Polym. Bull. (2010) 65:495–508
DOI 10.1007/s00289-010-0264-3

ORIGINAL PAPER

Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals

Jesús E. Peñaranda A. · Marcos A. Sabino

Received: 6 October 2009 / Revised: 26 February 2010 / Accepted: 7 March 2010 /

Abstract The adsorption of metal ions Cu^{2+} and Ni^{2+} from contaminated simulated water was studied using new starch/acryl amide-based hydrogels in the presence of lignin or peat to create an interpenetrating polymer network (IPN). The chemical structure of the materials was studied using infrared spectroscopy and their morphology was observed by scanning electron microscopy (SEM). The behavior of hydrogels in water and the water transport mechanisms were characterized using Fick's law. Metal ion sorption was analyzed using inductively coupled plasma spectrometry. Hydrogels showed maximum water absorption values at about 100 h and all of them showed a Fickean water transport mechanism. On one hand, SEM confirmed that the new material is in fact an IPN and, on the other, that the internal porosity shown is responsible for the water absorption. On the other hand, the hydrophobic nature of the dispersed phase and its concentration in the hydrogel formulation seem to influence this process, which could also influence or facilitate the diffusion/sorption of metal ions. Peat-containing hydrogels showed a slightly lower absorption capacity of these ions than lignin-containing formulations. These hydrogels have a high potential to obtain metal ion-collector membranes.

Keywords Interpenetrating polymer network · Peat · Lignin · Isotherm · Sorption · Heavy metals

Introduction

Hydrogels are natural or synthetic crosslinked polymeric materials which, when coming in contact with water, swell and become soft and elastic. A significant part

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J. E. Peñaranda A. · M. A. Sabino (✉)
Departamento de Química, Grupo B5IDA, Universidad Simón Bolívar, Apdo. 89000,
Caracas 1080-A, Venezuela
e-mail: msabino@usb.ve

of them does not dissolve [1] because of the crosslinks and, due to the flexibility of the polymer chains, it is possible for solvent molecules to enter the three-dimensional structure.

Within the hydrogel classification, there is a specific group called interpenetrating polymer networks (IPNs) [2], which are a combination of two or more polymer networks synthesized in juxtaposition, i.e., a blend of two or more crosslinked polymers, which may be incompatible, but are physically interlocked, forming a three-dimensional structure between its constituent phases. Therefore, several kinds of IPN architectures exist, among them non-covalent IPN materials. For example, a wide variety of organic–inorganic compounds have been formulated in an effort to improve material properties or create new materials [1–3].

Recent investigations [3, 4] have been focused on reducing the impact of the acrylic components, which are generally used as starting monomers to obtain these materials. The incorporation of fractions of natural polymers [5], which provide properties for different applications, has been suggested as a result. In our case, we are particularly interested in including natural compounds such as starch and lignin to obtain hydrogels and studying their potential use in the absorption of heavy metal ions. However, in this research work we would like to specifically focus on studying the effect of the presence of peat (an organic material having a high lignin content) as the interpenetrated phase in acrylamide-based hydrogels, which could have a high potential to obtain metal ion-collector membranes.

Peat is a fibrous structure of decomposed organic matter blended with a mineral substance which is in conditions of permanent water logging (flooding of an agricultural land due to an increase of the groundwater level or to excessive irrigation), and whose is of dark organic matter content higher than 30% [6]. It forms as a result of the partial carbonization and decay of vegetation in the acid water of bogs, marshes, and wetlands. Necrotic plant tissues resulting from said decay process are basically constituted by cellulose, hemicellulose, lignin, and relatively high concentrations of lipids, proteins, tannins, and aliphatic biopolymers [6, 7]. Some works have pointed out that peat has a great potential to be used in the removal of heavy metal ions from contaminated liquid effluents or wastewater [8–10].

