Heavy metal ions removal from water using a smart polyurethane/acrylic hybrid

F. M. Pardini [ID],[1,2] P. A. Faccia,[1,2] J. I. Amalvy [ID][1,3,4]

[1]Grupo (Nano)Materiales Poliméricos - Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), (CCT La Plata CONICET - Universidad Nacional de La Plata), Diag. 113 y 64, B1904DPI, La Plata, Argentina
[2]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[3]Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), Argentina
[4]Centro de Investigación y Desarrollo en Ciencia y Tecnología de Materiales (CITEMA), (CIC - Facultad Regional La Plata, Universidad Tecnológica Nacional), 60 y 124, 1900, Berisso, Argentina
Correspondence to: Javier I. Amalvy (E-mail: jamalvy@gmail.com).

ABSTRACT: Heavy metal contamination is certainly one of the most serious environmental problems today. In the present work, polymer films with pH-responsive properties were used for the removal of heavy metals from aqueous solution. These polymers were prepared using different amounts of 2-(diethylamino)ethyl methacrylate (DEA), and a polyurethane based on isophorone diisocyanate (PU) to obtain pH-responsive hybrid films of PU/DEA. Equilibrium sorption characteristics of Cu^{2+} and Zn^{2+} on polymer films were evaluated through batch studies. Hybrid systems were characterized by using FTIR, UV–Visible and microscopy techniques. The effect of pH, initial metal ion concentration and hybrid film composition on the extent of sorption were investigated. Maximum removal of Cu^{2+} and Zn^{2+} in hybrid systems was at pH 4.0, for 250 mg/L initial concentration of each ion, and for the hybrid system with more proportion of DEA (50 wt. %). Polymer systems showed greater selectivity for Zn^{2+} than for Cu^{2+}, and the equilibrium sorption data were satisfactorily fitted to Langmuir sorption isotherm model. Characterization techniques revealed that functional groups of DEA, in hybrid systems, are the main sorption sites for the metal ions. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2018**, *135*, 46874.

INTRODUCTION

Common sources of wastewater containing large quantities of metals such as chromium, cadmium, copper, mercury, lead and zinc come mainly from industries such as mining, smelting metals, fuel and energy production from petroleum, fertilizer industry, etc.[1] These residues containing heavy metals end up being transferred to the environment due to an incorrect treatment or final disposal. Additionally heavy metals are not degradable by chemical or biological means, so they can be transported to sites far from the point of origin of the contamination, usually through watercourses, causing serious environmental consequences for the ecosystem.[2]

There are several methods for removing heavy metals from aqueous solutions, among them: ion exchange,[3] adsorption on activated carbon,[4,5] solvent extraction,[6] chemical precipitation,[7] nanofiltration,[8] reverse osmosis[9] and adsorption.[10–12] However, many of these methods lack the necessary efficiency and can be very costly.[13]

In recent years, alternative treatments such as sorption of metals using accessible materials with specific characteristics began to be investigated. The focus was on numerous sorbents with the ability to bind metals in order to remove them from aqueous solutions of interest and at a low cost.[14] Among these materials called "low-cost sorbents", there are natural polymers like chitosan, synthetic responsive polymers, inorganic materials like zeolites[14] and radiation grafted materials.[15]

Within the low-cost sorbent systems of heavy metals, polymers with large surface areas and porous structures proved to be good candidates.[13,16–18] Yun Tian showed that the polycationic synthetic polymer poly (dimethylamino ethyl methacrylate / 2-hydroxyethyl methacrylate) P(DMAEMA / HEMA) was able to remove more than 99.5% of the nitrate ions from the aqueous solutions,[19] while Kirupha et al. demonstrated that a novel polyurethane synthesized by poly-condensation can be used to remove copper and lead ions.[20]

Despite the number of recent studies incorporating heavy metals into the sorbent, the interaction between the matrix and metal ions receive limited attention in the literature and it is often overlooked. That is why in this work we intended to analyze also

polymers performance and their interactions with the copper and zinc by using FTIR and UV–Visible analysis.

Polymers that can selectively absorb metal ions usually have at least two types of monomers, each exerting a different function. One of the monomers usually forms a complex with the target metal (exerting the absorption function) and the other must allow the polymer to expand or swell reversibly in response to a change in the medium (responsive function). Generally, monomers of the methacrylate family are those chosen as responsive monomers[13,21] and sometimes the same monomer can play those two functions. It is also sought to complement the system with a supporting polymer that improves the performance of the system in terms of stability, durability, mechanical properties, etc.[22,23]

We have reported the synthesis and characterization of news pH-sensitive hybrid polymers of polyurethane (PU) and 2-(diethyl amino) ethylmethacrylate (DEA)[22] with adequate film and mechanical properties and with potential applications as drug delivery systems.[24] The possibility of forming complexes between metal ions and the amino functional groups of the hybrids makes of interest the analysis, characterization and evaluation of these responsive polymers and generate favorable expectations for their use as heavy metal uptake systems. The cationic pDEA is pH-responsive and expands upon lowering the pH [25] having an amino group that could interact with metal ions to form metal-polymer complexes. Since metal ions are generally dissolved at acidic pH (they are practically insoluble at alkaline pH) and most contaminated effluents present water with pH values below 7, a system that responds to a decrease in the pH of the medium would be very advantageous. In PU/AC systems, the polyurethane portion will act as a supporting polymer which provides good mechanical stability and film properties suitable to function properly in aqueous solutions, while the acrylic component (DEA) will act as the responsive part of the system and as the responsible part of the metal removal.

