$ were calculated by Eqs. (7) and (8), respectively:

$$n_r = \frac{(c_0 - c_{eq})V}{200.7 \times 10^3} \tag{7}$$

$$n_{1\text{-VI}} = \frac{0.4 \cdot m}{94} \tag{8}$$

where the factor 0.4 is introduced because the membrane contains 40% (wt/wt) PVI, 94 g mol^{-1} is the molar mass of 1-VI, the factor 10^3 is introduced because c_0 is in mg L^{-1} instead of g L^{-1}.

The desorption of Hg(II) ions was achieved by using HNO_3 as the desorbing agent. The initial sorption step was carried out during 24 h in solutions of Hg(II) (c_0 = 100 mg L^{-1}, V = 50 cm^3, pH 2.5). Then, the loaded membrane was placed in the desorption medium (V = 50 cm^3) and stirred at a stirring rate of 10.4 rad s^{-1} up to 24 h. The desorption ratio D was calculated by Eq. (9) [16,27]:

$$D = \frac{n_d}{n_r} \times 100 \tag{9}$$

where n_r is the quantity (mol) of Hg(II) retained in the membrane and n_d is the quantity of desorbed Hg(II), calculated from the final Hg(II) concentration in the desorption medium. The concentrations of Hg(II) in the solutions were determined by AAS.

2.4. Frontal filtration experiments

The filtration experiments were performed using the thermostated (25 ± 0.5 °C) two-chamber cylindrical cell (V = 450 cm^3) previously described [26]. The membrane (effective area, 28.3 cm^2), was weighed when dry (m) 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 = 17.5 or 91.6 mg L^{-1}). The filtration experiment was started by applying pressure (0.30 ± 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 analysed by AAS.

Table 1
Optimisation of the crosslinking conditions for the PVA/PVI membrane: influence on the swelling ratio S_w of the crosslinking time t with gaseous DBE at 140 °C.

	t (min)					
	30	60	120	180	240	300
S_w	0.85	0.79	0.71	0.68	0.50	0.54

Accuracy: S_w ±5%.

3. Results and discussion

3.1. PVI polymerisation

The yield of the free-radical polymerisation of PVI was 91% (wt/wt). The dn/dC value for the synthesised polymer was 0.207 cm^3 g^{-1} in 0.1 M NaCl solution. Hence, the value for $\overline{M_w}$ was 52,000 ± 5000 g mol^{-1}, in close agreement with the reported value [23].

3.2. Film crosslinking with gaseous DBE

Crosslinking of the PVA matrix by reaction with gaseous DBE at 140 °C was performed because both water-soluble polymers would dissolve when the membrane is placed in contact with aqueous solutions. After crosslinking, the membrane interaction with water is limited to swelling. Thus, the swelling ratio S_w is a good indicator of the efficiency of the crosslinking reaction. The smaller the S_w value, the better the crosslinking. On the other hand, the extent of swelling must be limited (S_w < 0.7) in order to retain the complexing properties of the membrane. Accordingly, most commercial ion-exchange membranes are designed with S_w > 0.2, because below this value, the membranes generally are rigid and show insufficient flow rates. Besides, the evaluation of the efficiency of the crosslinking of films must take into account their tanning, their rigidity, and their deterioration. It was thus necessary to seek a compromise between the S_w value and these qualitative criteria in order to determine the optimal time for the DBE crosslinking reaction.

Measurements of S_w were carried out on the membrane to investigate the efficiency of the DBE crosslinking reaction. Various crosslinking times were tested (Table 1), showing that S_w reached a constant value, close to 0.5, after 240 min crosslinking. Thus, a crosslinking time of 4 h was used for the preparation of all membranes.

3.3. Film and membrane characterisation

Since PVA was crosslinked at 140 °C for 4 h, the thermal stability of a PVA/PVI film was studied at this temperature by TGA. The experimental procedure was similar to the experimental conditions of crosslinking: (i) rise in temperature from 30 °C to 140 °C at 10 °C min^{-1}, (ii) isotherm at 140 °C for 240 min. Fig. 2 shows a loss of weight (about 7.5%) in the first heating step. This mass loss was attributed to a physical dehydration (desorption of water molecules adsorbed on the film). Observation of the isotherm at 140 °C shows that the mass decreased slowly, revealing excellent thermal stability of the PVA/PVI film for 240 min at 140 °C.

The efficiency of the DBE crosslinking of the PVA/PVI membrane was investigated by comparing its FTIR spectra before and after crosslinking (Fig. 3). In the spectrum after crosslinking, new peaks detected at 1182 cm^{-1} indicated the formation of ether links between the hydroxyl groups of PVA. This spectrum also showed a decrease in the intensity of the band located at 3200 cm^{-1}, attributed to the stretching vibration of the hydroxyl groups. This modification proved that the PVA chains were crosslinked by DBE, forming a network in which the PVI is entrapped.

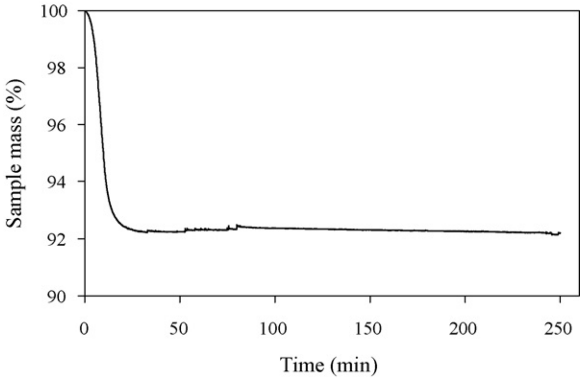

Fig. 2. The FTIR spectra of PVA/PVI films before (- - -) and after (—) DBE crosslinking (4 h, 140 °C).

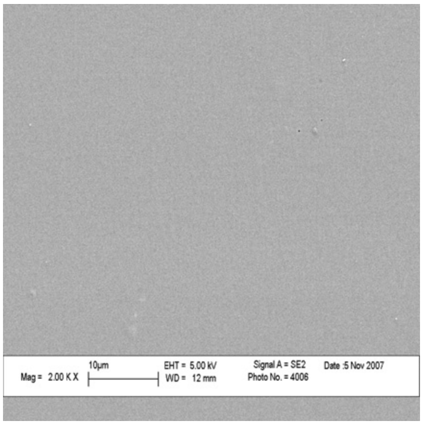

Fig. 5. SEM image (2000×) of a PVA/PVI film surface before crosslinking.

The morphology of a PVA/PVI membrane was examined by SEM. Fig. 4 shows views of the section and surface of the membrane. The SEM observation of the section (a) shows a compact, dense and homogeneous material. This image reveals no nodule or aggregate, and the absence of cavities, indicating that the mixture of polymers is compatible. In contrast, the image of the surface (b) shows regular folds and sinuous paths. A likely interpretation of this unevenness is that the crosslinking treatment at 140 °C resulted, at the surface, in a tightening of the PVA network. To confirm the hypothesis that the surface contracts during curing by DBE, images of the film before crosslinking of the membrane were examined (Fig. 5). This film did not present the characteristic undulations of the membrane, which is consistent with the idea that the crosslinking process caused the unevenness. These results demonstrate that the PVA/PVI membrane, although totally homogeneous, had a heterogeneous surface.