Several materials, among them peat, exhibited the ability to remove metals from aqueous solutions to at least some degree, with the reported sorption capacities ranging from 1 to 400 mg/g adsorbent, depending on the metal and the adsorbent in question. These materials, although capable of removing metallic species from solutions, have been difficult to apply in an industrial setting. This is mainly due to the difficulties in handling and contacting the biomass with the process streams. Biomass tends to be very fragile and is often used in the form of dried powders. This small particle size is necessary to increase the available adsorbent surface area, but also makes handling very difficult. One method of overcoming these obstacles is to transform the biomass into a form whose physical characteristics are more attractive. Immobilization of the biomass within a polymer matrix (for example, some kind of IPN hydrogel) is a proven method of achieving this transformation.

The main objective of this research work is to synthesize IPN hydrogels using lignin and peat as the interpenetrated phase into an acrylamide–starch matrix, to characterize them and to measure their absorption capacity of the metal ions present in simulated water contaminated with nickel (Ni^{2+}) and copper (Cu^{2+}).

Materials and methods

Materials

Acrylamide (AA: Molecular Biology Grade, Promega Corporation) was used as a monomer for the preparation of the hydrogels. To obtain the other formulations, the following natural polymers were added: cassava starch (for commercial use), lignin (extracted from black liquor), and peat (from the Orinoco River, Venezuela). Ammonium peroxydisulfate (Fisher Scientific) was used as initiator for the polymerization process, and *N*,*N′*-methylene-bis-acrylamide (Bio-Rad Laboratories) was employed as the crosslinking agent. The amount of initiator and crosslinker used were determined based on the amount of the AA monomer in each formulation. Copper sulfate ($CuSO_4 \cdot 5H_2O$) and nickel sulfate ($NiSO_4 \cdot 6H_2O$), respectively, were used to prepare the solutions based on copper and nickel metal ions (simulated wastewater).

Experimental procedure

Hydrogels synthesis

Different types of hydrogels were prepared using acrylamide, starch, lignin, and peat, in the amounts shown in Table 1.

Hydrogels were prepared by adding the synthetic monomer (AA), in the amounts described before, in test tubes with 20 mL of distilled water in each one until the monomer was dissolved. Then, the natural polymers were incorporated under constant mechanical stirring until the mixture components were homogeneously distributed. After that, the initiator and the crosslinking agent, which were previously diluted in distilled water, were added under constant mechanical stirring (using a vortex), and slight heating. Then, the test tubes were placed in a water bath at 85 °C until the gels were formed. Once the hydrogels were obtained, they were removed from the test tubes, cut with a nylon thread in disc-like pieces with similar

Table 1 Composition of each formulation evaluated

Formulation	F1	F2	F3	F4	F5
Acrylamide (g)	2	2	2	2	2
Starch (g)	0	2	2	2	2
Lignin (g)	0	0.5	0	0.75	0
Peat (g)	0	0	0.5	0	0.75
[Initiator] (%)	0.5	0.5	0.5	0.5	0.5
[Crosslinker agent] (%)	3	3	3	3	3

thickness and washed during 24 h with distilled water. Finally, the hydrogels were dehydrated to constant weight at room temperature.

Characterization by Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained from samples on potassium bromide (KBr) disks. First, hydrogels were frozen in liquid nitrogen and then, they were ground to a fine powder using a mortar and pestle. Translucent disks were obtained using a mixture of 10 mg of each powdered formulation with 90 mg of KBr, respectively. Then, infrared spectroscopy analysis was made using a Fourier Transform Infrared Spectrometer (Nicolet Magna 750) at a resolution of 4 cm^{-1}.

Morphological characterization (SEM)

Disks of each formulation were freeze dried (lyophilization process, using an equipment Labconco Freeze-Dryer-12) and then fractured under cryogenic conditions to determine the morphology of the hydrogels. The internal faces of the several fragments obtained were observed under scanning electron microscopy (SEM). To make this possible, each fragment was gold-coated using a Baltec SCD-050 (Tempotac, SAIA) ionic coating system. Finally, the morphology of the hydrogels was studied in detail using an JEOL (model JSM-6390) Electron Microscope with an accelerating voltage of 15 kV and different levels of magnification.

