

# PVA Cryogel Membranes as a Promising Tool for the Retention and Separation of Metal Ions from Aqueous Solutions

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**ABSTRACT:** The sorption and transport of metal ions by poly(vinyl alcohol) hydrogel membranes (PVA HG), obtained by physical crosslinking through the freezing/thawing method, was analyzed using aqueous nitrate solutions of copper, lead, and nickel, at concentrations ranging from 1 to 100 mM, at 25°C. The sorption of heavy metal by PVA HG has been characterized by swelling and loading degrees. The effect of the heavy metals incorporation on the chemical properties of PVA HG matrices has been studied using SEM, to observe changes in the surface morphology of PVA HG membranes, and FTIR-ATR, aiming to monitor the heavy metals ions sorption

into PVA hydrogel membranes. The analysis of permeation and diffusion coefficients of 100 mM aqueous solutions of Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> show that the diffusion process may be mainly described by hydrodynamic models; however, the transport process shows that the distribution coefficient for the different heavy metals are always higher than one, in agreement, with the sorption studies. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1567–1573, 2010

**Key words:** hydrogel; metal ions; sorption; diffusion; membrane

## INTRODUCTION

Heavy metals ions, with many applications in industry and consequently in our daily life, are very harmful for environment if they are discharged into soils or natural water resources. For example, lead, nickel, and copper ions have been classified as priority pollutants by the US Environmental Protection Agency (US EPA).<sup>1</sup> These particular ions have potential noxious health effects causing disturbances in the central nervous system, renal and hepatic disturbances, and convulsions, respectively.<sup>2</sup> Therefore, the separation/retention followed by recovering and recycling of heavy metals ions is a very important demand to control water pollution and to protect water resources and human health.

Polymer sorbents, besides the most common methods (metal ion precipitation and ion-exchange/chelation), have been developed as an alternative approach to reduce cation concentration in wastewaters. Such polymeric materials are based on a synthetic polymer containing, e.g., macrocycles,<sup>3,4</sup> such

as calixpyrrole<sup>5,6</sup> or calixarenes,<sup>7,8</sup> in such a way that ions are retained and separated from the solution, essentially by coordination.

Among polymers, hydrogels have been successfully used for removal and separation of metal ions.<sup>9–13</sup> However, we should note that there are few studies involving poly(vinyl alcohol) (PVA) gels, in spite of their exceptional properties.

PVA membranes obtained by irradiation crosslinking<sup>14</sup> or by PVA grafting with acrylic acid and styrene<sup>15,16</sup> have been studied for the removal of heavy metal ions (Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>) from aqueous solution. PVA, as a well-known biomaterial, has also been used as a matrix for immobilization of, e.g., bacteria,<sup>17</sup> fungi,<sup>18</sup> for the removal of metal ions by biosorption or bioaccumulation.<sup>19,20</sup>

In this article, we report experimental results on the sorption efficiency of metal ions, such as Cu<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup>, by cryogel PVA membranes. The effect of these ions on the gel structure was monitored by FTIR-ATR, SEM, and swelling measurements. These gels, obtained by a freezing–thawing method,<sup>21,22</sup> exhibit higher mechanical strength than PVA gels crosslinked using chemical or irradiative techniques, because the mechanical load can be distributed along the crystallites of the three-dimensional structure.<sup>23</sup> Some characteristics of these “physically” crosslinked PVA gels include a high degree of swelling in water, a rubbery and elastic

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nature, and high mechanical strength.<sup>24</sup> Furthermore, the transport by diffusion of those metals has been evaluated by the time lag method.

## MATERIALS AND METHODS

### Materials and membrane preparation

Poly(vinyl alcohol) (PVA), industrial grade (polimerization degree  $\sim 900$ ; hydrolysis degree 98 mol %; polydisperse), was supplied from Chimica Râșnov-Romania.

Lead, nickel, and copper nitrates (Merck, pro-analysis) were used without further purification. All solutions have been prepared with distilled water.

The PVA cryogel membranes were prepared as follows: a PVA solution of 14 wt % concentration was prepared by dissolving a certain amount of PVA in distilled water at 80°C under continuous stirring for 3 h. The obtained solution was cast in Petri boxes and submitted to freezing for 12 h at  $-20^{\circ}\text{C}$  and, after that, thawed for 12 h at  $+25^{\circ}\text{C}$ . The cycles of freezing and thawing were repeated three times. The obtained PVA hydrogel (PVA HG) membranes show a good mechanical resistance and a white and opaque appearance caused by a heterogeneous structure.<sup>25</sup>

### Sorption studies

The sorption of heavy metal ions by PVA HG has been quantified in terms of the loading (LD) and swelling ( $Q$ ) degrees.