Because both polymers present in the membrane are hydrophilic, they may partially dissolve when the membrane is in lengthy contact with aqueous solutions. Hence, the stability of the membrane in contact with water was studied by monitoring the appearance of carbon and nitrogen in water with time, with a COT analyser. The yields of nitrogen and carbon losses were calculated as the ratio of the element mass present in the water at time *t* to

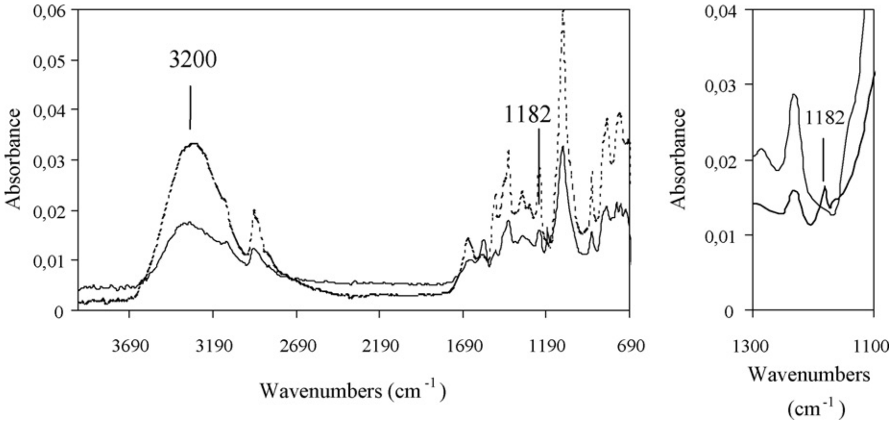

Fig. 3. TGA curve of a PVA/PVI film, 30–140 °C in 11 min, then at 140 °C for 240 min.

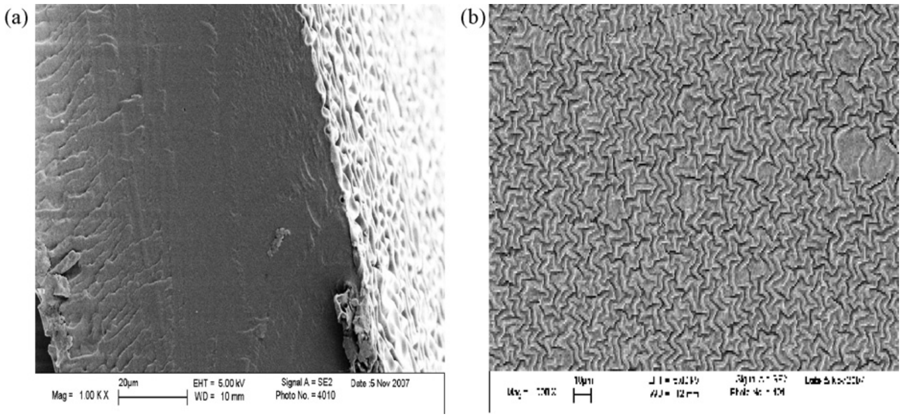

Fig. 4. SEM images of the section (1000×) (a) and surface (500×) (b) of a PVA/PVI membrane.

Table 2
Dissolution in water of PVA and PVI polymers from the membrane.

Time (days)	Nitrogen dissolved (%)	Carbon dissolved (%)	PVI dissolved (%)	PVA dissolved (%)
1	4.3	11.0	4.3	5.2
4	6.5	15.7	6.5	7.2
7	7.0	16.7	7.0	7.6
14	7.9	19.1	7.9	8.8
70	8.1	20.3	8.1	9.6

$m \approx 100$ mg, $V = 100$ cm^3. Accuracy: nitrogen ±2.5%, carbon ±5%. Temperature 20 °C.

the element mass initially present in the PVI, known from the composition of the membrane. Since the PVA matrix was crosslinked, it was assumed first that only PVI dissolved. If it was the case, the yields of N and C losses would have been equal, but in fact, the yield found for carbon loss was larger than that for nitrogen loss, showing that PVA also dissolved. Since only PVI contains nitrogen, the dissolution yield of PVI equals the yield of nitrogen loss. Then, by difference between total dissolved carbon and carbon generated from PVI dissolution, the mass of carbon due to PVA dissolution was calculated, and finally the yield of PVA dissolution. The results given in Table 2 show that the matrix gradually dissolved, releasing PVA as well as the entrapped PVI. The dissolution yields of both polymers vary in similar way at any time of contact, that of PVA being slightly larger than that of PVI, in agreement with their 60/40 mass ratio in the membrane. The initial losses of polymers (PVA 5% and PVI 4% after 1 day) are probably due to the dissolution of the few uncrosslinked parts of the membrane. After this fast dissolution, subsequent dissolution was slower (it doubled in 70 days), showing a very low degradation rate of the membrane. Thus, crosslinking of the PVA/PVI membrane lead to almost complete immobilisation of PVI, as shown by the slow rate of polymers loss.

Another way to test the stability of the PVA/PVI membrane on the long term was to measure its efficiency for sorption of Hg(II) ions after a stay in water. The experiments were performed with the membrane samples used in the previous experiment ($m \approx 100$ mg), that had remained in water from 1 to 70 days. These membranes were used for the sorption of a Hg(II) solution ($c_0 \approx 100$ mg L^{-1}, $V = 50$ cm^3, pH 2.5). For each membrane, the values of the retention ratio R and the mass of mercury sorbed at equilibrium par g of membrane, q, were determined using Eqs. (4) and (5). Table 3 summarises the results. The membranes almost retained their sorption capacity after a residence time of 70 days; the maximum loss being 3%. In relation with the results of the previous experiment, this finding shows that a fraction of PVI, up to 8%, may dissolve without important decrease of the retention ratio, which remained in the range 94–91%.

Finally, the concordance of the results obtained for the PVA/PVI membrane stability in water show that the crosslinking of the membrane was sufficient to allow its use, for at least 2 months, without appreciable loss of performance.

Mercury removal by the membrane is based on a complex-forming reaction that involves the nitrogen atoms of PVI. These nitrogen atoms are also involved in ion-exchange phenomena, that are usually characterised by the exchange capacity of the membrane. The apparent exchange capacity C_p (mmol g^{-1}) is the amount of available nitrogen atoms per unit mass of membrane, determined by titration with a strong acid. The theoretical exchange capacity of the membrane, C_{th}, is the number of moles of PVI monomer unit contained in a mass m of membrane, because is known that, although an imidazole ring contains two nitrogen atoms, only one is involved in proton exchange or metal complexing [34].

The theoretical and apparent (experimental) exchange capacities of the membrane are reported in Table 4, with the acidity constant of PVI and the results obtained for the sorption of Hg(II) ions after immersion in water for 1 day. However, the conditions for sorption of mercury, at $c_0 \approx 100$ mg L^{-1}, did not correspond to the saturation of the membrane. The results show that the value of C_p was much lower than that of C_{th}. The reasons are, first, that most sites are not accessible to proton exchange, and second, that the entrapment of PVI in the PVA network is not complete and allows partial dissolution. We have shown that immobilization of PVI in the PVA matrix is incomplete, with a 4.3% loss during the first day of immersion in water.

It could have been expected that, since the proton is a hard acid, and ions of heavy metals are soft acids, the affinity of PVI for ions such as Hg(II) might be greater than for the proton. However, the sorption capacity for Hg(II) ions was even lower than the apparent exchange capacity. A reason for this discrepancy may be differences between the size and coordination number of the exchanged ion. One can foresee that some sites accessible to the small proton cannot accommodate the large mercury ion. We can also assume that the Hg(II) ion, with maximum coordination number 6, may bind with several nitrogen atoms, while the proton binds only with one nitrogen atom. In conclusion, the apparent exchange capacity of the PVA/PVI membrane represents 8% of the theoretical capacity, which shows that 92% of the complexing sites of the PVA/PVI membrane are unavailable or inaccessible, even to the small proton. Why the amount of mercury sorbed is smaller (0.23 mmol g^{-1} vs. 0.33 mmol g^{-1}) than the apparent exchange capacity is probably due to the fact that the experimental conditions did not correspond to saturation of the membrane. It may also be due to the fact that the sorption of Hg(II) ions is restricted to a fraction of sites that possess a sufficient size for accommodation of the large mercury ion.