In this contribution, we propose to evaluate these pH-sensitive hybrid polymers of PU/DEA as metal ions sorbents in water solutions taking advantage of their ability to modify their structure to a given stimulus. Copper (Cu^{2+}) and zinc (Zn^{2+}) were selected as model metal ions for their abundance and for their hazardousness in aqueous effluents from multiple users like residential, industrial, agricultural, etc.[2,26–28] The effect of pH, PU/DEA ratio and initial metal ion concentration on the sorption capacity of polymer films were studied. The Langmuir isotherm model was used to describe equilibrium data. The sorption mechanisms of metal ions from aqueous solutions on hybrid films were also evaluated in terms of thermodynamics. Scanning Electron Microscopy (SEM) was used to characterize morphological modifications of hybrid systems in response to changes in pH conditions. Finally, polymer films with Cu^{2+} and Zn^{2+} incorporated were characterized by FTIR and UV–Visible spectroscopy to determine the influence of the metal type and the interactions between the matrix and metal ions.

EXPERIMENTAL
Materials
2-(diethylamino)ethyl methacrylate (DEA, 99%) was purchased from Scientific Polymers Products. The monomer was treated with basic alumina to remove the inhibitor. Isophorone diisocyanate (IPDI, 98%, Aldrich), 2-hydroxy ethyl methacrylate (HEMA, 97%, Aldrich), poly(propylene glycol) diacrylate (PPGDA, 98%, Aldrich), ammonium persulfate (APS, 98%, Fisher), ethylene diamine (EDA, 99%, Aldrich), dibutyltin dilaurate (DBTDL, 95%, Aldrich) and sodium dodecyl sulfate (SDS, 90%, Anedra) were of analytical grade and were used as received. Monomethoxy-capped poly-(ethylene glycol) methacrylate (PEGMA) macromonomer ($Mn = 2000$; $Mw/Mn = 1.10$) was supplied by Cognis Performance Chemicals (Hythe, U.K.) as a 50 wt. % aqueous solution. Polypropylene glycol 1000 (PPG1000, Voranol 2110) was of technical grade and triethylamine (TEA, 99%) was provided by ADELFA S.A. PPG1000 was dried and degassed at 80 °C at 1–2 mmHg before used. Dimethylol propionic acid (DMPA, 98%, Aldrich) was dried at 100 °C for 2 h in an oven. TEA was also dried before use. $CuSO_4.5H_2O$ (99%, Anedra) and $ZnSO_4.7H_2O$ (99%, Mallinckrodt) were used as received. Metal-bearing stock solutions were prepared (1000 ppm of $Cu2+$ and $Zn2+$)) by dissolving the metal salts in distilled water. All the working solutions were obtained by diluting the stock solution with distilled water.

Synthesis of PU/DEA Hybrids Dispersions
A detailed synthesis of PU/DEA hybrids was reported in a previous work.[22] Briefly, in a 1 L six-neck separable flask, PPG1000 and DMPA were charged and the mixture heated to 90 °C and bubbled dried air for 60 min. Then a mixture of IPDI and DBTDL catalysts was added and after 2 h of reaction; the prepolymer was cooled to 45 °C and HEMA dissolved in acetone was incorporated. Later, the temperature was raised to 60 °C and kept constant (for 90 min) until the isocyanate (NCO) content reached the desired value (ca. 4.7%). Next, the mixture was cooled to 55 °C and TEA (in acetone) was added. After neutralization, the temperature was lowered to room temperature and an aqueous dispersion of PU was obtained by adding the PU prepolymer to water containing the appropriate amount of EDA to perform the chain extension reaction. The resulting product was a stable dispersion with a solid content of about 30 wt. % and it was divided into several parts and added different amounts of DEA, PPGDA as the cross-linking agent and PEGMA as the steric stabilizer. The polymerization of PU/DEA/PPGDA/PEGMA mixtures was performed in batch mode using a glass reactor (1 L) with a water jacket for temperature control. The mixture was degassed with nitrogen gas and then the dispersion was polymerized at 80 °C using APS (0.015 wt. % on DEA monomer base) as an initiator.

The polymerization leads to the formation of PU/DEA hybrids having a chemical bond between polyurethane and DEA moieties. The resulting product was a stable dispersion with a solid content of approximately 30 wt. %. Hybrid dispersions with 10, 30 and 50 wt. % of DEA were prepared, and a short notation was used. Thus, "H90/10" denotes a hybrid system containing 90 wt. % of PU and 10 wt. % of DEA monomer. Pure PU dispersion was also prepared, in the same way as the hybrids systems without the addition of the DEA monomer, and it was used as a reference material for comparison with the hybrid systems. The synthesis of polymer dispersions is illustrated in Figure 1.
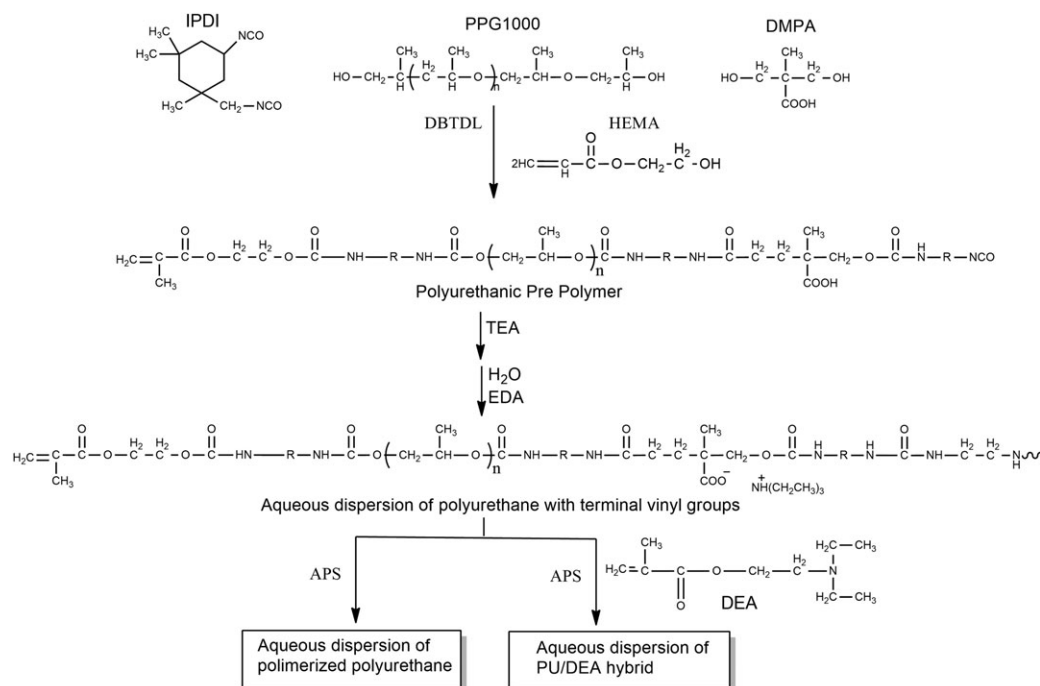
Figure 1. Synthesis of polymer dispersions.