Water absorption of the hydrogels

In order to study the behavior of hydrogels in water, it was necessary to weight a dry sample (two disks) of each formulation. Then, samples were immersed in distilled water to study the swelling process and obtain the absorption isotherm at room temperature. Weight was measured as a function of time in order to determine the swelling ratio up to the equilibrium (using Eq. 1). Analogously, water desorption was measured from maximum swelling of samples to their total dehydration (constant weight). Both processes were done at room temperature and the samples were placed on a thin wire mesh to allow all the faces of the sample to be in contact with the air.

$$\text{swelling ratio} = (\text{wet weight} - \text{dry weight}) * 100/(\text{dry weight}). \tag{1}$$

Then, the process of water diffusion inside the hydrogel network was explained using the Fick theory described in Eq. 2 employing data collected from the weight changes during the water sorption process.

$$K * t^n = W_t/W_\mathrm{f}, \tag{2}$$

where W_t/W_f is the medium penetration coefficient, K is a constant which incorporates characteristics of this network, and n is the diffusion exponent.

Metal ion sorption

To verify the influence of pH a suspension of different pH values of approximately 2–8 were attained by adding either HNO_3 or NaOH. During the shaking, the pH values were measured at certain intervals and readjusted if necessary. An aliquot of Ni and Cu (50 μL) as sulfate salts was then added to get the initial metal concentration of 1×10^{-4} mol L^{-1}. pH of the suspension was adjusted again and then shaken for another 24 h. At the end of the shaking period, the pH of suspension was measured and then filtered through a cellulose acetate membrane. This experiment were carried out using hydrogels formulations F1, F4, and F5.

For the kinetic sorption study, standardized aqueous solutions with an initial concentration of 8 mM of Ni and Cu were prepared using copper sulfate ($CuSO_4 \cdot 5H_2O$) and nickel sulfate ($NiSO_4 \cdot 6H_2O$), respectively, following the procedure described by Guo et al. [7] at room temperature. pH value of the solutions was then set at 5.9 ± 0.4 using NaOH, because as shown that pH values above 5 could favor the maximum ion metal absorption at the equilibrium [8]. After that, the hydrogel samples were placed into the ion solutions at room temperature. Then, aliquots of the solutions were taken 12 and 98 h after the hydrogels were incorporated into the solutions in order to determine the change of the solution concentration.

All the samples were analyzed using inductively coupled plasma (ICP) spectrometry using a ICP Spectrometer Thermo Scientific (ICAP 6000 Series) with a radio frequency power of 1,300 W, a nebulizer gas flow rate of 0.55 L/s, an auxiliary gas flow of 0.5 L/s and a plasma axial view. For each sample, the process was repeated three times with a sample flush time of 30 s.

Results

Characterization by FT-IR

FT-IR spectra were obtained for all of the prepared formulations as well as for the pure natural polymers. Each spectrum (although not all spectra are shown in this article) was analyzed to see if structural changes have occurred and/or if there is evidence of possible interactions that might occur between phases during polymerization.

The FT-IR spectrum of formulation F1 (corresponding to a typical spectrum of an acrylamide hydrogel) was used as a standard and presented the characteristic bands of the functional groups present in these type of polymers, i.e., N–H stretching (3550–3340 cm^{-1}), C–H stretching (2960 and 2870 cm^{-1}), amide II band or C=O stretching (1730 cm^{-1}), amide I band or N–H bending (1640 cm^{-1}), C–N stretching (1470–1370 cm^{-1}), C(=O)–O–C(=O) (1290 and 1245 cm^{-1}) stretching, asymmetric C–O–C stretching (1190 cm^{-1}), out-of-plane C–H bending (1110 and 1050 cm^{-1}), and out-of-plane C–N rocking (850–670 cm^{-1}).

