

Heavy metal removal using hydroxypropyl cellulose and polyacrylamide gels, kinetical study

José Luis Zamarripa-Cerón, Juan Carlos García-Cruz, Alfredo Carlos Martínez-Arellano, Carlos Fernando Castro-Guerrero, Marisela Estefanía Ángeles-San Martín, Ana Beatriz Morales-Cepeda

División De Estudios De Posgrado E Investigación Del Instituto Tecnológico De Ciudad Madero, Juventino Rosas Y Jesús Urueta Col. Los Mangos, Ciudad Madero Tamaulipas CP 89440, Mexico

Correspondence to: A. B. Morales-Cepeda (E-mail: abmoralesc@itcm.edu.mx)

ABSTRACT: In this article we report the removal of Pb, Ni and Cu using a hydrogel made with hydroxypropyl cellulose (HPC) and polyacrylamide (PAAm). The hydrogel successfully removed those metals, as shown by the results of atomic absorption spectroscopy; the polymer removed 53% of Pb, 52% of Ni and 51% of Cu. Different pHs were tried for these polymers. The highest metal removal was found at 40°C. The adsorption kinetics fitted Langmuir and Freundlich isotherms. Metal particles were detected on the hydrogel with electron microscopy and energy-dispersive X-ray spectroscopy, confirming that the gel removed the metals from the testing solutions. This polymer is a good option for treating wastewater and industrial waters as it removes metals and is composed of nontoxic materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43285.

KEYWORDS: applications; kinetics; microscopy; swelling

Received 25 July 2015; accepted 2 December 2015

DOI: 10.1002/app.43285

INTRODUCTION

Water is essential for life and is a very important asset in current life, as it is used in domestic and industrial processes. Due to the importance of water, the limited amount of freshwater, and the growing world population, the treatment of wastewater is of great importance, as it can be recycled or safely disposed to the environment. Heavy metals are among the pollutants of freshwater, as they are dangerous to health,¹ this problem has become a priority in water treatment.² Lead is one of the heavy metals found in water, it is a dangerous element as it is neurotoxic and harmful to health.¹ Other elements often found in water are nickel³ and copper.^{4,5}

Hydrogels are materials that have the ability of absorb and desorb water. During the water absorption process, hydrogels can also adsorb water soluble species and retain them on the surface. This characteristic can be used for treating waste-water and remove pollutants from it,⁴ by means of an adsorption process. Many papers deal with the issue of heavy metals in water. Usually they focus on the synthesis of materials that can remove heavy metals from water in a safe manner.^{6–9} Heavy metals form coordination complexes with electron rich atoms, as nitrogen, oxygen, sulfur, etc.,¹⁰ this makes some hydrogels suitable to remove heavy metals from wastewater, forming a chelate.⁴

This research shows the use of a hydrogel made with polyacrylamide (PAAm) and hydroxypropyl cellulose (HPC) for the adsorption of lead, copper, and nickel metallic ions in aqueous solution. Polysaccharides, as HPC, have been reported on the literature to remove heavy metals from aqueous solutions.^{4,11,12} Previous work reported these gels,^{13,14} and described their characteristics and properties such as their lower and upper critical solution temperatures.

The use of HPC and PAAm guarantees the adsorption of metals due to the capacity of both chemicals for forming chelates with metals, making composites of those materials an option of use in the pharmaceutical industry, as well as in the removal of metals from wastewater. Although there are papers using composites of these polymers for drug release,^{15,16} or similar compounds for mucoadhesive films,¹⁷ there are no papers using these composites for metal removal. PAAm is a polymer having a very high water absorbing capacity; this quality makes PAAm a suitable material for both water and metal adsorption.⁵ HPC is a polymer derived from cellulose, it is nontoxic, readily available,^{18,19} it is used as food additive and also in the pharmaceutical industry. HPC has the ability to change its water absorption capacity, due to the presence of a lower critical solution temperature and forms chiral nematic phases.²⁰ Cellulose, the material from which HPC is derived, also forms chiral nematic

Additional Supporting Information may be found in the online version of this article.

© 2015 Wiley Periodicals, Inc.

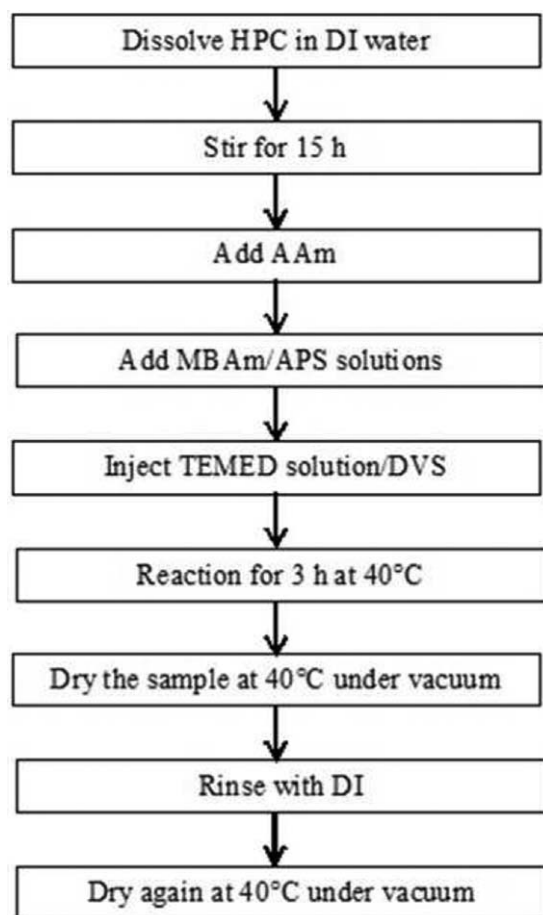


Figure 1. Scheme for the synthesis of the HPC/PAAm polymer.

phases.^{21–25} The results presented in this study show that the HPC/PAAm gel can adsorb Pb, Ni, and Cu from test solutions and keep it on the surface after drying. The polymer showed a high metal adsorption capacity, thus making it suitable for water treatment.