Table 3
Sorption of Hg(II) ions by the PVA/PVI membrane after lengthy immersion in water.

Time (days)	R (%)	q (mg g^{-1})
1	94.2	46.5
4	94.7	46.7
7	92.9	45.9
14	92.7	45.7
70	91.5	45.2

$c_0 \approx 100$ mg L^{-1}, $V = 50$ cm^3, $m \approx 100$ mg, pH 2.5, Accuracy: R ±3%, q ±1.5%.

Table 4
Exchange capacities of the PVA/PVI membrane.

C_p (mmol g^{-1})	0.33
C_{th} (mmol g^{-1})	4.25
C_p/C_{th} (%)	8
pK_a of PVI	4.9–5.45 [35]
Fixed mass of Hg(II)	
q (mg g^{-1})	46.5
q (mmol g^{-1})	0.23

Value of q in mg g^{-1} from Table 3. Accuracy: C_p ±1%, q ±1.5%.

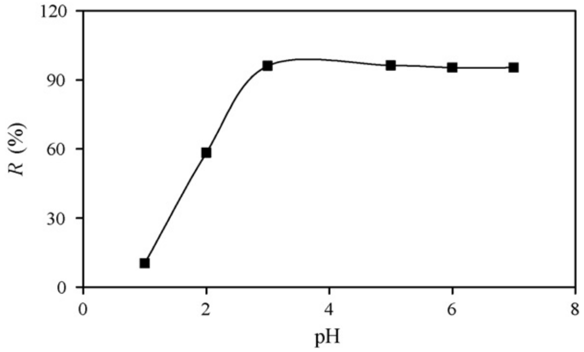

Fig. 6. Effect of pH on the retention ratio R of Hg(II) by PVA/PVI membrane.

3.4. Sorption experiments

3.4.1. Effect of the pH

The complexation of heavy metal ions by a chelating ligand strongly depends on pH. The medium pH also affects both the solubility of metal ion and the protonation state of the donating groups on the membrane. Moreover, the hydrolysis and precipitation of the metal ions are affected by their concentrations. In the present study, we changed the pH between 1.0 and 7.0. Experimental results for the effect of pH on Hg(II) ($c_0 \approx 100\,\mathrm{mg\,L^{-1}}$, $V = 50\,\mathrm{cm^3}$) sorption by the PVA/PVI membrane ($m \approx 100\,\mathrm{mg}$) are presented in Fig. 6. The retention ratio of the membrane clearly increased with increasing pH, reaching a constant value ($R \approx 97\%$) from pH 3.0 to 7.0. At pH <3, the retention ratio decreased rapidly when the acidity increased. Clearly, it is the competition between H^+ and Hg(II) ions for the same donating atoms that caused the decrease of R at low pH, because most of the nitrogen atoms were in protonated form. This is in agreement with the pKa value of PVI (pK_a = 4.9–5.45 [35]). In the second zone (between 3 and 7), the acidity decreased sufficiently for the nitrogen atoms to be deprotonated. The masses q of mercury sorbed at equilibrium per g of membrane at pH 3 and 7 were $44\,\mathrm{mg\,g^{-1}}$ and $45\,\mathrm{mg\,g^{-1}}$, respectively. Because the pH of the solution also affected 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. As a compromise, the optimum working pH for sorption of Hg(II) by the membrane was set at pH 2.5. At this acidity, Hg(II) ions would not precipitate if their concentration is lower than $2000\,\mathrm{mg\,L^{-1}}$. This limit was calculated using the value of the solubility product (pKs = 25.0) reported for $Hg(OH)_2$ [37]. Moreover, since precipitation was not instantaneous, experiments could be performed even at $c_0 = 4000\,\mathrm{mg\,L^{-1}}$. For all subsequent experiments, the optimal pH 2.5 value was used.

3.4.2. Sorption kinetics

The sorption rate was studied in order to determine an optimal contact time for the sorption of Hg(II) ions by PVA/PVI membrane from an aqueous solution, $c_0 = 221.2\,\mathrm{mg\,L^{-1}}$, $V = 230\,\mathrm{cm^3}$ and pH 2.5. The concentration, c_t, of Hg(II) decreased with time until reaching a plateau. Fig. 7 shows a rapid sorption within 60 min, whereas sorption equilibrium is attained within 120 min. At the end of the kinetic experiment, after 24 h contact time, the mass q of mercury sorbed at equilibrium per g of membrane was $76\,\mathrm{mg\,g^{-1}}$. Under our experimental conditions (Table 5), the proportion of occupied sites was small (the metal ion retention efficiency ratio of the membrane was $f = 9\%$) and therefore, the concentration of complexing sites of PVI was almost unchanged. It follows that the sorption step should be of pseudo-first order with respect with Hg(II), as demonstrated by a linear plot of Ln $(c_t - c_{eq}) = f(t)$. The results are given in Table 5 for first-order kinetics. The rate constant k was calculated and the half-reaction time ($t_{1/2} \approx 23.4$ min) was consistent with the reaction being complete in about 2 h.

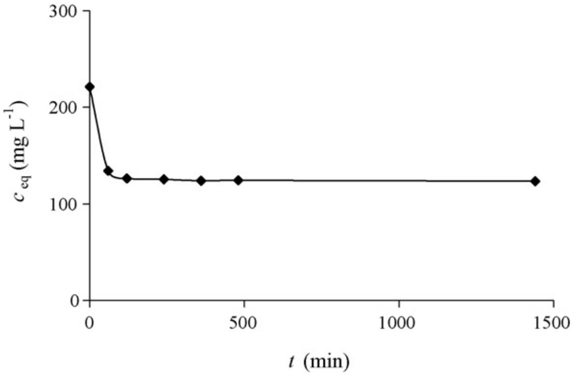

Fig. 7. Kinetics of sorption of Hg(II) by the PVA/PVI membrane. Concentration c_t of Hg(II) vs. time t.

Table 5
Yields and kinetics of sorption: rate constant k and half-reaction time $t_{1/2}$.

m (mg)	294.7
c_0 (mg L^{-1})	221.2
c_{eq} (mg L^{-1})	123.4
f (%)	9
q (mg g^{-1})	76
k ($\times 10^4$ s^{-1})	5.0
$t_{1/2}$ (s)	1404.7
r^2	0.9806

Room temperature, $V = 230\,\mathrm{cm^3}$, pH 2.5, accuracy q ±2.0%, k ±20%, i.e. $\pm 0.2 \times 10^{-4}\,\mathrm{s^{-1}}$.

3.4.3. Effect of the mass of membrane

Fig. 8 shows the results of sorption experiments, as a function of membrane mass (m, 50–500 mg), from an aqueous solution of Hg(II) ($c_0 \approx 100\,\mathrm{mg\,L^{-1}}$, $V = 50\,\mathrm{cm^3}$) at pH 2.5 during 24 h. When m increased, the retention ratio R increased up to 100 mg and then remained constant ($R = 96 \pm 2\%$), in agreement with increasing the number of complexing sites. For masses smaller than 100 mg, there was a significant reduction in the sorption. When m increased, the mass of mercury fixed at equilibrium increased and reached a maximum value, while the mass q of mercury fixed per gram of membrane decreased (Table 6). This result was expected, because the same amount of Hg(II) ions reacted with an increasing quantity of sites, resulting in a lower ratio of occupied sites. It is clear that, for a maximum sorption of Hg(II), a minimum membrane mass of 100 mg was required. Accordingly, a mass of 100 mg of membrane was used for the sorption of Hg(II) in all subsequent experiments.