The LD, defined as the mass of metal ions sorbed by 1 g of PVA HG, was measured by immersing a PVA HG sample in 10 mL of electrolyte solution (0.001, 0.01, and 0.1  $M$ , respectively), and left to reach the equilibrium (2 weeks). The amount of metallic ions sorbed by the membrane was calculated by measuring the concentration of those species in the supernatant aqueous solution before and after the sorption experiments, by using UV-visible spectroscopy.

The swelling degree of PVA HG samples, in equilibrium with electrolyte solutions,  $Q$ , was calculated from the mass of the swollen gel, after being in equilibrium with an electrolyte solution,  $m_{el}$ , and in equilibrium with water,  $m_w$ , according to  $Q = m_{el}/m_w$ . The equilibrium is attained after 2 weeks. Each experiment was repeated at least three times and they were carried out at  $25^{\circ}\text{C}$ .

### Permeability technique

Permeability of heavy metal ion salts through PVA HG membranes was measured using a diffusion cell similar to that reported elsewhere.<sup>26,27</sup> This consists

of two 250 mL compartments filled with electrolyte solution (the donor compartment) and water (the receptor compartment). These two compartments were connected by two horizontal tubes, with a permeation area,  $A = 0.659 \text{ cm}^2$ . The PVA HG membrane previously swollen in water was placed between the two compartments. Solutions in both cells were stirred at ca. 200 rpm by using a F20 FALC magnetic stirrer. Constant temperature, ( $25.0 \pm 0.1^{\circ}\text{C}$ ), was maintained throughout the experiments by immersing the permeation cell in a thermostat bath (Velp Scientifica).

The flux of metal ions through the PVA HG membranes was quantified as follows: every 20 min, 4 mL of sample were collected from the receptor compartment. The amount of metal ions that permeates the membrane was quantified by two different techniques: atomic absorption spectroscopy (Perkin-Elmer Analyst spectrophotometer with graphite furnace) for lead ( $\lambda_{\text{Pb}} = 283.3 \text{ nm}$ ) and copper ( $\lambda_{\text{Cu}} = 324.7 \text{ nm}$ ), and visible absorption spectroscopy by using a Hanna Instruments spectrophotometer for copper (HI 95,747) and nickel (HI 93,726).

On the basis of these measurements, the integral diffusion,  $D_{\theta}$ , and the permeation,  $P$ , coefficients of metal ions through PVA HG membranes were calculated<sup>28</sup> using the equations

$$D_{\theta} = \frac{l^2}{6\theta} \quad (1)$$

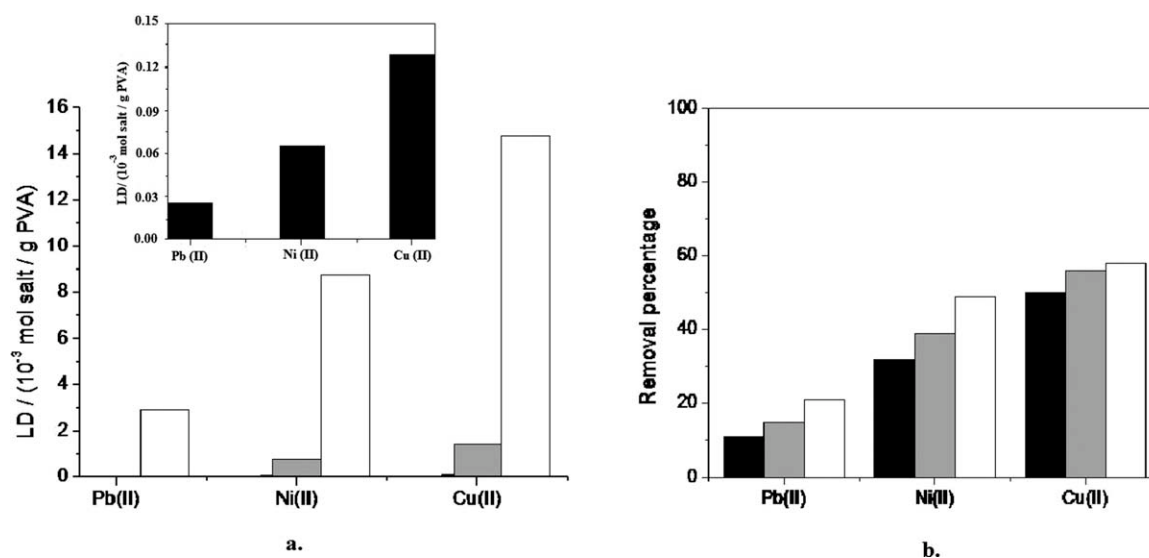
$$P = \frac{Vl}{Ac_i} \frac{dc}{dt} \quad (2)$$