Sorbent Film Formation

Polymer films were prepared by casting the aqueous dispersions on Petri dish. After drying at 30 °C for 24 h, the films were cut into circular pieces (about 22 mm diameter) with a cork borer and cured at 60 °C for 48 h; and finally stored in desiccators with silica gel.

Sorption Studies

Sorption experiments were performed under agitation on mechanical shaker at 400 rpm by the addition of the dry polymer film $(0.1 \pm 0.05 \text{ mg})$ to 80 mL of metal solution (50, 100, 150, 200 and 250 mg/L of Cu^{2+} or Zn^{2+} in a 150 mL glass bottle at room temperature $(25.0 \pm 0.5 \text{ °C})$. The pH was adjusted using a solution of 0.1 M HNO_3 in the range of 2.0 to 6.0; and was measured using an InstruLab Alpha Altronix pH meter, Argentina. Sorption time was set at 24 h, where all systems evaluated reached a constant concentration value. Then, films were removed from the metal solutions and proceeded with the atomic absorption analysis of the remaining solution. Metal uptake was calculated from the difference in the metal contents in the aqueous solution (mg/L), before and after sorption. Before carrying out the measurements, solutions were subjected to digestion in HNO_3 to remove the present organic matter. Metal ion concentrations of the solutions were determined using a Varian SpectrAA 300 Plus spectrophotometer, USA. Standard solutions of copper and zinc were used to prepare the corresponding calibration curves. Experimental values of metal uptake capacities were the results of triplicate measurements reported as means.

The amount of metal uptake per unit mass of sorbent at equilibrium, Q_e (mg/g) was obtained using Equation 1.

$$Qe = \frac{(C0 - Ce)}{M} \qquad (1)$$

where C_0 and C_e denote the initial and equilibrium metal ion concentrations (mg/L), respectively. 'V' was the volume of the solution in liters and 'M' was the mass of the polymer film used (g).

The sorption percentage of metal ion at equilibrium (A_e) from polymer films (mass of films $0.1 \text{ g} \pm 0.05$) was calculated as follow:

$$Ae = \frac{(C0 - Ce)}{M} x100 \qquad (2)$$

where, again, C_0 and C_e are the initial and final metal ion concentrations, respectively.

Sorbent Film Characterization

After sorption experiments, the soaked films, with metal ions incorporated, were gently washed with distilled water to eliminate any superficial residue. Then, films were dried at 30 °C for 24 h before performing the characterization experiments.

Fourier transform infrared (FTIR) studies. FTIR spectra of films were run using a Ge MIRacle™ Single Reflection, attenuated total reflection (ATR) accessory from Pike Technologies, USA, in a FTIR Nicolet 380 spectrometer, Thermo Scientific, USA. FTIR spectra were obtained by recording 64 scans between 4000 and 500 cm^{-1}, with a resolution of 4 cm^{-1}; and they were processed and corrected using the Advanced ATR Correction facility of the EZ Omnic software.

UV–visible spectroscopy and light transmission. UV–visible spectra were determined on dried free-standing films, before and after metal ions uptake, and were normalized by the thickness of films. The transmittance from 200 to 800 nm was measured with a Nicolet Genesys 10 spectrophotometer, USA.
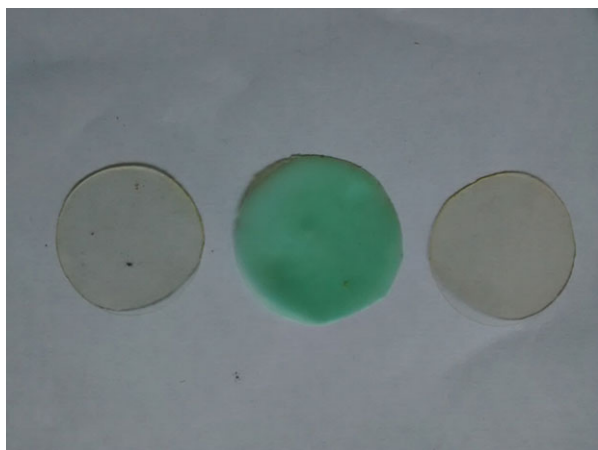
Figure 2. Hybrid films without metal ions (left), with copper (center), and with zinc (right). [Color figure can be viewed at wileyonlinelibrary.com]

Scanning electron microscopy (SEM). The morphology of polymers was observed by SEM with an FEI-Quanta 200 (The Netherlands) instrument, in high vacuum mode and operated at 15–20 kV acceleration voltage. PU and PU/DEA films were equilibrated during 24 h in a buffer solution at pH 4.0, and then were frozen at -40 °C in an alcoholic solution followed by lyophilization under vacuum for 24 h. To prevent sample-charging effects during the observation, fractured pieces of samples were previously mounted onto the surface of an aluminum SEM specimen holder and sputter coated with a thin overlayer of gold.