When the other formulations were analyzed, no significant changes were observed in the aforesaid bands in the formulations containing lignin and peat (F2, F3, F4, and F5). This suggests that the presence of these constituents does not

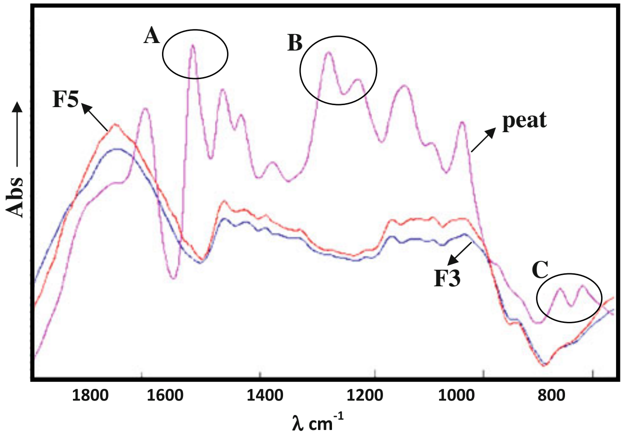

Fig. 1 Comparison of FT-IR spectra of peat with F3 and F5 formulations in the presence of peat in different proportions

favor chemical reactions or strong interactions between polymer–matrix and disperse phases. However, to the contrary, these components (lignin or peat) might be incorporating as a dispersed and incompatible phase, forming a type of non-covalent IPN.

However, when the spectra of F3, F5, and peat are compared, some changes can be observed in the bands at about 1530–1500 cm^{-1}, 1300–1200 cm^{-1}, and 900–800 cm^{-1}, and these changes can be seen in Fig. 1.

In this figure, it can be observed that the bands identified in regions A, B, and C have disappeared. Region A refers to N–H stretching at 1515 cm^{-1}, while region B normally shows –OH stretching of secondary alcohols and, at last, C–H rocking vibrations appear in C. This behavior shows a reduced molecular mobility of these groups, probably due to chemical interactions with the chemical environment of the synthetic hydrogel network. Hence, in our case it could be said that the peat might be inducing some kind of chemical interactions with the synthetic network at the interface which might favor its anchoring on the available spaces of the network.

Morphological characterization by scanning electron microscopy

All hydrogel formulations were observed by SEM to study their morphological characteristics in order to establish the presence or absence of possible physical interactions between their components and thus confirm the suggestions made from the FT-IR results regarding the possible forms of interaction between the components and the incorporation of them in the hydrogel network, as well as the kind of surface they show, the dispersion, the porosity, etc.

First, we analyzed the SEM micrographs of the hydrogel formulation F1 used as a standard. Being an acrylamide-based homopolymer network, it showed a fairly homogenous morphology with a continuous, homogenous, and brittle cut surface as can be seen in Fig. 2.

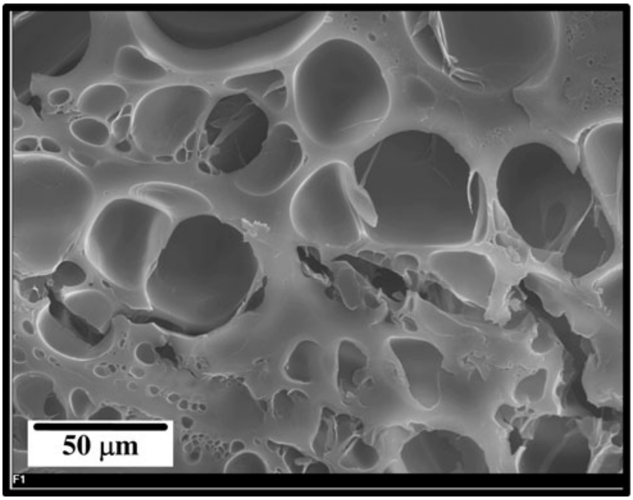

Fig. 2 SEM micrographs of internal morphology of F1 hydrogel formulation

Then, we analyzed the morphology of the formulations containing peat (F3 and F5). As can be seen in Figs. 3 and 4, the different phases can be clearly distinguished in both cases.

Figure 3 shows a plane of the cut surface, which is brittle and has drop-like pores which have a large base diameter ranging from 200 to 700 μm. Dispersed phases of the starch and the peat present in the formulation can also be seen, evidencing that they are included in the synthetic network forming IPN hydrogels, as has been discussed in this section.