where  $l$  is the membrane thickness,  $\theta$  is the time lag,  $t$  is the time,  $dc/dt$  is the metal ion permeation rate, and  $V$  and  $c_i$  are the initial volume and concentration of the heavy metal ion solution (200 mL and 10 mM, respectively) in the donor compartment.

### PVA HG membrane characterization

The surface morphology of PVA HG membranes has been analyzed by scanning electron microscopy (SEM) with a Jeol model 5130 scanning microscope operating under low vacuum at 25 kV. The membranes were submitted to a fast cryogenic treatment by diving gel samples into liquid nitrogen at  $T = -195^{\circ}\text{C}$  for about 30 sec, and left into a freeze dryer (Free Zone 4.5 - Labconco) for 12 h before coated with a gold film.

The incorporation of heavy metal ions into PVA HG membranes was confirmed by infrared spectroscopy using a FTIR PerkinElmer spectrometer with ATR device. The FTIR spectra were obtained by using xerogel PVA samples.



**Figure 1** (a) Loading degree and (b) removal percentage, of nitrate solutions of metal ions by PVA HG, at 25°C. Black bars,  $c = 1$  mM (Inset figure); gray bars,  $c = 10$  mM; and white bars,  $c = 100$  mM.

## RESULTS AND DISCUSSIONS

### Sorption capacity of PVA HG membranes

The effect of the initial concentration of metal ions (from 1 to 100 mM) on the sorption capacity of PVA HG membranes has been evaluated. Figure 1 shows that the sorption capacity of PVA HG increases by increasing the concentration of salt aqueous solutions, with loading degrees (LD) following the order:  $LD(\text{Pb(II)}) < LD(\text{Ni(II)}) < LD(\text{Cu(II)})$ . This result is in agreement with that reported for the extraction of transition metal ions by gel chitosan membranes.<sup>29,30</sup>

Taking into account the initial amount of metal ions in solution, their removal percentage, from aqueous solution, by the PVA HG can be calculated and are shown in Figure 1(b). The dependence of the removal percentage of metal ions on the initial concentration of salt aqueous solution is higher for Pb(II) and Ni(II) than for Cu(II); that is, an increase in the initial concentration of metal ions in two orders of magnitude leads to an increase of removal percentage of 1.4 and 1.5 folds, for Pb(II) and Ni(II), respectively, and only about 1.0 for Cu(II).

The removal capacity of metal ions shown by PVA HG is higher than that obtained by other materials as, for example, alginate-based gels.<sup>31</sup> A possible explanation for that comes from the high affinity shown by divalent cations to PVA. In fact, LD values [shown in Fig. 1(a)] are higher than those found for symmetric 1 : 1 electrolytes.<sup>25</sup> It should be stressed that such affinity of PVA towards metal ions has been previously observed, especially for Cu(II), and can be justified by the formation of a PVA-Cu(II) macro complex<sup>32</sup> – (see Scheme 1).

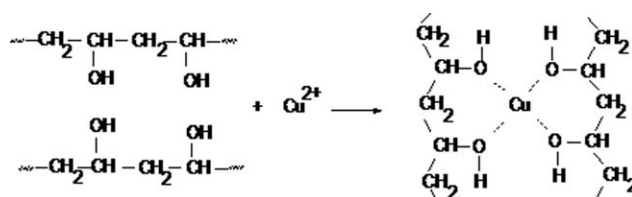
However, it is known<sup>32</sup> that such interaction occurs preferentially at pH higher than 8, which is

not the case in this study. On the other hand, it should be expected that the formation of such complex (Scheme 1) would lead to a more tightly packed structure<sup>33</sup> and, consequently, a more rigid structure will be formed, affecting the swelling and permeation properties of the gels. Both these parameters will be discussed in the following sections.