RESULTS AND DISCUSSION

Visual Observations
The evaluation of visible changes in hybrid films revealed the metal uptake capacity of these systems. Hybrid films with copper incorporated present a light blue/green color indicating the formation of copper complexes (Figure 2). For polymer films with zinc, no coloration was observed, which is logical since the complexes of this metal are colorless.

Effect of pH on Metal Ion Sorption Capacity
Conditions of the loading medium directly influence the amount and efficiency of metal sorption in the matrix.[29] In this way, pH of the aqueous solution was an important variable, which controls the uptake of the metals on the solid–water interfaces. The effects of hydrogen ion concentration from pH 2.0 to 4.0 on the extent of adsorption in polymer hybrid films are shown in Table I.

The extent of metal uptake by films varies with pH, showing the same behavior for both metal ions. The use of pH values higher

or equal than 5.0, resulted in the formation of metal hydroxide precipitates. Thus, these results are not shown in this work.

At pH 2.0, the incorporation percentage decreases compared to pH 4.0 (pH value where the maximum load is given). These results are probably due to the competition between protons and metal ions for the polymer binding sites. At low pH values, hydronium ions are adsorbed more than other ions, since they have a higher concentration and more tendencies to be adsorbed.[30,31] Also, amino and hydroxyl groups at this pH, have a higher degree of protonation, so there are less available to retain the metal ions.[29]

Regarding the effect of PU/DEA ratio, as expected, the increment in DEA proportion improves the sorption capacity for all pH values because the presence of more binding sites and a higher free volume of the matrix as show in SEM images. About the type of ion, zinc was more strongly attracted to the sorbent, with higher removal percentages at the same pH, compared to copper.

Results showed that metal ion adsorption on hybrid films is pH dependent. As was also observed by Zouboulis et al. with modified polyacrylonitrile-immobilized fungal biomass,[32] pH affects the availability of metal ions in solution and the metal binding sites of the adsorbent. Based on the results obtained, pH 4.0 was selected as the optimum pH of loading for the subsequent metal uptake experiments.

Effect of pH 4.0 in Film Morphology
SEM is one of the best methods for characterizing the polymer structure because it offers information on surface porosity, amorphous and crystalline regions, particle size and phase separation.[33] Morphologic changes of lyophilized polymer films, after exposing them to a buffer solution at pH 4.0, have been examined by SEM technique (Figure 3).

The surface of the PU shows a collapsed state with almost a featureless structure. For H90/10, the surface shows an increment in the rugosity, however, despite presence of DEA component, no major changes in the polymer structure is observed, probably due to the low percentage of this component in the systems (10 wt. %). On the contrary, for H70/30 and H50/50 systems, the surface shows an open morphology state with a porous structure, thin walls, and a predominant free space as a consequence of the matrix expansion.[34]

As was described in a previous work,[22] PU/DEA hybrid systems have high water absorption capacity at pH 4.0, 150 wt. % and 280% for H70/30 and H50/50, respectively. This condition is related to the protonation of amino groups of DEA and to the consequently electrostatic repulsion between them. The

Table I. Values of Cu^{2+} and Zn^{2+} Incorporated (%) at Different pH Using a Loading Solution of 250 mg/L and at 25 °C, for PU/DEA Films

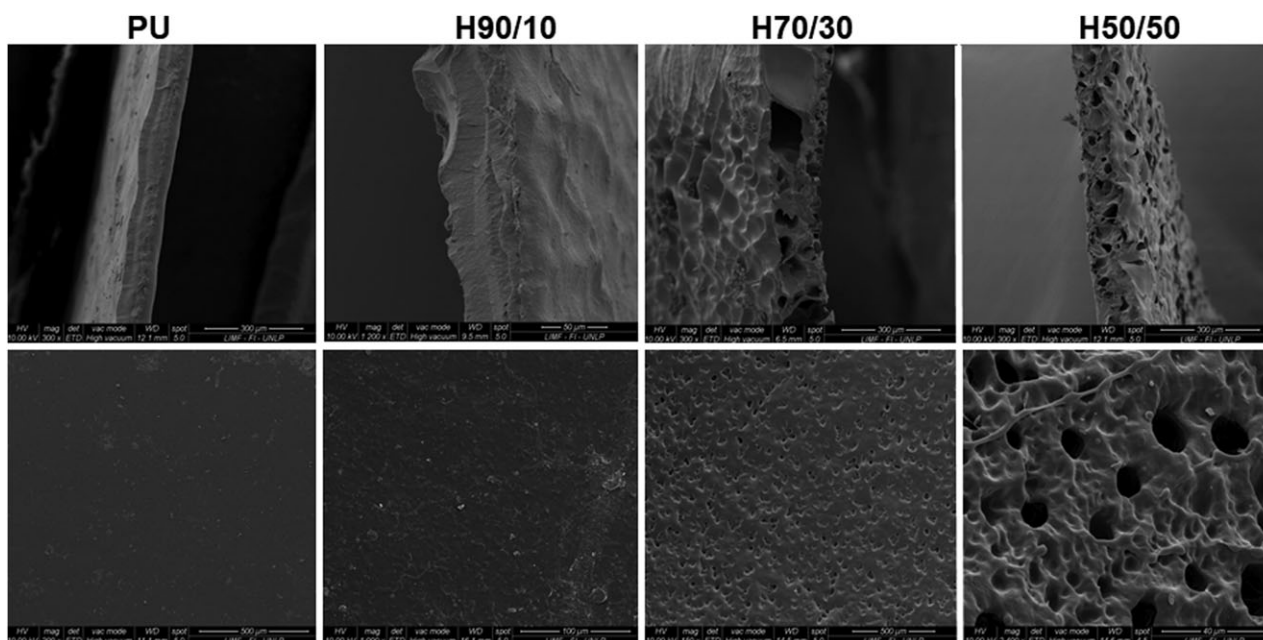|	Cu^{2+}			Zn^{2+}		
pH	H90/10	H70/30	H50/50	H90/10	H70/30	H50/50
2.0	8.5 ± 0.9	12.0 ± 1.1	18.5 ± 2.0	11.5 ± 0.9	15.0 ± 1.1	24.6 ± 1.8
3.0	27.5 ± 1.2	42.0 ± 2.8	57.5 ± 2.4	50.0 ± 1.3	66.0 ± 2.1	81.0 ± 2.1
4.0	31.0 ± 1.4	52.0 ± 2.6	64.0 ± 1.9	57.0 ± 2.0	74.0 ± 2.5	85.0 ± 2.0

Figure 3. Surface (down) and cross-section (up) SEM images from PU and hybrid films previously swelled at pH 4.0.

mentioned electrostatic force increases the network space, and in turn, allows water to get into the matrix. This behavior could favor the entrance of metallic ions into the polymer matrix, especially when DEA content is 30 wt. % or higher.