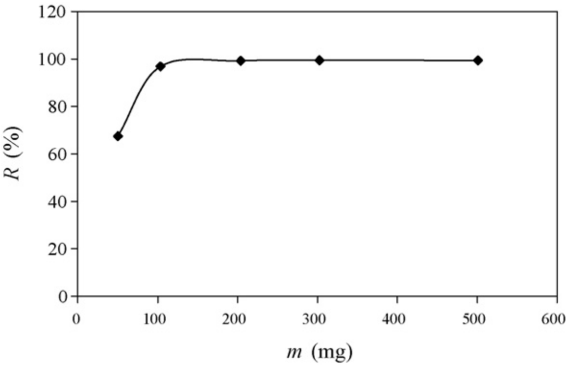

Fig. 8. Influence of the mass m of membrane on the sorption of Hg(II). Retention ratio R vs. m.

Table 6
Effect of mass *m* of PVA/PVI membrane on the sorption of Hg(II) ions.

	m (mg)				
	50.2	103.5	203.8	302.5	501.0
c_{eq} (mg L^{-1})	30.5	3.0	0.8	0.5	0.6
Mass of Hg(II) fixed (mg)	3.2	4.5	4.6	4.7	4.7
q (mg g^{-1})	63.0	43.9	22.8	15.4	9.3

$c_0 \approx 100$ mg L^{-1}, $V = 50$ cm^3, pH 2.5, $t = 24$ h. Accuracy: q ±1.5%.

3.4.4. Effect of the initial concentration of Hg(II) ions: sorption isotherm

A sorption isotherm describes the sorption capacity for a given system (membrane/solute) at a fixed temperature. It expresses the mass of solute fixed per unit mass of membrane, q, versus its equilibrium concentration c_{eq}. The initial concentration c_0 was varied in the 17–3640 mg L^{-1} range at pH 2.5. The values of q for the PVA/PVI membrane are plotted versus c_{eq} of Hg(II) in Fig. 9. The values of q increased and reached a limiting value q_{lim} that corresponds to the saturation of all available complexing sites of the membrane. The maximum sorption capacity was $q_{lim} \approx 120$ mg g^{-1}. For comparison, the theoretical value of q_{lim} was calculated as follows. The theoretical exchange capacity of the membrane is $C_{th} = 4.25$ mmol g^{-1} (Table 4). Since an average complexing site contains a single nitrogen atom, the maximum retained amount of Hg(II) ion should be C_{th}. The theoretical mass of Hg that can be retained in 1 g of membrane was finally calculated, knowing the molar mass of Hg(II). This theoretical mass is $q_{th} = 4.25 \times 200.7 = 853$ mg g^{-1}, which is not in agreement with the experimental value ($q_{lim} \approx 120$ mg g^{-1}). The experimental mass is 7 times smaller than the calculated value, confirming that many sites are inaccessible to Hg(II) ions. The theoretical value favourably compares with data reported for the chitosan adsorption capacity for Hg(II): 361.1 mg g^{-1} at pH 2.5, when chitosan was in the form of flakes [8]. For adsorption of Hg(II) on PEI-attached PHEMA gel beads (PEI is poly(ethyleneimine) and PHEMA is poly(2-hydroxyethylmethacrylate)), the maximum adsorption capacity was 334.9 mg g^{-1} [9]. When chitosan was used in the form of glutaraldehyde-crosslinked membrane or beads, larger adsorption capacities were observed, at pH 6: 888 and 648 mg g^{-1}, respectively [10].

The experimental value q_{lim} of Hg(II) was also compared to the apparent exchange capacity value determined for the PVA/PVI membrane (Table 4). Since $C_p = 0.33$ mmol g^{-1}, the theoretical mass of mercury sorbed would be $0.33 \times 200.7 = 66.2$ mg g^{-1}, which is smaller than the experimental value ($q_{lim} \approx 120$ mg g^{-1}). By comparison with the experimental data in Table 4, with did not correspond to membrane saturation, the mass of Hg sorbed was larger, as expected because saturation of the membrane was obtained.

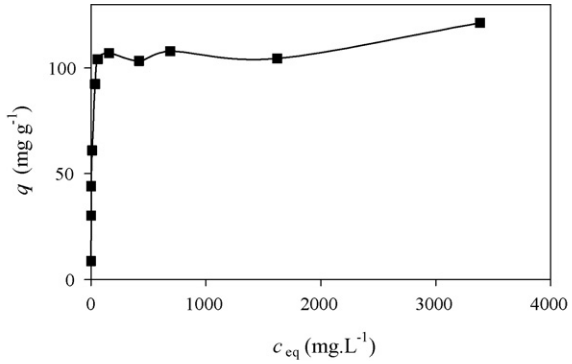

Fig. 9. Sorption isotherm of Hg(II) on a PVA/PVI membrane. Influence of the initial concentration c_0 on the sorption of Hg(II).

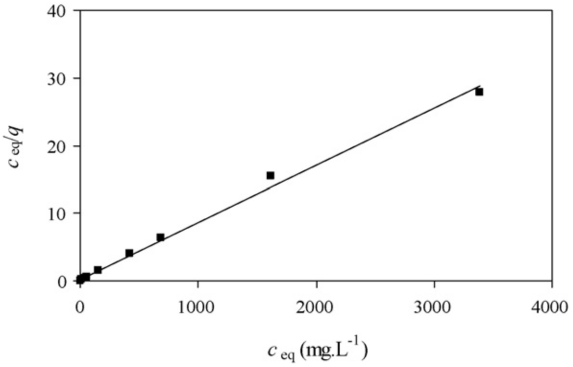

Fig. 10. Langmuir plot for the sorption of Hg(II) on a PVA/PVI membrane at room temperature.

However, the mass of Hg sorbed was twice larger than that calculated from C_p. Hence, the hypothesis that the number of nitrogen atoms available for mercury is smaller than that of atoms available for protons, because of the difference in size, is not verified. Another explanation would be that, contrary to protons that bind with a single N atom of imidazole, two mercury ions would bind with an imidazole ring, by using the two N atoms.

The sorption isotherm was used to characterise the interaction of Hg(II) with the membrane. It provides a relationship between the concentration of Hg(II) in the aqueous solution and the amount of Hg(II) sorbed by the membrane (solid-phase) when the two phases are at equilibrium. Sorption data are usually represented by the Langmuir isotherm. The Langmuir equation [10,27,28] is given below:

$$q = \frac{q_{max} b c_{eq}}{1 + b c_{eq}} \tag{10}$$

where q_{max} and b are the maximum sorbed mass at saturation (mg g^{-1}) and the sorption coefficient (L mg^{-1}), respectively. The values of q_{max} and b were determined from the linearised form (11) of Eq. (10):

$$\frac{c_{eq}}{q} = \frac{c_{eq}}{q_{max}} + \frac{1}{b q_{max}} \tag{11}$$

In agreement with Eq. (11), a plot of c_{eq}/q versus c_{eq} gave a straight line with a slope $1/q_{max}$ and intercept $1/b\ q_{max}$.

The essential characteristic of a Langmuir isotherm is generally expressed in terms of a dimensionless constant called the equilibrium parameter, R_L, defined by relation (12) [27]:

$$R_L = \frac{1}{1 + b c_0} \tag{12}$$

It was stated that the value of R_L indicates that the isotherm is either unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [27].

The sorption isotherm was modelled by the Langmuir model. Fig. 10 shows the linear plot for Hg(II) sorption by PVA/PVI membrane. The equilibrium data fitted very well the Langmuir isotherm, with a correlation coefficient $r^2 = 0.9953$. Calculation of the Langmuir parameters gave the data presented in Table 7. The maximum

Table 7
Langmuir parameters for the sorption of Hg(II) by the PVA/PVI membrane.

Experimental	Langmuir		
q_{lim} (mg g^{-1})	b (L mol^{-1})	q_{max} (mg g^{-1})	r^2
120	6451	118.3	0.9953

Room temperature, $m \approx 100$ mg, $c_0 = 17$–3640 mg L^{-1}, pH 2.5, accuracy: q_{lim} ±1.5%, q_{max} ±1.5%.