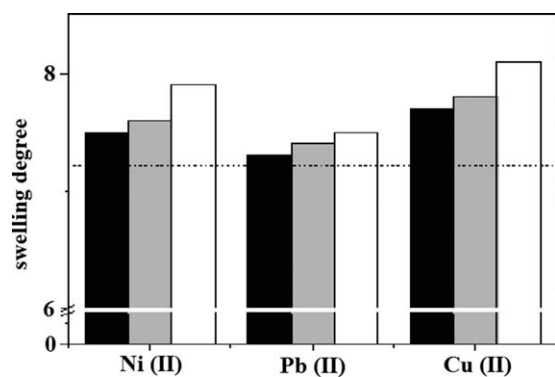
### Effect of metal ion salts on the swelling degree of PVA HG

Figure 2 shows the effect of metal ion aqueous solutions on the swelling degree ( $Q$ ) of PVA HG. Two different observations can be done from the analysis of this figure: (a)  $Q$  values increase with salt concentration, and they are higher than  $Q$  value for PVA HG in water ( $Q = 7.2$  - see dashed line in Fig. 2); and (b) the swelling degree is not dependent on the type of metal ion (considering that the maximum error in the swelling degree determination is 5%).

In a first approach these results seem to contradict the previous hypothesis. However, if a considerable salting-in phenomena occurs, as due to the interaction of metal cations with PVA HG structure, the electrolyte concentration inside gel matrix rises, as well as the concentration of the counter-ions, the difference between the internal and external ion



**Scheme 1** PVA-Cu(II) macro complex.<sup>32</sup>



**Figure 2** Swelling degree of PVA HG in aqueous solutions of divalent metal ions, at 25°C. The dashed line represents the swelling degree of PVA HG in water.

concentrations increases, and the gel swells due to an increase in osmotic pressure.<sup>34,35</sup>

Such swelling behavior is also observed in PVA HG in equilibrium with, e.g., NaCl, although not so significantly; for example, the immersion of PVA HG in a 0.1M NaCl solution results in an increase of  $Q$  from 7.2 (in water) to 7.5.<sup>36</sup> These results suggest that the mechanism of interaction between metallic ions and PVA HG, if exists, is based on weak interactions once they do not resemble the effect of further crosslinking on a gel matrix.

Another hypothesis, taking into account that when polymers in solution or hydrogels are in contact with electrolytes solutions, according to the Hofmeister series, is that the nitrate ions (chaotropic species in Hofmeister series) determine the salting-in processes and, as consequence, the hydrogel swelling. So, the resulted water flux will bring into the gel higher amount of salt. If there is no chemical affinity between them, ions will diffuse through the gel, until the equilibrium is reached.

### Permeation of aqueous solutions of metal ions through PVA HG membranes

The analysis of permeability ( $P$ ) and diffusion ( $D_0$ ) coefficients of aqueous solutions of metal ions through PVA HG (Table I) will allow us to infer about the transport mechanism of those metal ions inside the gel matrix and have been calculated using a time lag technique under steady-state conditions.

The analysis of diffusion coefficients shows that the diffusion process inside PVA HG matrices is one order of magnitude lower than in aqueous solution (e.g.,  $D(\text{Pb}(\text{NO}_3)_2)$  in water is  $1.132 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),<sup>38</sup> suggesting that the diffusion of this salt is controlled by the properties of the electrolyte in aqueous solutions.<sup>39</sup> In fact, a linear relationship between the logarithm of  $D_0$  and the square of the hydrated cation radius,  $r_H$ , is found [Fig. 3(a)]. The decrease of  $D_0$  with an increase of  $r_H$  can be explained by an increase in the coefficient to resistance, which is a measure of the friction acting on a solute as it moves through a solvent,<sup>40</sup> and/or by a decrease in the effective free volume. The former is easily explained once the friction acting in a larger ion is greater than in a corresponding smaller ion and, consequently, the diffusion process is less effective; however, the latter deserves further discussion. To check the effect of free volume on the transport properties, the polymer volume fraction ( $\phi$ ) has been calculated using<sup>41</sup>

$$\phi_p = \{1 + [(Q - 1)\rho/d]\}^{-1} \quad (3)$$

where  $\rho$  is the polymer density,  $\rho$  ( $1.17 \text{ g. cm}^{-3}$ )<sup>36</sup> and  $d$  is the density of the metal ion salt in aqueous solution.<sup>42</sup> Surprisingly, the diffusion coefficients decrease by decreasing the polymer volume fraction (Table I). However, it should be stressed that taking into account experimental data obtained from different techniques the increase in swelling degree is a consequence of an increase of the osmotic pressure resulting from a significant ionic sorption. Consequently, by increasing the salt concentration inside gel diffusion coefficient tends to decrease.<sup>43</sup>