EXPERIMENTAL

Materials and Synthesis

Totally, 2 g of HPC (Aldrich M_n 10,000 g/gmol, MS 3.6) were dissolved in 20 mL of deionized water (DI) for 15 h. 2 g of acrylamide (AAm, Aldrich, 97%) were added, and the solution was stirred until complete dissolution was achieved. At the beginning of the reaction, 8 mL of water containing 2 mg of methylenebisacrylamide (MBAm, Aldrich, 99%) and 40 mg of ammonium persulfate (APS, Sigma-Aldrich, 98%) were added. Then, 40 mg of tetramethylethylenediamine (TEMED, Sigma-Aldrich, 99%) dissolved in 8 mL of water and 0.36 g of vinyl sulfone (DVS, Aldrich, 97%) were injected, and the mixture was allowed to react for 3 h at 40°C in an inert atmosphere with constant stirring. After the desired reaction time, the solution was poured on silicon Petri dish, and it was allowed to dry at 40°C under vacuum, rinsed with DI water, and allowed to dry again^{13,14} under vacuum. The synthesis is resumed in the scheme in Figure 1.

Characterization

The adsorption of metals was evaluated by means of Atomic Absorption using a spectrophotometer GBC model 932AA. The heavy metal solutions were prepared at a concentration of 10 ppm of each aforementioned material. They were mixed for a few hours, and the conditions of pH and temperature were set in the experiment. 1 g of absorbent hydrogel sample was added, and then 10 mL aliquots were taken and analyzed in the atomic absorption spectrophotometer. Microscopic studies of the gel were carried out at room temperature with a Hitachi STEM S-5500 using an elemental detector Bruker X Flash 4010, the samples were observed with the STEM on carbon tape; the samples observed on the SEM were those dried samples after adsorption at pH 4 and 40°C, except for Pb, that was observed after adsorbing at pH 4 and 25°C.

Adsorption Experiments

A stock solution of each metal, Pb(II), Ni(II), Cu(II) (Accu Standard, 1000 ppm diluted in 2% nitric acid solution) was diluted to 10 ppm solution, adjusting the pH to the desired value.

The gels were left to absorb water containing the metals. A sample of the gel was cut (measuring 1.0 cm × 1.3 cm),^{26,27} and deposited in the solution to be analyzed. The metal content was analyzed with the aforementioned Atomic Absorption spectrophotometer.

With the data obtained, Freundlich and Langmuir adsorption models were tried.²⁸ The equilibrium isotherms are used in order to determine the biosorbent capacity for the metallic ions. The relationships between the quantity of metal adsorbed and the metallic concentration remaining in the solution are described by an isotherm.^{29,30}

The equations that describe the Langmuir and Freundlich adsorption models are, (1) and (2), respectively:

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{bKc} \quad (1)$$

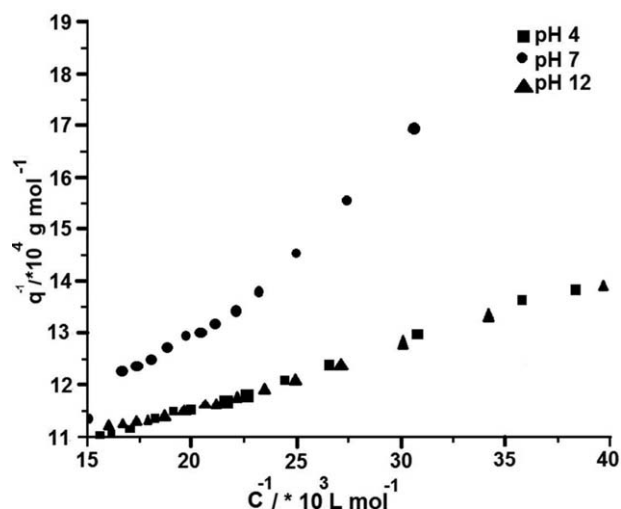


Figure 2. Langmuir isotherms for the Pb²⁺ adsorption on the HPC/PAAm gel at different pHs and room temperature.

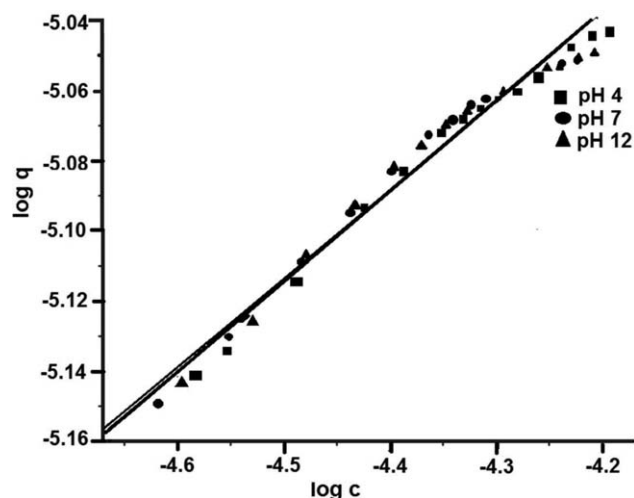


Figure 3. Freundlich isotherms for the Pb^{2+} adsorption on the HPC/PAAm gel at different pH's and room temperature. The units for q and c are mol g^{-1} and mol L^{-1} , respectively.

$$q = kc^{1/n} \quad (2)$$

Where q is the quantity of metal adsorbed (mol/g), c is the residual quantity of the solute in the solution (M), K is the adsorption equilibrium constant (L/mol), b is the maximum adsorption capacity, and k and $1/n$ are arbitrary values.