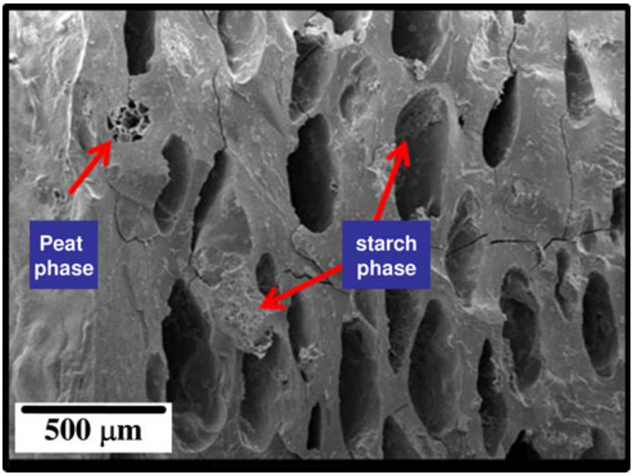

Fig. 3 SEM micrographs of internal morphology of F3 hydrogel formulation

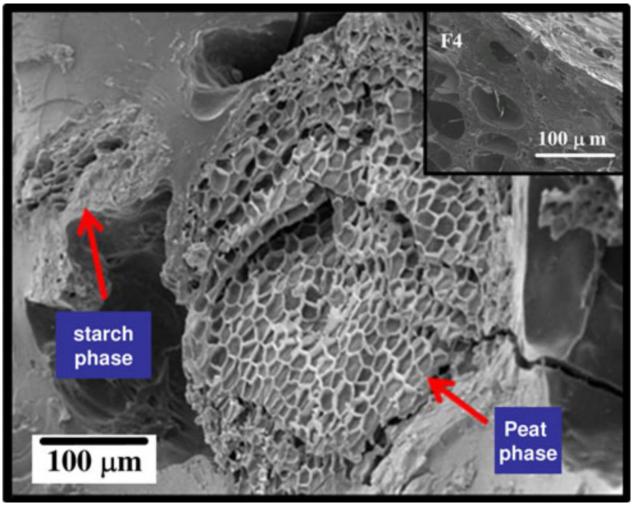

Fig. 4 SEM micrographs of internal morphology of F5 hydrogel formulation. Top right F4 hydrogel internal morphology

Figure 4 is the micrograph of formulation F5, which shows a flat ductile cut resulting from the fracture of the samples, with large microcavities; the interpenetrating phases of peat and starch can also be clearly seen. It is possible to see that that the peat grains or particles are very well anchored to the synthetic matrix, which supports the discussion made during the FT-IR analysis. The morphology of F4 is included on the top of Fig. 4 as a means of comparison. This formulation has a lignin interpenetrated phase which is very well dispersed in the synthetic matrix and is porous like the other formulations.

Behavior of hydrogels in water

Water absorption of the hydrogels

When the hydrogels of each formulation were submitted to the water absorption process, their dimensions and their weight increased with time, evidencing that they were indeed swelling. At the end of the tests, the samples of all the formulations kept their shape (cylinders or discs) and their dimensional stability. However, the gels of formulation F2 showed a certain degree of brittleness in their swollen state; thus, they were handled very carefully in order to avoid their possible disintegration or loss of some mass fractions.

The swelling index according to Eq. 1 was plotted for each formulation in order to establish the influence of the monomers used in each formulation on the water absorption and swelling of the hydrogels. Most of the tested samples attained their maximum water absorption percentage at about 100 h, when it reached the equilibrium.

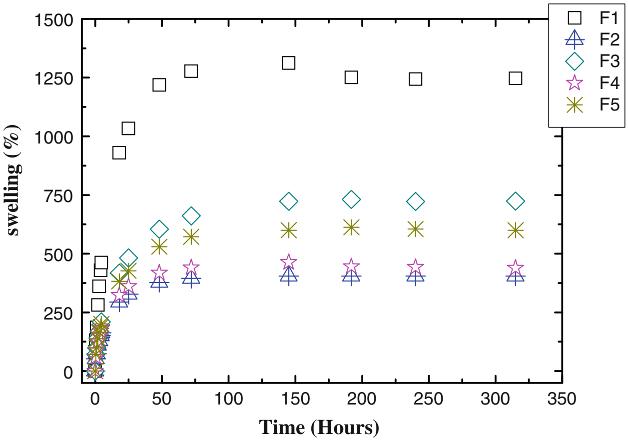

Fig. 5 Variation of swelling index (% weight) for each formulation as a function of time