After this discussion, two other points remain unaddressed: (a) if the solvent plays the main role in the diffusion process, it should be expected that the transport process could be modeled by, e.g., the free volume model,<sup>44</sup> where the hydrogel membrane is considered to be a homogeneous hydrated network; and (b) how can we justify the high retention of metallic ions as seen by AAS with a transport process mainly controlled by water as a solvent?

The analysis of free volume model equation predicts that the logarithm of the permeability coefficients have a linear relationship with the reciprocal of

**TABLE I**  
Transport Properties of Electrolyte from 10 mM Aqueous Solutions Through PVA HG Membranes, at 25°C

	$\theta$ ( $\pm s$ )/s	$D_0/(10^{-6} \text{ cm}^2 \text{ s}^{-1})$	$P/(10^{-6} \text{ cm}^2 \text{ s}^{-1})$	$\phi_p^a$	$r_H^b/\text{nm}$
Pb(NO <sub>3</sub> ) <sub>2</sub>	1526 ( $\pm 183$ )	1.44	1.43	0.122	0.401
Ni(NO <sub>3</sub> ) <sub>2</sub>	1684 ( $\pm 120$ )	1.31	4.23	0.113	0.404
Cu(NO <sub>3</sub> ) <sub>2</sub>	2143 ( $\pm 262$ )	1.03	5.03	0.109	0.419

<sup>a</sup>  $\phi_p$ , polymer volume fraction calculated from eq. (3)

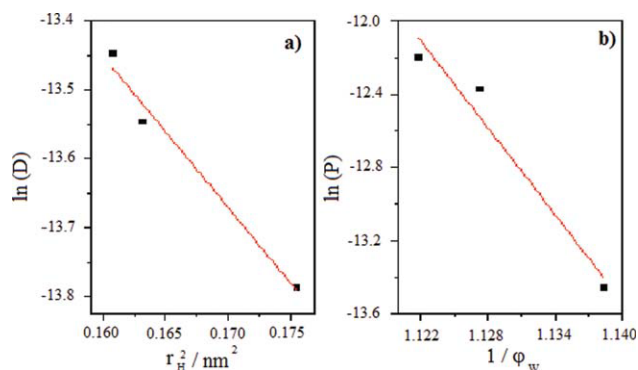
<sup>b</sup> hydrated radius of ionic cations.<sup>37</sup>

water volume fraction ( $\phi_w = 1 - \phi_p$ ). From Figure 3(b), we can observe that, although there is an increase of  $P$  with an increase in the gel hydration, there is a poor correlation to a linear relationship. Such deviation from linearity can be justified by the existence of specific interactions between the solute and the membrane.<sup>29</sup>

Generally, with steady-state transport processes through membranes, there is a time lag ( $\theta$ ) associated with the dissolution of the permeant species to a constant level before the steady-state is achieved. In addition, an increase in the induction period may be found with an increase in the interaction between the permeant species and the polymeric matrix.<sup>45,46</sup> On the other hand, the quantification of the amount of electrolyte retained by the polymeric matrix can be calculated by the distribution coefficients,  $K$  ( $K = P/D_0$ ), and they were found to be equal to 0.99, 3.32, and 4.89 for Pb(II), Ni(II), and Cu(II), respectively. These data should be considered only qualitatively, once they are calculated assuming that the transport process is Fickian; even so, they show a similar trend of retention capacity similar to those found by sorption analysis.