RESULTS AND DISCUSSION

Adsorption Experiments

In Figure 2 are presented the lead adsorption isotherms of the HPC/PAAm gel at room temperature. The highest percentage of lead adsorption was obtained in the acidic pH, while the lowest was that of the alkaline pH. At neutral pH, the solution's adsorption was between the acidic and the alkaline; the highest percentages were determined with the data of the adsorption experiment (see Figure S1 in Supporting Information); at pH 4 it was 53 wt %, at pH 7 it was 49 wt % and at pH 11 it was 47 wt %. This behavior was observed in other reports,^{31,32} where PAAm gels absorbed a higher quantity of metal ions in acidic pH, while they absorbed less in alkaline pH. It has been explained that at alkaline pH, COONH_2 groups dissociate, increasing the content of ions, which causes a change of the ionic strength of the solution³³ and a decrease of osmotic pressure³²; solution pH affects the amine and hydroxyl functional groups of the polymer,³⁴ see Figure S2 in Supporting Information for a graph showing the point of zero charge of the HPC/PAAm polymer. Composites of polyacrylamide and hydroxyl

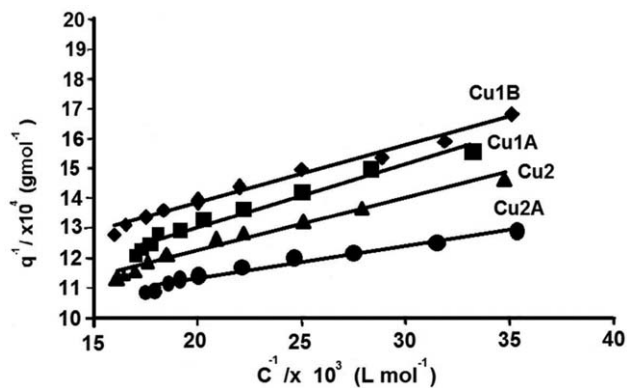


Figure 4. Langmuir isotherms applied to the Cu^{2+} solutions. Notation of samples: Cu1A 25°C pH 4, Cu1B 40°C pH 4; Cu2A 25°C pH 7; Cu2B 40°C pH 7.

bearing-benzoquinone derivatives have also shown a decreased adsorbing capacity at higher pH's,³⁵ with the ionic strength of the solution playing a role on the metal adsorption, and Na^+ ions showing affinity to the adsorbing sites, because Na^+ ions have a higher mobility.

The Langmuir and Freundlich adsorption isotherms for Pb^{2+} ion are shown in Figures 2 and 3, respectively. The parameters obtained from both isotherms are summarized in Table I. The Pb adsorption experiments were done using a standard sample with 1000 ppm of $\text{Pb}(\text{NO}_3)_2$, which was diluted in water to 10 ppm. 50 mL of solution were extracted and 200 mL were left for analysis. The Langmuir and Freundlich adsorption isotherms exhibit an almost lineal behavior for all pHs. The value of K is large, and that of $1/n$ is between 0.1 and 0.5, which indicates that the adsorbents have a high adsorption capacity.^{36,37} It is also observed that the Langmuir parameters are not sequential, while the Freundlich parameters are, and the correlation coefficient in general is better for the Freundlich model. The $1/n$ parameter is an indication of the affinity between the adsorbent and the adsorbed.³⁸ Its value and that of k go in the following order: acidic pH > neutral pH > alkaline pH, which means that the quantity of lead adsorbed decreases in that order. The behavior of the isotherms is similar in the three cases, but the $1/n$ and k values indicate that the gel in an acidic environment is the most effective adsorbent of the three for the removal of the lead ion, although, the other two adsorption conditions are good for removing the lead ion.

The gel adsorbs lead due to the OH, NH C=O, and C—O—C groups present in the polymer. The free electrons of the

Table I. Pb^{2+} Adsorption Parameters on the HPC/PAAm Gel for Various pH's

pH	Model						
	Langmuir			Freundlich			
	$K/[\text{L/mol}]$	$b [\text{mol/g}]$	r^2	K	$1/n$	r^2	r^2
Acid	9.708×10^4	1.037×10^{-5}	0.972	1.148×10^{-4}	0.262	0.994	
Neutral	9.960×10^3	2.322×10^{-5}	0.992	1.111×10^{-4}	0.258	0.989	
Basic	9.773×10^4	1.047×10^{-5}	0.987	1.055×10^{-4}	0.253	0.986	

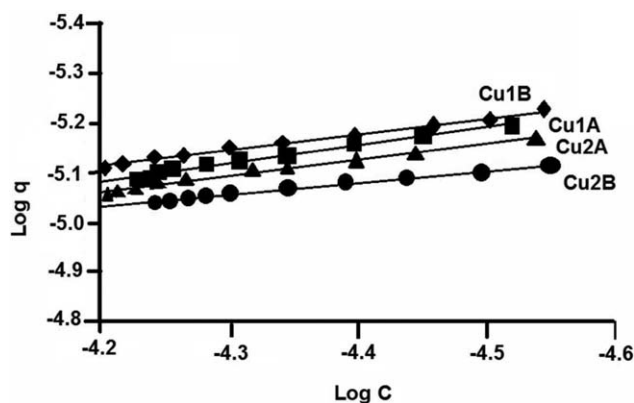


Figure 5. Freundlich isotherms applied to the Cu^{2+} solutions. The notation of samples is the same as Figure 3.

aforementioned groups retain the metal dissolved in the water and a complex called chelate is formed between the gel and the metal.^{39,40}

Adsorption tests for the Cu^{2+} and Ni^{2+} cations at pH 4 and at pH 7 were carried out at 25 and 40°C, with the aim of determining the quantity of metal adsorbed in the HPC/PAAm hydrogel. In Figures 4 and 5 are shown the results obtained for the copper solutions after applying the models previously described.