Table 8
Values of thermodynamical parameters for the sorption of Hg(II) by the PVA/PVI membrane.

T (K)	b (L mol^{-1})	q_{max} (mg g^{-1})	r^2	ΔG° (kJ mol^{-1})	$-T\Delta S^\circ$ (kJ mol^{-1})
288	5260	120	0.9989	–20.5	–39.9
298	6329	118	0.9917	–21.7	–41.3
308	7305	112	0.9995	–22.8	–42.7
318	11,618	106	0.9995	–24.8	–44.1
328	12,551	92	0.9996	–25.8	–45.5
338	17,314	90	0.9981	–27.4	–46.8

$c_0 \approx 100$–2000 mg L^{-1}, $V = 50$ cm^3, $m \approx 100$ mg, pH 2.5. Accuracy: b ±5%; ΔG° ±1%, q_{max} ±9%. $\Delta H^\circ = 19.6 \pm 2.0$ kJ mol^{-1}, $\Delta S^\circ = 138.6 \pm 3.0$ J K^{-1} mol^{-1}.

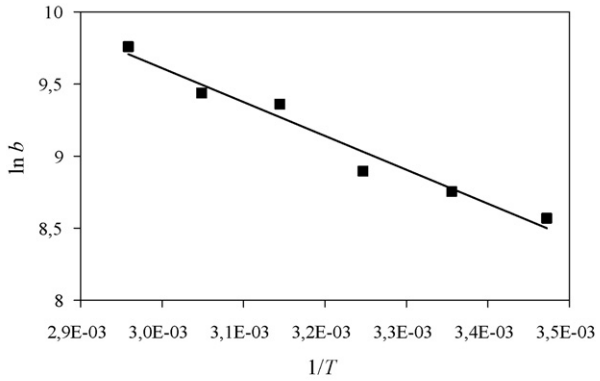

Fig. 11. Plot of ln b vs. $1/T$ for sorption of Hg(II) by the PVA/PVI membrane.

sorbed mass of Hg(II) was 118 mg g^{-1}, in close agreement with the experimental value, 120 mg g^{-1}, within the uncertainty range (±2 mg g^{-1}). All the values of R_L obtained at different initial concentrations were in the 0.0085–0.63 range, indicating favorable sorption of Hg(II) by the PVA/PVI membrane. In conclusion, the good agreement of the isotherm with the Langmuir model is consistent with the hypothesis that the sorption of Hg(II) ions by the membrane is limited by the saturation of the complexing sites of PVI.

3.4.5. Effect of temperature and thermodynamical parameters

A study of the temperature dependence of sorption gave valuable information about the corresponding enthalpy and entropy changes. The effect of temperature on sorption was studied by carrying out a series of isotherms at 288, 298, 308, 318, 328 and 338 K. At each temperature, samples of the PVA/PVI membrane ($m = 100$ mg) were equilibrated during 24 h with 50 cm^3 of Hg(II) solutions ($c_0 = 100$–2000 mg L^{-1}) at pH 2.5.

The results are shown in Table 8. The isotherm data obtained at different temperatures fitted well the Langmuir equation. The temperature dependence of b was used to determine the thermodynamical parameters. The free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for Hg(II) sorption by the PVA/PVI membrane were determined using Eqs. (13)–(15) [28]:

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

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

$$\Delta G^\circ = -RT \ln b \qquad (15)$$

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

The plot of ln b versus $1/T$ (Fig. 11) was linear over the entire range of temperatures (288–338 K). The values of ΔH° and ΔS° (Table 8) were calculated from the slope and intercept of this plot, respectively.

The negative ΔG° values indicate that the sorption process is favorable. The values of b increased when T increased, showing that the sorption reaction is endothermic for the PVA/PVI membrane. In contrast, opposite results were found for the PVA/PEI [27] and PVA/P$_4$VP [28] membranes. The values of q_{max} decreased with increasing temperature, which is in apparent contradiction with the increase of b. This decrease of the mass of mercury sorbed by the membrane, while b increases, would suggest that the number of available sites in the membrane decreased.

The value of ΔH° was calculated to be 19.6 kJ mol^{-1}. Obviously; the positive value of ΔH° indicates the endothermic nature of sorption process and could correspond to a physisorption. Besides, the large positive value of ΔS° (138.6 J K^{-1} mol^{-1}) shows that the sorption of Hg(II) ions by the membrane is accompanied by a considerable decrease in the order in the system. It may indicate a release of protons by the sites which complex Hg(II) ions. If the three membranes PVA/PVI, PVA/PEI and PVA/P$_4$VP are compared, the effect of temperature on the sorption of Hg(II) ions shows important differences. The variations of the sorption coefficient b, which decreases with increasing T for two membranes (PVA/PEI [27] and PVA/P$_4$VP [28]), are not always reflected by changes in ΔG°. The study of thermodynamical parameters explains this divergence by showing that changes in ΔG° with T result from the variations of two terms, ΔH° and $T\Delta S^\circ$, whose second can become predominant. In other words, the sorption can be favoured either because the phenomenon is exothermic, or because the fixation of Hg(II) ions leads to the release of protons, with an increase in disorder in the system. The comparison of the three membranes shows that for the PVA/PVI membrane, the sorption of Hg(II) ions has an unfavorable enthalpic term (it is endothermic), but is strongly favored by the entropic term, consecutive to the release of protons when Hg(II) ions bind with the complexing sites.

3.4.6. Effect of the water hardness

The sorption of mercury cations may be hampered by competition with high concentrations of alkaline or alkaline earth salts in wastewaters.

The interfering effect of water hardness was studied by varying the concentration of Ca(II), the typical representative ion. The studies were carried out using a sample volume of 50 cm^3 of a solution containing 100 mg L^{-1} of Hg(II). The results presented in Table 9 show that Ca(II) did not cause a significant reduction in the sorption of mercury. The presence of Ca(II) at low concentrations (20–100 mg L^{-1}) did not decrease the retention ratio of Hg(II) ($R \approx 97\%$). At higher concentration of Ca(II) ions (200 mg L^{-1}), R

Table 9
Effect of the presence of Ca(II) ions on sorption of Hg(II) by the PVA/PVI membrane.

Concentration of Ca(II) (mg L^{-1})	R (%)	q (mg g^{-1})
0	98.6	45.5
20	98.2	40.5
40	97.8	40.8
100	97.2	42.5
200	92.3	39.3

$c_0 \approx 100$ mg L^{-1}, $V = 50$ cm^3, $m \approx 100$ mg, pH 2.5, room temperature. Accuracy: R ±3%, q ±1.5%.

Table 10
Effect of NaCl concentration on sorption of Hg(II) by the PVA/PVI membrane.

NaCl concentration ($g\,L^{-1}$)	R (%)	q ($mg\,g^{-1}$)
0	98.6	45.5
0.005	97.3	42.9
0.05	98.1	43.4
0.5	98.0	42.2
10	91.1	40.6

$c_0 \approx 100\,mg\,L^{-1}$, $V = 50\,cm^3$, $m \approx 100\,mg$, pH 2.5, room temperature. Accuracy: R ±3%, q ±1.5%.

decreases only to 92%. This small variation indicates that no competition occurred between the two metal ions, probably because the imidazole ligand has no affinity for the Ca(II) ion. The membrane insensitivity to Ca(II) is comparable to that reported for the PVA/P_4VP membrane [28], whereas the PVA/PEI membrane [27] was quite sensitive to water hardness.

In conclusion, the presence of Ca(II), even at high concentrations, had little influence the retention of Hg(II) by the PVA/PVI membrane. Thus, this membrane is well adapted to the treatment of hard wastewaters containing Hg(II) ions.