Figure 5 shows the maximum water absorption and swelling values for each formulation. It can be clearly observed that these values change significantly according to the composition of the formulations [11, 12]. As has been previously mentioned water diffusion and absorption of the formulations will proceed through a different mechanism depending on the chemical nature of their components and the degree of crosslinking [13]. Hence, the swelling of the hydrogels provides an idea of the degree of crosslinking the gels have reached. Low swelling percentages are obtained by those samples whose structure is sufficiently crosslinked, considerably limiting their chain mobility, making the gels more rigid (small pores) and, thus, making water diffusion through the network difficult. Likewise, samples showing high swelling percentages have a more flexible network structure and a lower crosslinking density, thus allowing higher chain mobility due to a lower number of anchorage points (or entanglements) between them.

According to Fig. 5, the gel of formulation F1 was the one with the highest swelling percentage. This compound was highly hydrophilic, a characteristic that favors the absorption of high amounts of water. On the other hand, when peat or lignin are incorporated, the water absorption percentages of the formulations are considerably lower than those of the hydrogels used as standards. This might be due to the fact that IPN hydrogels might be forming in both cases. Lignin, as well as peat, forms a dispersed phase which is anchored on part of the free portions of the network, thus stiffening it and making it significantly more difficult for water to pass through the structure of said hydrogels. In addition, these components are not very hydrophilic. This limits their interaction with water considerably, resulting in the trend shown in the swelling index versus time plot.

When studying the effect of the presence of both these components on the water absorption of hydrogels in the presence of a starch phase, it can be seen that hydrogels with peat (F3 and F5) have a higher swelling index than those with lignin (F2 and F4). This could be explained through the SEM results. The hydrogel samples containing peat show highly porous structures that might favor the water flow through the hydrogel. This phenomenon might be associated to the fact that, as has already be mentioned, due to the nature of its components, in this case lignin have more hydrophilic character than peat [6, 7]. Also peat particles have more heterogeneities, which might be favoring the formation of large pores through which water can flow more easily, because there is more free volume available and the crosslinking density of the synthetic matrix is being reduced by the size of the particles of the peat phase.

Water transport mechanisms in hydrogels

The water transport process in hydrogels can be described by Fick's law of diffusion (Eq. 2) [1, 5, 7, 8, 13]. We plotted the natural logarithm of weight gain with time versus the natural logarithm of time ($\ln W_t/W_\mathrm{f}$ vs. $\ln t$) for W_t/W_f values under 0.6 ($0 < W_t/W_\mathrm{f} < 0.6$), and found the values of n and K which are summarized in Table 2.

When $n = 0.50$, this indicates a Fickean type diffusion mechanism, while when $0.50 < n < 1$, this indicates a non-Fickean type or abnormal diffusion. In the special case where $n = 1$, this mechanism is called type II transport mechanism [1, 5, 13].

As can be seen for all the formulations studied, generally n is about 0.5, which according to what has been discussed so far, means that during the first stage of water absorption ($W_t/W_\mathrm{f} < 0.6$) water transport occurs predominantly by diffusion through the polymer network. This is known as Fickean behavior and is characterized by a linear dependence between the absorption of the solvent and the square root of time ($t^{1/2}$), and happens for all the formulations during the first stage of water absorption.

Then the constant n can describe the process of water transport within the hydrogels [13–15]. Although the value of the constant n is almost similar, indicating that all the hydrogels behave Fickiano, the presence of a dispersed phase seems to influence the value n, because it tends to decrease slightly from the formulation does not interpenetrated (F1). Also with increasing the concentration of these dispersed phases that value decreases slightly more (F4 and F5). Then the hydrophilic character seems to be influencing the process of diffusion of water into the hydrogel.