In the results summarized in Table II, the quantity of the Cu^{2+} ion adsorbed is observed to be higher in the acidic pH than in the neutral one and performs better at a temperature of 40°C. This indicates that the gel is sensible to the pH and to the osmotic pressure of the solution.

The gel is thermo-swelling, that is to say, the macromolecular network is stimulated upon increasing the temperature of the systems, which provokes a softening in the gel's chains, achieving a greater uptake of aqueous solution.²⁷ On the other hand, functional groups present in the gel's structure (OH, NH, C=O, and C—O—C groups) have affinity with the metals dissolved in water, the metallic ions are retained in the gel by the interaction of the free electrons of d orbitals with the functional groups present in the gel, they form a complex between the gel and the metal, a chelate is formed.^{39,40}

Figures 6 and 7 show the Langmuir and Freundlich isotherms of the gels after adsorbing Ni^{2+} . In Figure 7, a tendency to adsorb the metallic ion quickly is observed, but as the time

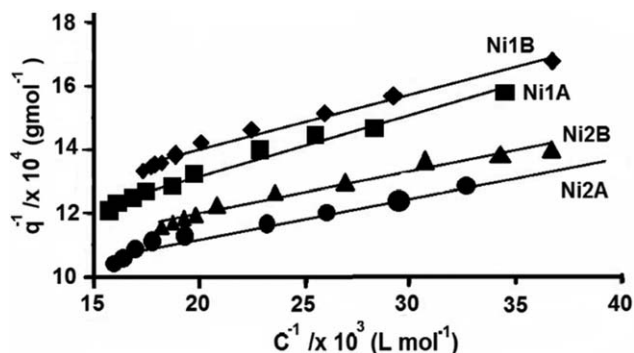


Figure 6. Langmuir isotherms applied to the Ni^{2+} solutions. Notation of samples: Ni1A 25°C pH 4, Ni1B 40°C pH 4; Ni2A 25°C pH 7; Ni2B 40°C pH 7.

increases, the adsorption line has an asymptotic behavior; that is to say, the polymer achieves saturation equilibrium in its network.

Analyzing the results obtained for the models with respect to the Ni^{2+} (Table III), it is initially observed that the correlation coefficient values are very high for both isotherms, greater than 95%. For this reason, both models are adequate. Likewise, the same tendency is noted on the graphs: at the beginning of the analysis the highest quantity of heavy metal is adsorbed, in this case Ni^{2+} , and as the experiment goes on, the metal uptake via the hydrogel becomes very slow.

The percentage of removal of cations from the aqueous solutions was calculated individually, this was found to be 53% for lead, 52.24% for nickel, and 51.09% for copper. The percentage of metal adsorption of the HPC/PAAm hydrogel is similar to chitosan/poly(vinyl alcohol) (PVA) composites,⁴¹ polymers having the same functional groups as the hydrogel of this study. However, for the chitosan/PVA system the adsorption/desorption is fit into the pseudo second order model^{41,42}; chitosan has also been fitted in that kind of model and into the Langmuir isotherms.⁴³ The effect of temperature and pH is similar to works with modified cellulose and polymethacrylic acid⁴⁴; this system had COOH groups but no amine groups, it was found that the metal removal increases with both pH and temperature, a conclusion similar to our findings.

Influence of pH

The pH of the test is important because it affects the sorption process,¹⁸ and the adsorption of heavy metals in water due to

Table II. Cu^{2+} Adsorption Parameters with the Freundlich and Langmuir Models

pH	T, °C	Model						
		Langmuir			Freundlich			
		$K/[\text{L/mol}]$	$b [\text{mol/g}]$	r^2	K	$1/n$	r^2	
Acid	25	42.02×10^4	1.13×10^{-5}	0.972	2.87×10^{-4}	2.73	0.982	
Acid	40	52.08×10^4	1.00×10^{-5}	0.983	1.63×10^{-4}	3.17	0.988	
Neutral	25	83.73×10^4	1.09×10^{-5}	0.964	8.21×10^{-5}	4.29	0.981	
Neutral	40	49.63×10^4	1.14×10^{-5}	0.974	2.07×10^{-4}	3.06	0.989	

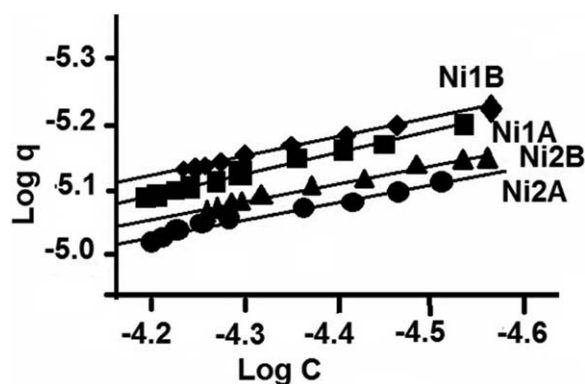


Figure 7. Freundlich isotherms applied to the Ni^{2+} solutions. The notation of samples is the same as Figure 6.