3.4.7. *Effect of the presence of chloride ions*

The presence of complexing anions such as Cl^-, that simultaneously increase the ionic strength of the aqueous solution, is an important variable that influences the sorption of Hg(II) ions by membranes. The effect on the sorption of Hg(II) ions from an aqueous solution ($c_0 \approx 100\,mg\,L^{-1}$, $V = 50\,cm^3$, pH 2.5) by the PVA/PVI membrane during 24 h was studied by conducting experiments at varying concentration of NaCl (0.005, 0.05, 0.5 and $10\,g\,L^{-1}$). The results are presented in Table 10. No significant reduction in the recovery of mercury was detected for the Cl^- concentrations range 0.005–0.5 $g\,L^{-1}$. The retention ratio of Hg(II) ions by the PVA/PVI membrane was constant ($R \approx 98\%$) up to a NaCl concentration of $0.5\,g\,L^{-1}$. In the presence of $10\,g\,L^{-1}$ NaCl, the PVA/PVI membrane had a smaller retention ratio ($R \approx 91\%$), indicating that the formation of the strong chlorocomplexes of mercury displaces the complexation equilibrium between Hg(II) and the membrane. Compared to the PVA/P_4VP membrane [28], the new membrane shows a similar insensitivy to chloride ions up to $0.5\,g\,L^{-1}$ but inferior results in $10\,g\,L^{-1}$ NaCl. With respect to the PVA/PEI membrane [27], the PVA/PVI membrane efficiency in the presence of NaCl was much larger. Another striking result is that the effects of ionic strength, which caused an increase of R at large salt concentrations for the PVA/PEI membrane [27], were not observed with the PVA/PVI membrane. These results prove the significant potential of this membrane to treat saline waters polluted by mercury.

3.4.8. *Regeneration of the membrane with nitric acid*

In order to check its reusability, the regeneration of the PVA/PVI membrane after sorption of Hg(II) ions was studied. Desorption was carried out with nitric acid, the most common non-complexing desorbing agent for metal ions. In this study, the effect of acid concentration on the desorption ratio was examined, the possibility of carrying out repeated cycles of sorption–desorption was studied, and the contact time necessary for complete desorption was determined. The initial sorption step was carried out during 24 h in solutions of Hg(II) ($c_0 = 100\,mg\,L^{-1}$, $V = 50\,cm^3$, pH 2.5). The PVA/PVI membrane loaded with Hg(II) was agitated with $50\,cm^3$ of HNO_3 solutions at various concentrations (0.5–0.01 M). Table 11 reports the effect of the concentration of nitric acid on the desorption ratio D, calculated using Eq. (9), with comparison to results reported for a previous membrane [28]. An interesting feature of the PVA/PVI membrane is that desorption in a 91% ratio is possible in 0.1 M HNO_3, whereas in the same medium, this ratio was only 44% for the PVA/P_4VP membrane [28]. Desorption in 0.1 M HNO_3 was also superior with PVI than with P_4VP. The minimum concentration of nitric acid for satisfying desorption of Hg(II) was 0.5 M. Therefore, subsequent desorption experiments were carried out with 0.5 M HNO_3.

Table 11
Effect of HNO_3 concentration on the desorption of Hg(II) from two membranes.

c_{HNO3} (M)	Membrane	
	PVA/PVI, D (%)	PVA/P_4VP [28], D (%)
0.5	96.7	99.9
0.1	90.9	44.3
0.05	33.7	9.6
0.01	19.8	0

Initial sorption step under the following conditions for both membranes: room temperature, $m \approx 100\,mg$, sorption at pH 2.5, $c_0 = 100\,mg\,L^{-1}$, $V = 50\,cm^3$. PVA/PVI membrane: $R = 93.4$–96.4%, $q = 43.4$–$44.3\,mg\,g^{-1}$. PVA/P_4VP membrane [28]: $R = 99.8$–99.2%, $q = 46.4$–$47.5\,mg\,g^{-1}$. Accuracy: R ±3%, D ±5%, q ±1.5%.

Table 12
Sorption–desorption cycles of Hg(II) ions with 0.5 M HNO_3.

Cycle	q ($mg\,g^{-1}$)	R (%)	D (%)
1	44.3	96.4	96.7
2	44.2	96.2	94.6
3	44.4	96.8	94.6
4	44.5	97.0	94.7
5	44.8	97.6	95.0

Room temperature, $m \approx 100\,mg$. Sorption at pH 2.5, $c_0 = 100\,mg\,L^{-1}$, $V = 50\,cm^3$. Accuracy: R ±3%, D ±5%, q ±1.5%.

In order to test the resistance of the membrane to degradation by concentrated nitric acid, consecutive sorption–desorption cycles with 0.5 M HNO_3 were repeated five times on the same membrane sample. The values of R and D for each cycle of sorption–desorption are presented in Table 12. The values of both R and D remained large and did not noticeably change during the repeated sorption–desorption operations. These results clearly show that the PVA/PVI membrane can be used repeatedly without losing its sorption capacity for Hg(II).

The rate of desorption of Hg(II) ions with 0.5 M HNO_3 had to be taken into account. For this purpose, the desorption kinetics were studied. A sample ($m = 100\,mg$) of membrane was loaded with Hg(II) ions as before, and placed in $50\,cm^3$ of 0.5 M HNO_3. Aliquots of the solution were withdrawn at known time intervals and analysed for the Hg(II) ions. The variations of the concentration of Hg(II) ions in the desorption medium versus time are illustrated in Fig. 12. Under these conditions, the final desorption ratio was $D = 93.6\%$. The desorption step was very fast, since all Hg(II) ions that could be extracted from the membrane were liberated in less than 120 min.

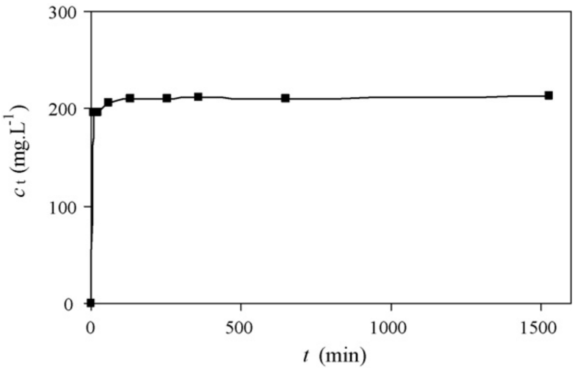

Fig. 12. Influence of the contact time on desorption of Hg(II) for the PVA/PVI membrane by 0.5 M HNO_3.

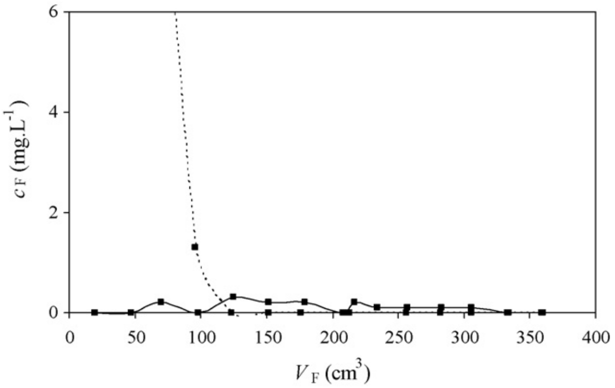

Fig. 13. Changes in concentrations of Hg(II) in the filtrate for the PVA/PVI membrane vs the volume of filtrate ($c_0 \approx 20$ mg L^{-1} (—) and 100 mg L^{-1} (- - -), pH 2.5, at room temperature).