Effect of Polymer Composition and Metal Ion Concentration on Sorption Capacity

Metal uptake by hybrid films was positively correlated with increasing metal ion concentrations as is shown in Figure 4. Since there are more ions in solution, the formation of metallic complexes in the polymer matrix is favored, due to a higher concentration gradient. Also, results from the Figure 3 indicate that the sorption capacity increases with an increase in DEA content. This behavior reveals that the metal ion removal by sorption on polymer films, was dependent on functional groups concentration as expected. By increasing the amount of DEA, the number of amine, carbonyl and ether groups, which can interact with copper and zinc, and therefore forming complexes, is higher. Fitting with

linear regression gave in all cases a R^2 greater than 0.9. For 70/30 and 50/50 systems, an almost constant ratio of metal sorption and metal concentration indicates a relation close to 1:1 between metal ions and DEA functional groups.

In the case of PU system, the reduced number of carboxylic groups available to coordinate metal ions, limits their complexation and therefore, the removal of metal ions is low. In addition, at pH 4, carboxylic groups are almost protonated and the contribution to the metal uptake of metal ions is still lower.

Sorption Efficiency

Sorption efficiency of metals ions (Figure 5), increases with the increment of DEA proportion, especially in H70/30 and H50/50 systems. The values obtained for both ions indicate that polymer systems have greater selectivity for Zn than for Cu. This behavior is probably related to the lower stability of the aquo-zinc complexes, $[Zn(H_2O)_6]^{2+}$, with respect to copper ones, $[Cu(H_2O)_6]^{2+}$,
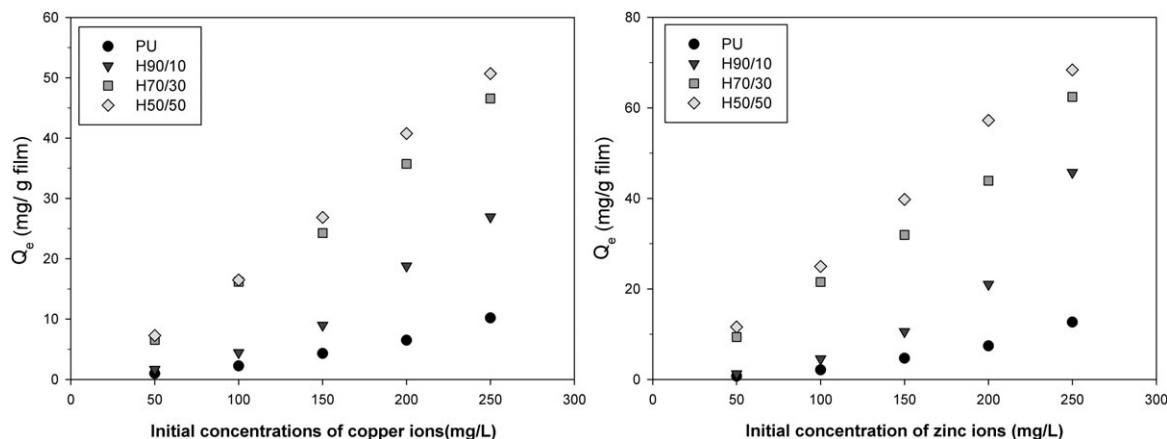

Figure 4. Effect of polymer composition on the sorption of Cu (left) and Zn (right) at different initial metal ions concentrations; and at pH 4.0 and 25 °C.
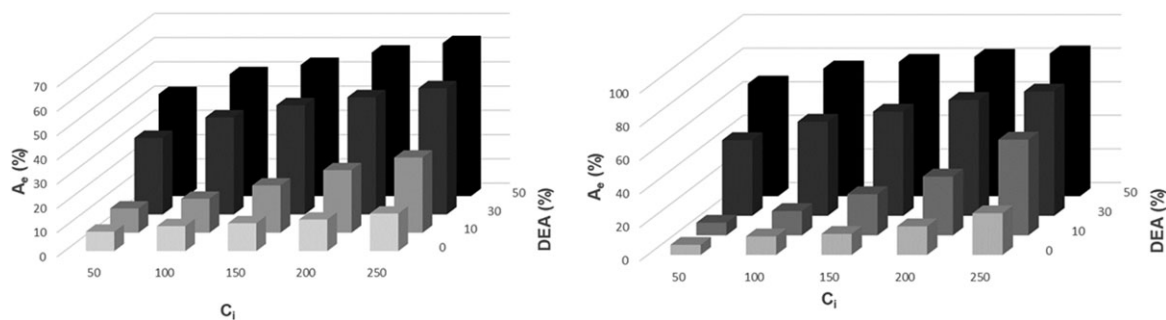
Figure 5. Sorption efficiency of Cu^{2+} (left) and Zn^{2+} (right) by polymer systems at pH 4.0 and 25 °C for different initial ion concentration.

which would favor the incorporation of Zn^{2+} to the polymeric matrix.[35]

Sorption Isotherms

Sorption capacity data at equilibrium of hybrid films can be analyzed using commonly known sorption isotherms, which provide the basis for the design of sorption systems. The most widely used isotherm equation for modeling of the sorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites and it is given by Equation 3.

$$Qe = \frac{b.Qm.Ce}{1 + b.Ce} \qquad (3)$$

where b is the sorption equilibrium constant including the affinity of binding sites (L/mg), Q_m is the maximum sorption capacity (mg/g), and C_e is the equilibrium metal ion concentration in the solution (mg/L). Equation 3 can be written as follows:[36]

$$\frac{1}{Qe} = \frac{1}{Qm} + \frac{1}{Qm.b.Ce} \qquad (4)$$

where Q_m and b can be determined from the intercepts and slopes of the linear plot of $1/Q_e$ versus $1/C_e$.