the influence on the adsorbent and dissociation and ionization of the species to be adsorbed,¹⁹ the dissociation of the functional groups of the adsorbent are also affected by the pH and this changes reaction equilibrium and kinetics of the sorption process.³⁴

In all experiments, the highest metal removal was at pH 4, suggesting that osmotic pressure and ionic strength plays a role in the adsorption process. The point of zero charge was determined to be 9.54 (see Figure S2 in the Supporting Information); however, the highest sorption values were found at 4, this is attributed to the chelating properties of the polymer,¹ as it has OH, COOH and NH groups^{13,14}; other works have observed this effect on EDTA–chitosan magnetic adsorbents composites for lead removal,¹ where the acidic pH favored the formation of EDTA–lead complexes. At alkaline pH the metals formed hydroxides and precipitated, this contributed to the observed lower adsorption of Pb at alkaline pH and prevented the experiment with the other metals at higher pH. The metal removal also increased when working with a higher temperature, this is attributed to the metallic ions having more kinetic energy and to an increase on the diffusion of the metal ions to the composite.⁴⁴ However, great care should be placed on increasing the temperature, as HPC/PAAM composites show an LCST that depends on factors such as the concentration of the polymer¹³ if this temperature is reached, there will be a phase separation of HPC.²⁰

The results obtained demonstrate that the hydrogel performs well in acidic and neutral environment. On the other hand,

these hydrogels are not selective to the metallic cation in comparison to previous works; but rather, they adsorb lead, copper, or nickel indistinctly.

SEM Characterization

Figure 8 shows the HPC/PAAM xerogel, in this figure, white lines are observed, they are attributed to the preferred orientation of the chains of the cellulose derivative.⁴⁵ Some orifices that are attributed to the water evaporation from the reaction during the drying that cross the gel's surface are also clearly observed. The micrographs were obtained from xerogel samples just after their synthesis, before testing them for removing the metal ions.

In Figure 9 is shown a sample after adsorbing lead and then drying. Lead crystals are clearly visible on the surface of the polymer. These crystals are similar in size and mainly rectangular, although there are some amorphous crystals. The crystals measured with the software of the STEM measured 2.5 microns wide, and 791 nm thick.

The accumulation of copper crystals is observed on Figure 10. Copper crystals are found dispersed in bi-dimensional and tri-dimensional shapes, without homogenous form between chains of the gel where they are deposited. In Figure 10(b) is observed a large aggregate, this feature is attributed to an agglomeration of copper on the surface of the gel. The crystals seen on the micrographs confirm that the gels removed copper in solution.

Figure 11 shows an EDX analysis of a gel containing copper, this sample was analyzed after adsorbing copper and then drying. Figure 11(a) shows the SEM micrograph of a gel, and Figure 11(b) shows the EDX mapping of the region shown in (a), copper, represented in blue turquoise, is present in the gel in a random distribution. Figure 11(c) shows the EDX spectrum of the same region, there are peaks corresponding to Cu, N, and O, these last two elements are expected to be present in a polymer containing PAAM and HPC; C is detected, but this corresponds to C of the gel and of the carbon tape. The Cu K_{α} peak is present, although it is observed as a small peak; this confirms the presence of Cu on the gel. According to the elemental analysis carried out in the sample of xerogel, 2.40 wt % of the sample is Cu^{2+} .

In Figure 12 is presented the SEM micrograph of the gel that contains the nickel cation. It is observed that copper is deposited on the network in bi-dimensional and tri-dimensional

Table III. Parameters of Ni(II) Adsorption with Freundlich and Langmuir Models

Medium	T	Model					
		Langmuir			Freundlich		
		$K/[L/mol]$	$b [mol/g]$	r^2	k	$1/n$	r^2
Acid	25	47.86×10^4	1.07×10^{-5}	0.982	1.99×10^{-4}	3.03	0.992
Acid	40	60.00×10^4	9.52×10^{-6}	0.983	1.35×10^{-4}	3.37	0.994
Neutral	25	65.76×10^4	1.15×10^{-6}	0.973	1.29×10^{-5}	3.72	0.982
Neutral	40	74.24×10^4	1.07×10^{-5}	0.968	1.25×10^{-4}	3.63	0.983

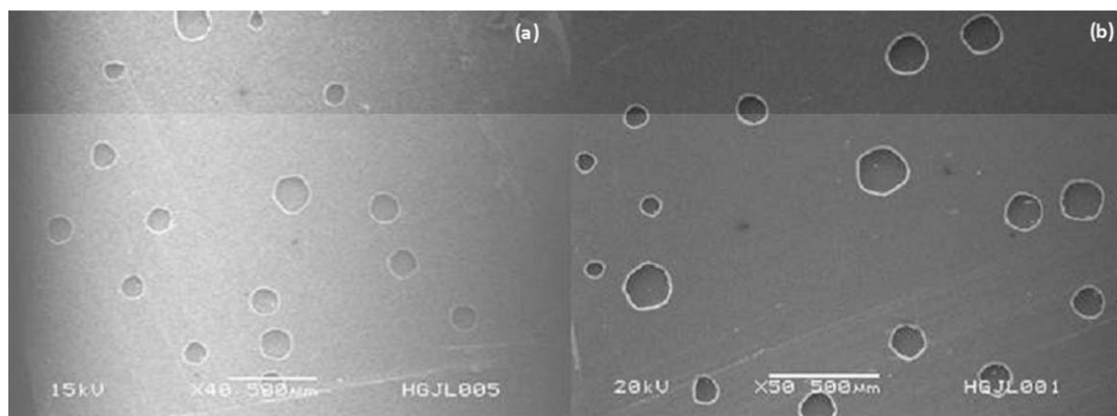


Figure 8. SEM micrographs of the xerogel's surface: (a) 40X and (b) 50X.

shapes in a dispersed manner in the gel. In Figure 12(b) a large agglomeration is observed, this is attributed to nickel on the surface of the gel, there is a difference in contrast between the agglomerate and the surface of the polymer, as in Figure 10(b).