These results were compared with those reported for other complexing membranes. The PVA/PEI membrane [27] was quickly degraded by nitric acid, even in 0.05 M concentration. In contrast, the PVA/P$_4$VP membrane [28] was remarkably insensitive to 0.5 M HNO$_3$ during five sorption–desorption cycles. An interesting feature of the PVA/PVI membrane is that desorption in 0.1 M HNO$_3$ was possible, with limited efficiency, which was not the case for the PVA/P$_4$VP membrane [28]. The peculiar resistance of the PVA/PVI and PVA/P$_4$VP membranes to oxidation by nitric acid may be attributed to the presence of an aromatic ring in the ligand structure, while PEI did not possess such a cycle.

3.5. Frontal filtration experiments

In order to study the performances of the PVA/PVI membrane under dynamic conditions, filtration experiments were carried out on Hg(II) feed solutions of initial concentrations $c_0 \approx 17.5$ and 91.6 mg L^{-1} ($V = 400$ cm^3). The pH of both solutions was adjusted to 2.5. The filtration efficiency was studied by monitoring the Hg(II) concentration c_F in the filtrate versus time. Because of the active area (28.3 cm^3) of the filtration membrane, the mass of membrane was larger than in sorption experiments, $m \approx 230$–260 mg. Each experiment lasted several days and was stopped when the volume of filtrate V_F was about 360 cm^3. The flow of filtrate was measured periodically in the stationary state: it was about 1.1 cm^3 h^{-1}. The variations of c_F versus V_F are shown in Fig. 13 for both experiments. The performances of the membranes were quantified by the elimination ratio E, defined by Eq. (16):

$$E = \frac{(c_0 - c_F)}{c_0} \times 100 \qquad (16)$$

The average values found for c_F (calculated from 15 measurements shown in Fig. 13, standard deviation 0.2 mg L^{-1}) were practically nil in both experiments, demonstrating the remarkable efficiency of the PVA/PVI membranes in removing Hg(II) ions. In the stationary state, for both c_0 (17.5 and 91.6 mg L^{-1}), the values of E were close to 100% (Table 13), showing that the PVA/PVI membrane could remove almost all Hg(II) ions present in these aqueous solutions.

Table 13
Filtration of aqueous Hg(II) solutions through the PVA/PVI membrane.

c_0 (mg L^{-1})	m (mg)	Flow rate (cm^3 h^{-1})	Average c_F (mg L^{-1})	E (%)
91.6	230.6	1.09	<0.1[a]	>99.4
17.5	260.0	1.10	0.1	99.4

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

For $c_0 = 91.6$ mg L^{-1}, the large concentrations found in the filtrate for $V_F < 30$ cm^3 (Fig. 13) were associated with a large flow rate that probably corresponded to the initial equilibration of the membrane. Such equilibration was not observed for $c_0 = 17.5$ mg L^{-1}. For both concentrations of Hg(II), no final peak corresponding to saturation of the PVA/PVI membrane was observed. This situation is similar to that found in filtration of Hg(II) solutions by the PVA/PEI [27] and PVA/P$_4$VP [28] membranes, but differs from the results found during filtration by a PVA/PEI membrane of solutions containing Cd(II) and Cu(II) ions at $c_0 \approx 100$ mg L^{-1} [36]. The absence of saturation peaks could be rationalized by calculating the theoretical volumes V_{calc} for these peaks. For these calculations, the mercury masses present in the filtrate were always neglected.

From the limiting value for the mass of mercury sorbed by the membrane, given in Table 7 (120 mg g^{-1}), determined from the sorption isotherm, the amounts of mercury that can be fixed by the membrane at saturation were calculated and the V_{calc} values were derived for both c_0 (Table 14). At both concentrations, saturation would occur for volumes of 0.30 L ($c_0 \approx 91.6$ mg L^{-1}) and 1.78 L ($c_0 \approx 17.5$ mg L^{-1}). In view of these data, it was surprising that saturation of the membrane was not observed for $c_0 \approx 91.6$ mg L^{-1} (no peak), since the filtration was stopped after recovery of 0.36 L of filtrate, i.e. after the theoretical saturation of membrane. The explanation is probably that the limiting value found in sorption experiments corresponds to uncomplete complexation by the membrane sites, especially because most internal sites are not accessible to mercury ions.

In filtration experiments, the situation is different from sorption, because the solution is forced under pressure through the membrane, and therefore, the internal sites are made available for complexation. If this hypothesis is true, the mass of mercury sorbed should be compared with that calculated from the theoretical complexing capacity of the membrane (853 mg g^{-1}), obtained by calculating the number of donating nitrogen atoms in Section 3.4.4. Using this value, the amounts of mercury that can be fixed by the membrane at saturation were calculated and the V_{calc} values were derived for both c_0 (Table 14). Now, the calculated volumes were so large that no saturation peak could be observed before stopping the experiments after recovery of 0.36 L of filtrate.

In conclusion, the membrane showed a large complexing capacity for Hg(II) ions. For example, a PVA/PVI membrane of mass 260 mg can treat a volume up to 12.7 L of 17.5 mg L^{-1} solution of Hg(II) before saturation. It also means that a larger PVA/PVI membrane with $m = 1$ g could be used for the treatment of almost 49 L of the same Hg(II) solution in a single operation.

Table 14
Theoretical volume of filtrate for saturation of the membrane in filtration experiments.

c_0 (mg L^{-1})	m (mg)	Mass of Hg sorbed (mg)	Quantity of Hg sorbed (mmol)	V_{calc} (L)
Membrane sorbing capacity: 120 mg g^{-1} (from Langmuir isotherm)				
91.6	230.6	27.7	0.138	0.30
17.5	260.0	31.2	0.155	1.78
Membrane sorbing capacity: 853 mg g^{-1} (theoretical)				
91.6	230.6	196.7	0.98	2.15
17.5	260.0	221.8	1.105	12.7

4. Conclusion

A novel complexing membrane for the removal of Hg(II) ions from aqueous solutions was prepared by the technique of semi-interpenetrated polymer networks. In this membrane, the complexing polymer, poly(vinylimidazole), is entrapped within a matrix of poly(vinylalcohol), crosslinked by gaseous dibromoethane. This membrane could be used in contact with aqueous solutions for 2 months, without appreciable dissolution, with almost complete preservation of its complexing ability. The removal of Hg(II) ions was investigated by performing sorption and filtration experiments. In all cases, the operating pH was 2.5, in order to avoid mercury precipitation and protonation of the complexing sites.

Modelling of the sorption equilibrium was satisfactory performed using the Langmuir model. The linear isotherms plotted at different temperatures allowed the calculation of the thermodynamical parameters. The sorption of mercury was characterised by a negative enthalpy change and a large positive entropy change that was ascribed to simultaneous proton release. Because application of the membrane would involve the treatment of industrial wastewaters, the effects of interfering species such as calcium and chloride ions were investigated. These ions had little influence on the retention ratio, showing that they did not compete with mercury ions for the complexing sites. A special attention was given to the conditions for membrane regeneration. Since the membrane contained very stable imidazole rings that resist oxidation, it could be desorbed several times with 0.5 M HNO_3, without losing its complexing properties. From the sorption isotherm at room temperature, the maximum retention capacity of the membrane was 120 mg Hg g^{-1} in sorption experiments, whereas the theoretical exchange capacity was 853 mg Hg g^{-1}, showing that most internal complexing sites of the membrane were not accessible to mercury ions.

When used in the filtration mode, the elimination ratio of Hg(II) was $\geq$99.4% for solutions containing 91.6 or 17.5 mg Hg L^{-1}. The absence of saturation peaks in filtration experiments showed that the retention capacity of the membrane was >120 mg Hg g^{-1}, indicating that the internal sites became available for complexation when the solution flowed through the membrane. It was calculated that a PVA/PVI membrane with $m = 1$ g might be used for the treatment of almost 49 L of a Hg(II) solution ($c_0 = 17.5$ mg Hg L^{-1}) in a single operation.