Results of sorption studies of separate solutions of Cu^{2+} and Zn^{2+} at different concentrations ranging from 50 to 250 mg/L on a fixed amount of sorbent, were expressed by Langmuir model using Equation 4 (Figure 6). Parameters of Langmuir sorption isotherms are presented in Table II along with the correlation coefficient.
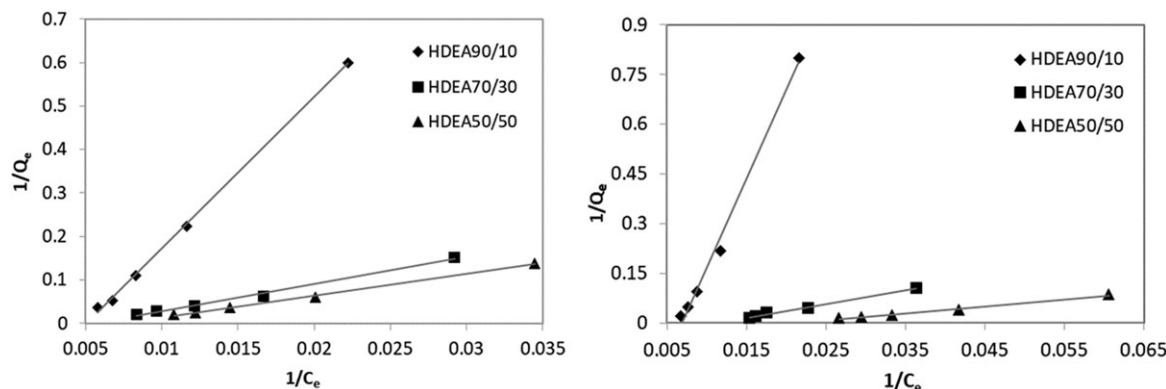
Langmuir model can fit the data adequately ($R^2 > 0.9$) for all systems. Q_m increases as the amount of DEA increases, indicating a greater uptake capacity in hybrids with higher DEA proportion. Coefficient b also increases with DEA content, indicating a greater affinity for the metal as the proportion of acrylic monomer increases. In addition, both Q_m and b are higher for Zn ions, which results in a higher polymer-metal affinity for the latter metal.

Hybrid systems developed in the present study exhibits similar or higher sorption capacity compared to other natural and synthetic sorbents, with data collected from the literature as can be seen in Table III.

One of the essential characteristics of the Langmuir equation could be expressed by dimensionless constant called equilibrium parameter, R_L.[42]

$$RL = \frac{1}{1 + b.C0} \qquad (5)$$

where C_0 is the initial metal ion concentration (mg/L) and b is the Langmuir constant previously calculated. The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).[43]

Also, using the b parameter of Langmuir, the spontaneity of the metal–ligand bond (ΔG), can be calculated from the following equation:

$$\Delta G = -RT.Ln(b) \qquad (6)$$

The Gibbs free energy change indicates if the adsorption process is spontaneous and higher negative value reflects a more

Figure 6. Langmuir sorption isotherms of Cu (left) and Zn (right) for hybrid films.

Table II. Parameters of Langmuir sorption isotherms for Cu^{2+} and Zn^{2+} ions in hybrid films

System	Metal	Q_m (mg/g)	b (L/mg) x 10^3	R^2
H90/10	Cu	26.95	1.07	0.999
	Zn	45.73	3.41	0.997
H70/30	Cu	46.56	3.41	0.991
	Zn	62.41	3.84	0.994
H50/50	Cu	50.67	3.95	0.998
	Zn	68.37	6.87	0.992

energetically favorable sorption.[44] ΔG and R_L values obtained for both metal ions are presented in Table IV.

The negative values of ΔG mean that the sorption of metal ions in hybrid films is spontaneous. ΔG values increase with DEA content, suggesting that there are strong interactions between the metal ion and the amino functional group. In addition, higher values of ΔG are observed in the case of zinc, indicating that the sorption of this metal is more favored than the copper, as could be seen in the previous sorption graphs.

Calculated R_L values (Table IV), indicate that the sorption of both metal ions in hybrid films is favorable for each concentration tested.

Fourier Transform Infrared (FTIR) Studies

Functional groups such as NH_2, OH, and CO are often involved in the bonding between the metal ions and the polymer matrix,[45] where different transport studies indicate that ions like Cu^{2+} and Zn^{2+}, are coordinated by NH and OH groups[46]. In this sense, it has been confirmed that amino groups are the most effective binding sites for metal ions, forming stable coordination complexes.[47] To study the chemical interaction between the polymer matrix and metal ions, FTIR studies were performed. FTIR spectra of PU films (Figure 7) and H50/50 films (Figure 8) with and without metal ions are shown.

In PU film with copper incorporated, the band centered at 1655 cm^{-1}, corresponding to the carbonyl group of urea, is not

observed; and the band corresponding to the amide II moves to smaller wavenumbers (from 1545 to 1533 cm^{-1}). The N-H band assigned to the free N-H stretching vibration and hydrogen-bonding N-H stretching vibration, show a narrow and a shift from 3343 to 3325 cm^{-1}, suggesting a decrease in freedom of movement.[22] On the contrary, no significant changes are detected in C-O-C vibration bands of the urethane and polyetherdiol (between 1175 and 1000 cm^{-1}). Therefore, spectra analysis would indicate that Cu^{2+} could be interacting with the carbonyl and amino groups of the urea.