Figure 13 shows the EDX analysis of a gel after treating water with Ni and then drying. Figure 13(a) shows the SEM micrograph of the analyzed region and Figure 13(b) shows the EDX

mapping of the same zone; this last figure shows that Ni, represented as pink dots, is present on the gel, having a random distribution. Figure 13(c) shows the EDX spectrum of the analyzed region, there are peaks of Ni, N, O, and C; as in Figure 11(c), N and O are due to the presence of PAAm and HPC on the gel, and C is due to both the polymer and the carbon tape. In Figure 13(c) can be observed a peak corresponding to Ni K_{α} , this

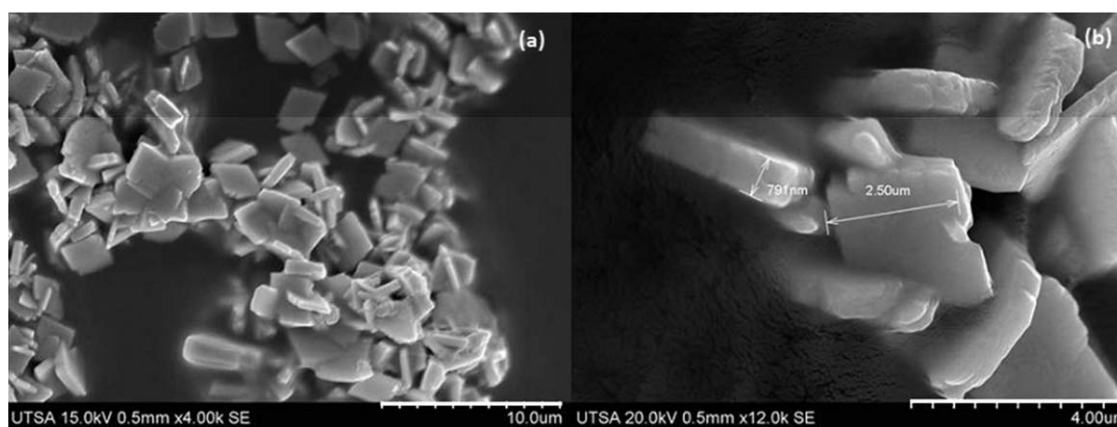


Figure 9. SEM micrographs of the gel with Pb^{2+} , (a) 4kX and (b) 12kX.

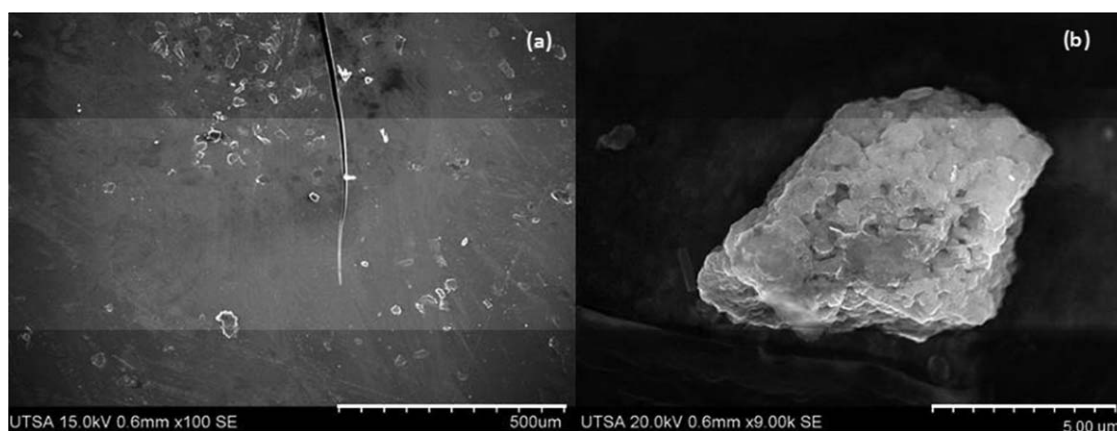


Figure 10. SEM micrographs of the gel with Cu^{2+} : (a) 100X and (b) 9kX.