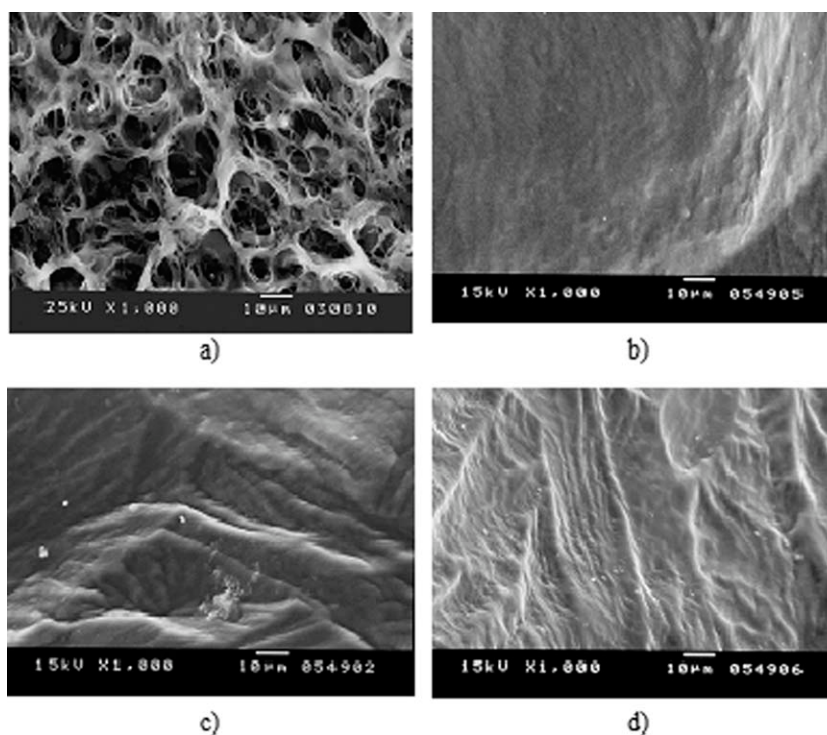
#### Effect of metal ions sorption on the PVA HG structure

The effect of the different cations on the morphology and structure of PVA HG membranes have been also studied by SEM and FTIR, respectively. Figure 4



**Figure 3** Effect of hydration radius of metal ions (a) and water volume fraction (b) on diffusion and permeability coefficients, respectively. Solid lines were obtained from fitting data points to a straight line equation; the following correlation coefficients were obtained: (a) 0.964 and (b) 0.919. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

shows the SEM micrographs of different PVA surface membranes. The PVA HG membrane [Fig. 4(a)] shows a very homogeneous porous surface.<sup>47</sup> However, the sorption of metal ions by the PVA HG membranes, when in equilibrium with 0.1M salt solution, promotes the occurrence of a nonporous, rather compact, and smooth wave surface morphology [Fig. 4(b–e)] of those surface membranes. These evidences clearly suggest that the metal ions have a nonneglected effect on the structure of PVA HG by “sealing” the porous.



**Figure 4** SEM micrographs for PVA HG in equilibrium with water (a) and in equilibrium with 0.1M salt solutions: (b)  $\text{Cu}(\text{NO}_3)_2$ , (c)  $\text{Ni}(\text{NO}_3)_2$ , and (d)  $\text{Pb}(\text{NO}_3)_2$ .