In PU film with zinc, in the high wavenumbers region, are an increase and a shift (from 3510 to 3490 cm^{-1}), of the shoulder assigned to the O-H stretching vibration of the DMPA.[48] The urethane N-H band moves from 3343 to 3349 cm^{-1} suggesting an increase of the free N-H stretching vibration. A shift (from 1110 to 1102 cm^{-1}) and a widening of the band corresponding to the C-O-C vibration were also detected. In addition, the band corresponding to the stretching vibrations of the C-H (2898 cm^{-1}) is not observed as result of its shift to higher wavenumbers. An increase in the absorbance of the band center at 2928 cm^{-1}, assigned to symmetrical stretching vibration of the methylene, was also detected. Unlike films with copper, no significant changes were observed in the amide I and II bands. Therefore, these results would indicate that Zn^{2+} interacts with the oxygen atoms present in the DMPA, polyol and acrylic groups of the PU.

In H50/50 film with copper incorporated, at high wavenumbers, a shift from 3334 to 3383 cm^{-1} of NH band is observed, indicating a decrease of the hydrogen-bonding of N-H groups,[22] and a shift of the shoulder from 3510 to 3544 cm^{-1}, suggesting also a decrease of the hydrogen-bonding of OH groups.[48] These results would indicate that the hydrogen-bonding interactions of the polymer are been affected by the metal absorption. Compared with PU, other changes associated with the vibrations modes of the DEA were found in H50/50 film. In the C-H zone (from 3000 to 2842 cm^{-1}), the shoulder assigned to the symmetrical stretching vibration of the methyl adjacent to the amine group of the DEA, rise and moves from 2872 to 2894 cm^{-1}. Changes associated with the bending vibration of methyl and methylene

Table III. Maximum Sorption Capacity, Q_m (mg/g), of Cu^{2+} and Zn^{2+} for the Different Systems
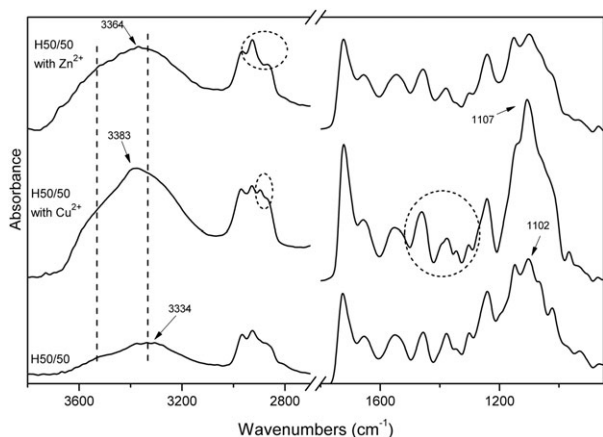
System	Cu^{+2}	Zn^{2+}	References
PU/DEA 50/50	50.67	68.37	This work
Poly(2-hydroxyethylmethacrylate)	0.84	-	13
Copolymer of 2-hydroxyethyl methacrylate/ methyl methacrylate	31.15	-	13
Ascophyllum nodosum (alga)	-	61.08	37
White corn	-	22.58	37
Saccharomyces cerevisiae (levadura)	-	63.50	37
Polyethyleneiminemethylene phosphonic acid	85.69	-	29
N-[3-(dimethylamino)propyl]methacrylamide	63.5	-	38
Polyamine-functionalized	64.77	-	39
Chlorella sp. (alga)	-	66.16	40
Poly(N,N-dimethylaminoethyl methacrylate)	31.46	-	41

Table IV. Values of R_L Parameter, at Different Metal Ion Concentration, and ΔG for Hybrid Films at 25 °C and pH 4.0

| System | Metal | ΔG (kJ/K.mol) | RL | | | | |
			50 (mg/L)	100 (mg/L)	150 (mg/L)	200 (mg/L)	250 (mg/L)
H90/10	Cu	−10.45	0.949	0.903	0.862	0.824	0.789
	Zn	−7.69	0.983	0.967	0.951	0.936	0.921
H70/30	Cu	−13.32	0.854	0.746	0.661	0.594	0.540
	Zn	−13.68	0.839	0.722	0.634	0.566	0.510
H50/50	Cu	−13.68	0.835	0.717	0.628	0.559	0.503
	Zn	−15.12	0.744	0.593	0.492	0.421	0.368
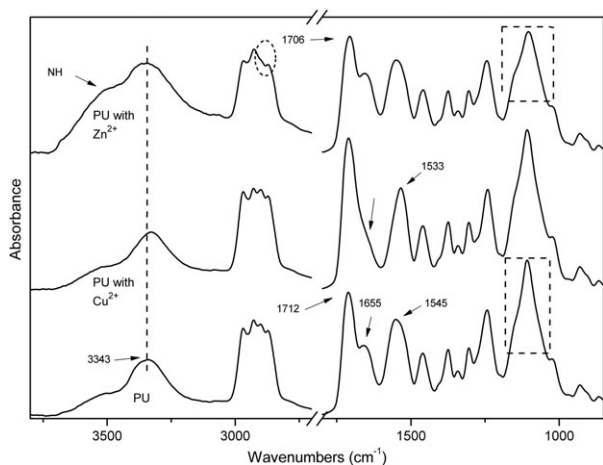
Figure 7. FTIR spectra of PU films with and without metal ions.

groups adjacent to the N atom of the DEA moiety are also detected in the fingerprint region (1500–500 cm^{-1}). Within those changes, the band assigned to the scissoring of the methylene groups moves from 1452 to 1460 cm^{-1}, and the band at 1344 cm^{-1} assigned to the symmetrical bending vibration of the methyl shows an increase in the intensity. In addition, the band at 1066 cm^{-1} corresponding to C-N stretching vibration moves to low wavenumbers and the C-O-C stretching vibration (at 1102 cm^{-1}) increase and moves to 1107 cm^{-1}. However, no

significant changes were appreciated in the amide II band of urethane and urea groups (at 1545 cm^{-1}), or in the carbonyl band of urea groups (at 1655 cm^{-1}). Hence, from the spectrum analysis, it can be concluded that copper would be interacting principally with the nitrogen of the DEA affecting therefore the vibrational modes of the acrylic group.