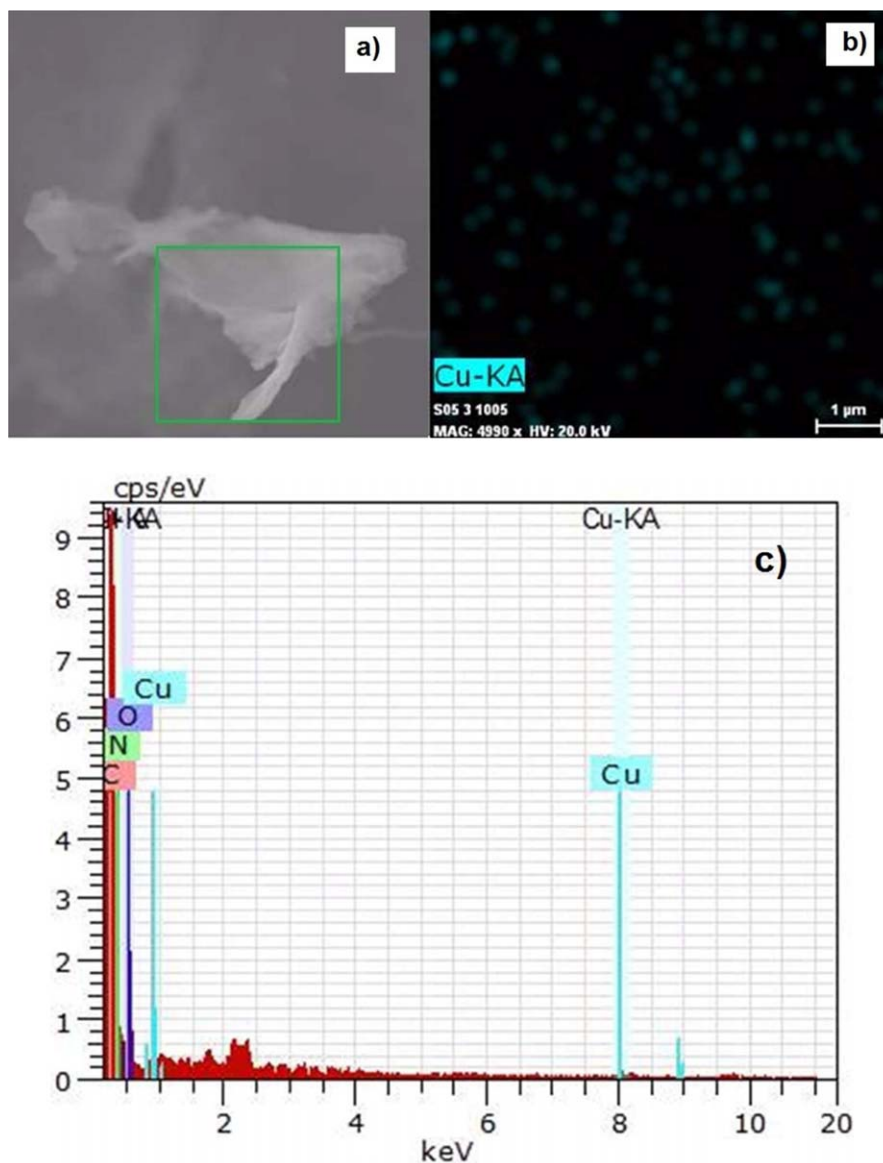


Figure 11. Analysis of the adsorption of Cu^{2+} in the gel, (a) SEM micrograph, (b) elemental mapping of the same region showing the distribution of Cu in the gel, (c) EDX spectrum of the sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

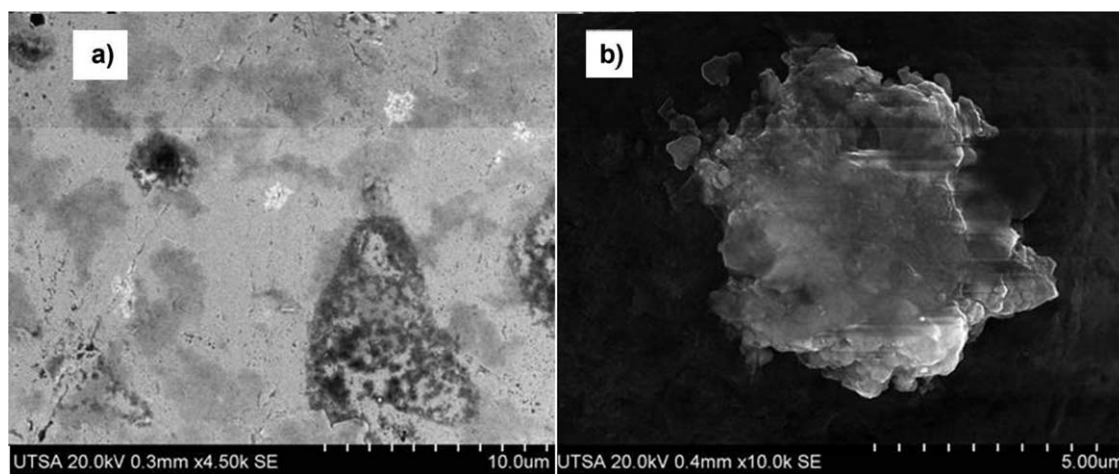


Figure 12. SEM micrographs of the gel with Ni^{2+} : (a) 4.5k and (b) 10kX.