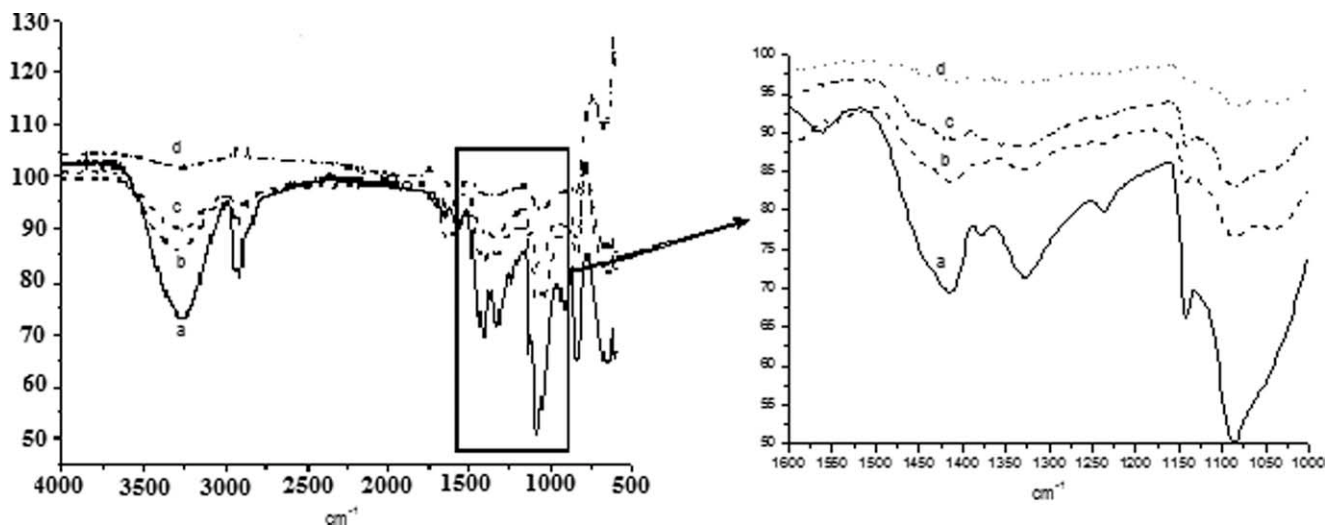


Figure 5 FTIR spectra for: (a) PVA, (b) PVA/Pb(II), (c) PVA/Cu(II), and (d) PVA/Ni(II) membranes.

Alteration in the structure of PVA HG upon sorption of metal ions has also been observed by FTIR spectroscopy. From the analysis of FTIR spectra (Fig. 5) the following characteristic vibrational bands of PVA are observed: at  $\nu = 3283 \text{ cm}^{-1}$  assigned to hydrogen bonds formed by  $-\text{OH}$  groups; the band at  $\nu = 2924 \text{ cm}^{-1}$  can be assigned to the stretching vibration of the alkyl groups ( $\text{C}-\text{H}$ )<sup>48</sup>; and the band at  $\nu = 1090 \text{ cm}^{-1}$  can be assigned to the vibration determined by the ( $\text{C}-\text{O}$ ) bond but also to the crystalline fraction of the PVA in the membrane and can be explained through hydrogen intra and intermolecular bonds formation between PVA chains.<sup>23</sup> However, it is worthwhile to note that comparing the vibration bands of PVA with those of PVA with sorbed metal ions no further band neither shift of the existing bands are occurring. Using a different approach, it is possible to estimate the effect of metal ions on the structure of PVA HG structure. In fact, the ratio of the heights of the peaks of the stretching vibration of  $\text{CH}_2$  group, at  $\nu_1 = 1417 \text{ cm}^{-1}$ ,  $h_1$ , and that of  $\text{C}-\text{O}$  stretch and  $\text{O}-\text{H}$  bend at  $\nu_2 = 1090 \text{ cm}^{-1}$ ,  $h_2$ , will give information on the interaction between metal ion and PVA HG membrane<sup>49</sup> (Table II).

From the analysis of data shown in Table II, we can conclude that there is a clear effect of metal cations on the structure of PVA; although the effect of

those ions, as seen by FTIR, does not exactly follow the swelling, sorption, and transport results, which may be justified by the method precision, they show that the sorption of metal ions is followed by an increase in the ratio of  $h_2/h_1$  of about 20%, when compared with PVA. Such increase justifies that the highly sorption capacity of PVA HG occurs not only by dissolution of those ions in the aqueous part of the gel but also by interacting with PVA structure.

## CONCLUSIONS

The sorption efficiency and the permeation of metal ions,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$ , by PVA HG membranes obtained through physical crosslinking has been successfully studied. The removal capacity of metal ions, from aqueous solutions, of PVA HG change from 11% (for Pb(II) with an initial concentration of 1 mM) to 60% (for an initial concentration of Ni(II) of 100 mM). The sorption process is accomplished by a high permeation rate (around  $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ). Although the sorption mechanism is not completely understood, it is suggested that the high capacity of PVA HG to sorbe those metal ions is due to a process comprising dissolution of metal ions on the PVA HG aqueous phase, and also interaction with nonbonding electrons of the oxygen, from the PVA hydroxyl groups, forming a supra molecular structure.

The data shown in this article show that the permeation and sorption of Cu(II), Ni(II), and Pb(II), coupled with the very good mechanical stability of PVA HG membranes, are promising results for the further development of more appropriated PVA matrices for separation/retention followed by recovering and recycling of heavy metals.

We thank Prof. Victor M.M. Lobo for useful discussions on the transport of electrolytes through gels.

TABLE II  
Comparison Between the Ratios of the Heights of the Specific Vibrational Peaks of PVA

	$h_1$ ( $\nu_1$ )	$h_2$ ( $\nu_2$ )	$h_2/h_1$
PVA	64.5	50.0	0.78
PVA/Pb(II)	83.7	76.5	0.91
PVA/Cu(II)	89.0	83.0	0.93
PVA/Ni(II)	96.5	93.6	0.97

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