Finally, for H50/50 with zinc, is observed an increase and a shift of the shoulder at 3510 to 3491 cm^{-1}, indicating an increment of the hydrogen-bonding of O-H groups. On the other hand, the urethane N-H band moves from 3334 to 3364 cm^{-1} suggesting an increase of the free N-H groups. In addition, there is a broadening and a shift to low wavenumbers of the band at 1102 cm^{-1} corresponding to C-O-C stretching vibration of the polyetherdiol and DEA proportion (1206–990 cm^{-1} region). In the carbonyl zone, the absorbance of the band at 1725 cm^{-1} decrease, suggesting a change in its chemical environment. In C-H zone, there are an increase of the band at 2926 cm^{-1} (symmetrical stretching vibration of the methylene), and a shift of the shoulder at 2872 cm^{-1}, assigned to symmetrical stretching vibration of the methyl adjacent to the amine group of the DEA. Hence, zinc would also be interacting principally with the functional groups of DEA and also with the oxygen atoms present in the DMPA and polyol groups.

Figure 8. FTIR spectra of H50/50 films with and without metal ions.
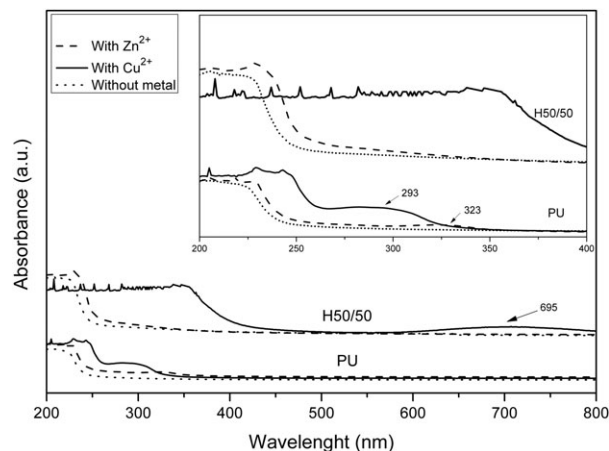
Figure 9. UV–visible spectra of PU and H50/50 films with and without metal ions. (Enlargement shows 200–400 nm region).

UV–visible spectroscopy and light transmission

In UV region (Figure 9), there is an increase in the absorbance intensities of all metal-loaded films, due to the electron transitions n→π* of the carbonyl groups, which are normally weak by the selection rules, increasing their intensity due to the loss of local symmetry around the carbonyl groups from the incorporation of the metal in the matrix.

In PU film with copper, the appearance of a band at 293 nm assignable to lower energy electron transitions of carbonyl groups interacting with metal ions can be appreciated. In PU film with zinc, also the appearance of a band at 323 nm corresponding surely to the interactions of the nitrogen of the urethane group and the carbonyls of the urea with the metal is observed. From 400 to 800 nm (visible region), the absorbance of PU films does not suffer modifications when incorporating the metal, which agrees with the colorless of these films.

On the other hand, H50/50 hybrid loaded with copper presents an absorption band with a maximum at 695 nm, characteristic of copper complexes. Bjerrum et al.,[49] obtained theoretical and experimental wavelengths of copper complexes and described how the incorporation of amino group as ligand into the complex, modifies the maximum absorbance of the band, displacing it from 790 nm in the hexaaquo complex ($[Cu(H_2O)_6]^{2+}$) towards shorter wavelengths.

In the present work, the maximum absorbance value obtained (695 nm) resembles the ones calculated and obtained by Bjerrum et al. when only one molecule of ammonium is present, therefore, the complex that would be forming in the hybrid film with copper, would be $[Cu(NR_3)(H_2O)_5]^{2+}$. This result follows the trend and behavior of the sorption studies previously analyzed, indicating that each copper molecule would be coordinating with the amino group of DEA portion. For the hybrid film with zinc, no changes are observed in the visible region of the spectra. This behavior is expected since complexes of zinc do not have coloration.

CONCLUSIONS

Sorption of Cu^{2+} and Zn^{2+} from aqueous solution into PU/DEA hybrids at different conditions such as pH, initial metal ions concentration, and polymer composition were studied to investigate optimum values of the mentioned conditions for the removal of metal ions. Changes in these variables affect the sorption process and therefore modify the obtained values of the number of metal ions uptake. Maximum removal of metal ions in hybrid systems was at pH 4.0, 250 mg/L initial concentration of each ion, and for the hybrid systems with more proportion of DEA (50 wt. %). Polymer systems showed greater selectivity for Zn^{2+} than for Cu^{2+} in all concentration tested.

Equilibrium sorption data were satisfactorily correlated by Langmuir isotherm equations. The negative value of the standard Gibbs free energy change revealed that the sorption procedure is a spontaneous one. R_L values indicated a favorable uptake process for each system.

SEM studies showed highly porous nature at pH 4.0 for H70/30 and H5/50 hybrid films. FTIR studies of loaded hybrid films indicated that the functional groups of the DEA are the main sorption sites for the metal ions. UV–Visible analysis indicated that

complexes that would form between copper ions and hybrid films could be of the $[M(NR_3)(H_2O)_5]^{2+}$ type.

The possibility of decreasing the amount of metal ions in solution using a stable and non-polluting system is of high importance for the treatment of contaminated water. The proposed pH-responsive hybrid systems are promising in this respect.

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