Acknowledgments

Funding of Hadd Bessbousse by a Bourse d'excellence Eiffel and UNESCO/Keizo Obuchi grant is gratefully acknowledged. Mr. J.-J. Malandain (Groupe de Physique des Matériaux, UMR 6634 CNRS/Université de Rouen, Saint-Etienne du Rouvray - France) is also acknowledged for the SEM pictures.

References

[1] F. Zahir, S.J. Rizwi, S.K. Haq, R.H. Khan, Low dose mercury toxicity and human health, Environ. Toxicol. Pharmacol. 20 (2005) 351–360.

[2] D.K. Goldblum, A. Rak, M.D. Ponnapalli, C.J. Clayton, The Fort Totten mercury pollution risk assessment: a case history, J. Hazard. Mater. A136 (2006) 406–417.

[3] J.J. Rytuba, Mercury mine drainage and processes that control its environmental impact, Sci. Total Environ. 260 (2000) 57–71.

[4] World Health Organization, International Standards of Drinking Water, WHO, Geneva, 1971.

[5] W. Mertz, The essential trace elements, Science 213 (1981) 1332–1338.

[6] L.I. Sweet, T.Z. Judith, Toxicology and immunotoxicology of mercury: a comparative review in fish and humans, J. Toxicol. Environ. Health 4 (2001) 161–205.

[7] P. Miretzky, A. Fernandez Cirelli, Hg(II) removal from water by chitosan and chitosan derivatives: a review, J. Hazard. Mater. 167 (2009) 10–23.

[8] E. Taboada, G. Cabrera, G. Cardenas, Retention capacity of chitosan for copper and mercury ions, J. Chile Chem. Soc. 48 (2003) 7–12.

[9] A. Denizli, S. Senel, G. Alsancak, N. Tüzmen, R. Say, Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine), React. Funct. Polym. 55 (2003) 121–130.

[10] R.S. Vieira, M.M. Beppu, Dynamic and static adsorption and desorption of Hg(II) ions on chitosan membranes and spheres, Wat. Res. 40 (2006) 1726–1734.

[11] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nat. Prot. 1 (2007) 2661–2667.

[12] V.K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Suhas, Low cost adsorbents: growing approach to wastewater treatment – a review, Crit. Rev. Env. Sci. Technol. 39 (2009) 783–842.

[13] V.K. Gupta, A. Rastogi, A. Nayak, Biosorption of nickel onto treated alga (*Oedogonium hatei*): application of isotherm and kinetic models, J. Colloid Interface Sci. 342 (2) (2010) 533–539.

[14] V.K. Gupta, P. Singh, N. Rahman, Adsorption behavior of Hg(II), Pb(II), and Cd(II) from aqueous solution on Duolite C-433: a synthetic resin, J. Colloid Interface Sci. 275 (2004) 398–402.

[15] D. Mohan, V.K. Gupta, S.K. Srivastava, S. Chander, Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste, Colloids Surf. A 177 (2001) 169–181.

[16] O. Genc, C. Arpa, G. Bayramoglu, M.Y. Arıca, S. Bektas, Selective recovery of mercury by Procion Brown MX 5BR immobilized poly(hydroxyethylmethacrylate/chitosan) composite membranes, Hydrometallurgy 67 (2002) 53–62.

[17] A. Oehmen, R. Viegas, S. Velizarov, M.A.M. Reis, J.G. Crespo, Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor, Desalination 199 (2006) 405–407.

[18] V. Smuleac, D.A. Butterfield, S.K. Sikdar, R.S. Varma, D. Bhattacharyya, Polythiol-functionalized alumina membranes for mercury capture, J. Membr. Sci. 251 (2005) 169–178.

[19] A. Bougen, M.R. Baudry, B. Chaufer, F. Michel, Retention of heavy metal ions with nanofiltration inorganic membranes by grafting chelating groups, Sep. Purif. Technol. 25 (2001) 219–227.

[20] H.A. Abd El-Rehim, E.A. Hegazy, A. El-Hag Ali, Selective removal of some heavy metal ions from aqueous solution using treated polyethylene-g-styrene/maleic anhydride membranes, React. Funct. Pol. 3 (2000) 105–116.

[21] M.G. Khedr, Membrane methods in tailoring simpler, more efficient, and cost effective wastewater treatment alternatives, Desalination 222 (2008) 135–145.

[22] P.S. Sudilovskiy, G.G. Kagramanov, V.A. Kolesnikov, Use of RO and NF for treatment of copper containing wastewaters in combination with flotation, Desalination 221 (2008) 192–201.

[23] L. Lebrun, N. Follain, M. Métayer, Elaboration of a new anion-exchange membrane with semi-interpenetrating polymer networks and caracterisation, Electrochim. Acta 50 (2004) 985–993.

[24] L. Lebrun, E. Da Silva, M. Métayer, Elaboration of ion-exchange membranes with semi-interpenetrating polymer networks containing poly(vinyl alcohol) as polymer matrix, J. Appl. Polym. Sci. 84 (2002) 1572–1580.

[25] W. Zuo, G. Zhang, Q. Meng, H. Zhang, Characteristics and application of multiple membrane process in plating wastewater reutilization, Desalination 222 (2008) 187–196.

[26] L. Lebrun, F. Vallée, B. Alexandre, Q.T. Nguyen, Preparation of chelating membranes to remove metal cations from aqueous solutions, Desalination 207 (2007) 9–23.

[27] H. Bessbousse, T. Rhlalou, J.-F. Verchère, L. Lebrun, Sorption and filtration of Hg(II) ions from aqueous solutions with a membrane containing poly(ethyleneimine) as a complexing polymer, J. Membr. Sci. 325 (2008) 997–1006.

[28] H. Bessbousse, T. Rhlalou, J.-F. Verchère, L. Lebrun, Novel metal-complexing membrane containing poly(4-vinylpyridine) for removal of Hg(II) from aqueous solution, J. Phys. Chem. B 113 (2009) 8588–8598.

[29] B.L. Rivas, E.D. Pereira, I. Moreno-Villoslada, Water-soluble polymer-metal ion interactions, Prog. Polym. Sci. 28 (2003) 173–208.

[30] M.C. Millot, B. Sebille, A. Halli, H. Hommel, A.P. Legrand, Chromatographic and EPR study of poly(vinylimidazole) copper(II) complexes supported on silica, Chromatographia 37 (1993) 584–592.

[31] M. Sato, K. Kondo, K. Takemoto, ESR studies on the dimer formation between copper ions in the poly(vinylimidazole) copper(II) complex, Polym. Bull. 2 (1980) 305–308.

[32] L. Martinot, D. Leroy, C. Jerome, O. Leruth, Complexation of uranyl ion by polyvinylimidazole: electrochemical preparation and leaching tests investigations, J. Radioanal. Nucl. Chem. 224 (1997) 7–76.

[33] S. Sjoberg, Critical evaluation of stability constants of metal-imidazole and metal-histamine systems, Pure Appl. Chem. 89 (1997) 1549–1570.

[34] B. Cabot, A. Deratani, A. Foissy, Adsorption of poly(vinylimidazoles) onto silica surfaces, Colloids Surf. A 139 (1998) 287–297.

[35] M. Suzuki, N. Yokoyama, M. Kimura, K. Hanabusa, H. Shirai, Solvent effects on quenching of partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes with viologens, React. Funct. Polym. 40 (1999) 97–105.

[36] H. Bessbousse, T. Rhlalou, J.-F. Verchère, L. Lebrun, Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix, J. Membr. Sci. 307 (2008) 249–259.

[37] A. Ringbom, Complexation in Analytical Chemistry (Les complexes en chimie analytique), Dunod, Paris, 1967, p. 320 (French translation).