On the other hand, the value of K gives an idea of the hydrophilic nature of the components of each formulation, which may reduce or increase the time necessary to reach the maximum absorption [5]. In our case, the values of K do not differ significantly between the formulations. However, the formulations with higher

Table 2 Results of the parameters (n and K) obtained after application of the Fick's law for each formulation considering the initial stage of absorption ($W_t/W_\mathrm{f} < 0.6$)

Formulation	n	$K \times 10^2$ (h^{-n})
F1	0.54 ± 0.01	15 ± 1
F2	0.53 ± 0.01	15 ± 1
F3	0.50 ± 0.01	16 ± 1
F4	0.49 ± 0.02	12 ± 2
F5	0.46 ± 0.03	14 ± 1

concentrations of hydrophobic components are those with lower values for this constant *K*.

Metal ion sorption (Cu^{2+} and Ni^{2+})

Adsorption of Ni and Cu increased with the increase of pH from 2 to 8 (Fig. 6). There was no obvious difference in adsorption of metals on the different formulations selects (F1 as control, F4 and F5 with ligning and peat interpenetrated phase, respectively). The pH value, at which 50% of the initial heavy metal ions were adsorbed, termed as pH_{50} [8], is a measure of the relative affinity of metal cations for adsorbent surface. Lower pH_{50} value indicates higher affinity of metals for the adsorbent surface, in this case the pH_{50} for this evaluated IPN hydrogels is around pH ≥ 4, because at pH <4 all formulations shown less than 50% of metal ions adsorbed, only for F4 result indicate a better affinity by niquel that cupper at pH_{50} value. However, results suggest that the affinity of Ni and Cu are similar in all pH range evaluated. The respective optimum pH for adsorption of both ions metal was graphically determined as pH >5, which correlated with others works into the literature [8, 16, 17], and for this reason the final pH consider for to continue these study was around 6.

To analyze the metal kinetics sorption of hydrogels, a sample of each of them was placed in a vessel with 100 mL of the solutions to be tested, having an initial concentration of 8 mM. Aliquots were taken 12 and 98 h after the hydrogels were incorporated, in order to measure the change in the solution concentration resulting from the metal sorption of the hydrogels; then, they were analyzed by ICP [7, 8]. Results obtained for each formulation were plotted and the trends are shown in Fig. 7.

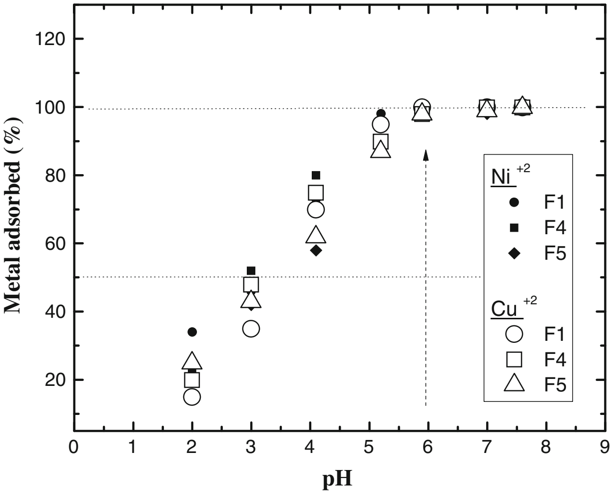

Fig. 6 Effect of pH on Ni^{2+} and Cu^{2+} adsorption using F1, F4, and F5 formulations

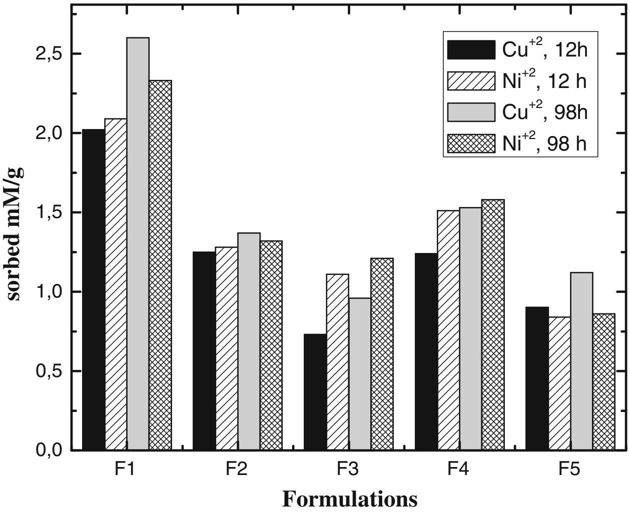

Fig. 7 Comparing absorption of Cu^{2+} and Ni^{2+} for all formulations at 12 and 98 h

When comparing the change of the amount of the two ions sorbed by each formulation in function of time, it was found that the formulations tended to preferably adsorb Ni^{2+} during the first stages of the process, while at longer sorption times the amount of ions sorbed were similar in both cases regardless of the type of ion, as can be seen in Fig. 7. This evidences the fact that under the experimental conditions used, the studied formulations have a higher affinity to the absorption of Ni^{2+}. However, this trend does coincide with the results of Guo et al. [7] who reported that the order of absorption preference for lignin-containing formulations is $Cu^{2+} > Ni^{2+}$ with 0.26 and 0.12 mmol/g, respectively. In our case, this may suggest that the presence of starch could somehow be creating or favoring the presence of sorption sites for Ni^{2+}. This could also be related to the atomic radius (slightly smaller for nickel than for copper, 1.24 vs. 1.28 Å, respectively) which would affect the availability of sites/diffusivity kinetics that favor nickel over copper.

As the results for both metal ions were similar, it could be said that the preference shown by the formulation used as a standard (F1) might result from the fact that in this case the effect of the water diffusion through the network would predominate over the absorption phenomenon and the former tends to stabilize as it approaches 100 h, until the formulations reach their maximum ion retention volume. On the other hand, in the case of the remaining formulations, there is a dispersed phase in the hydrogel network which hinders the ion flow through its structure despite the availability of functional groups (charge δ^{-}) that might capture these cations. However, lignin-containing formulations show a higher absorption than peat-containing formulations, because unlike lignin, peat shows a great number of heterogeneities which result in a smaller absorption capacity than lignin, as has already been mentioned [7–9].

Conclusions

The synthesized hydrogels showed a type of IPN structure in which the fractions of the natural components (lignin and peat) were found dispersed in a polymeric matrix (acrylamide). This kind of interpenetration could be proven through the morphological study by SEM, although the qualitative analysis by FT-IR showed no interactions between phases.

Most of the hydrogels showed maximum water absorption values at about 100 h and all the synthesized hydrogels showed a Fickean water transport mechanism at low swelling percentages with n values of about 0.5.

Adsorption of Ni and Cu increased with the increase of pH from 2 to 8, optimum pH for adsorption of Ni^{2+} and Cu^{2+} was graphically determined as 6.

In ICP studies with Ni^{2+} and Cu^{2+} metal ions, hydrogels showed a larger Ni^{2+} absorption capacity at low absorption times (12 h) and this trend was favored for the formulation used as a standard (F1), for which the diffusion phenomenon was predominant since it was a homopolymer network. In the meanwhile, peat-containing hydrogels showed a slightly lower absorption capacity that lignin-containing hydrogels, due to the presence of more heterogeneities which make the network more rigid, thus makes difficult in diffusion through the sample. Also functional groups in lignin allow such compounds to bind on active sites of peat.

However, although the presence of peat did not produce any significant change in the behavior of this type of IPN hydrogels when compared to the performance of lignin-containing hydrogels, the former compound could be used as a cost-effective and accessible alternative in the preparation of metal absorption materials (for example, membranes), with less ecological impact as a result of the lower amount of vinyl constituents in the formulations, also for the presence of starch phase that could be induce some biodegradability.

Acknowledgments Authors wish to thank specially to the Foundation Institute of Engineering in Caracas (F.I.I.) for allowing us to use the installations of the Center of Materials to make the ICP analyses. Polymer Group of Simón Bolívar University (GPUSB) for allowing the use of infrared spectrophotometer. At the same time, we wish to thank to Lic. Gleen Rodríguez from Center of Surface Engineering (C.I.S) of the Simon Bolivar University for SEM analyses. The authors also thank Decanato de Investigación y Desarrollo DID Universidad Simón Bolívar for financial support (Fondo de Trabajo PPI).

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