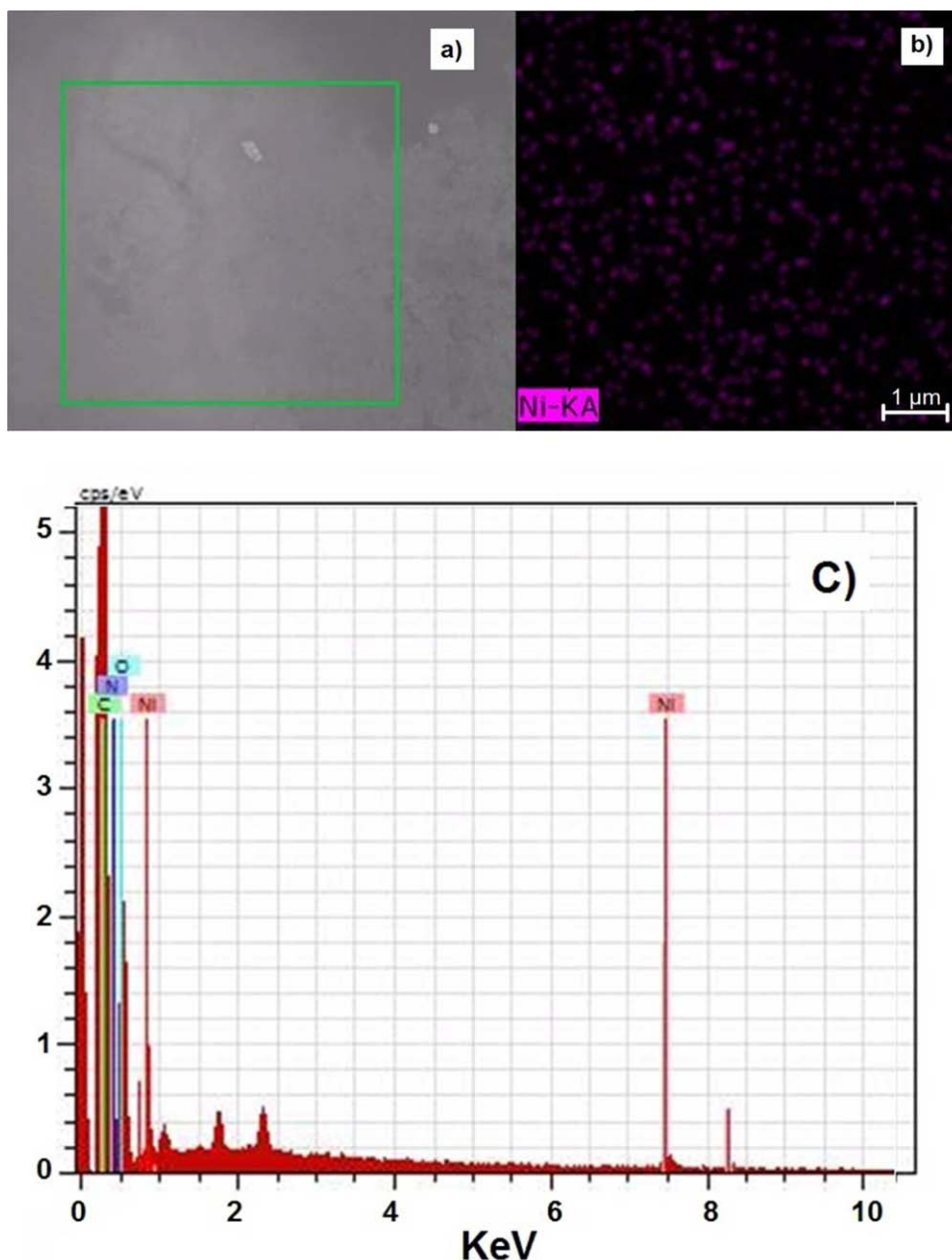


Figure 13. Analysis of the adsorption of Ni^{2+} in the gel, (a) SEM micrograph, (b) elemental mapping of the same region showing the distribution of Ni in the surface of the gel, (c) EDX spectrum of the sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

confirms the presence of Ni on the gel after treating an aqueous solution containing that metal. The quantity of nickel found in the sample was 1.17 wt %.

CONCLUSIONS

In this article HPC/PAAm gels were successfully used for removing heavy metals from water; lead, copper and nickel were the tested metals. Freundlich and Langmuir isotherms were applied for metal adsorption by the gels, and it was found that the gels had the highest adsorption at acidic pH. The micrographs showed the presence of agglomerations of metals on the surface of the gel, and the EDX of the hydrogels after treatment detected peaks corresponding to the metals; these two techniques confirmed that the

gel removed the metals from the solutions. The isotherms showed that the gels had a higher adsorption at acidic pH, as there is a higher osmotic pressure.³² Among the tested temperatures, the highest adsorption was observed at 40°C. The best conditions for metal removal among the tried were pH 4 and 40°C. These results strongly confirm that the HPC/PAAm polymer is a good option for removing metals from water and for wastewater treatment, due to the ability of the polymer of forming chelates with metallic atoms and its good water absorbing properties.

ACKNOWLEDGMENTS

J. L. Z. C. and J. C. G. C acknowledges the grant from CONACyT with number 253875 and 210322 respectively. A. C. M. A.

acknowledges the grant from DGEST (TNM) with number 452. The authors acknowledge the financial support of DGEST (TNM) No. 4519.12.13–PR. We also acknowledge the ICNAM and the Kleberg Advanced Microscopy Laboratory for allowing us the use of their facilities.

REFERENCES

1. Tan, Z.; Peng, H.; Liu, H.; Wang, L.; Chen, J.; Lu, X. *J. Appl. Polym. Sci.* **2015**, *132*, 42384.
2. Gadd, G. M.; White, C. *Trends Biotechnol.* **1993**, *11*, 353.
3. Oladipo, A. A.; Gazi, M. *J. Water Process Eng.* **2014**, DOI: 10.1016/j.jwpe.2014.12.002.
4. Wu, R.; Tian, L.; Wang, W.; Man, X. *J. Appl. Polym. Sci.* **2015**, *132*, 41830.
5. Oladipo, A. A.; Gazi, M. *J. Taiwan Inst. Chem. Eng.* **2015**, *47*, 125.
6. Xu, Z.; Bae, W.; Mulchandani, A.; Mehra, R. K.; Chen, W. *Biomacromolecules* **2002**, *3*, 462.
7. Cathell, M. D.; Szewczyk, J. C.; Bui, F. A.; Weber, C. A.; Wolever, J. D.; Kang, K.; Schauer, C. L. *Biomacromolecules* **2008**, *9*, 289.
8. Cervera, M. L.; Arnal, M. C.; Guardia, M. *Anal. Bioanal. Chem.* **2003**, *375*, 820.
9. Horzum, N.; Boyaci, E.; Eroglu, A. E.; Shawan, T.; Demir, M. M. *Biomacromolecules* **2010**, *11*, 3301.
10. Falcone, G.; Foti, C.; Gianguzza, A.; Giuffrè, O.; Napoli, A.; Pettignano, A.; Piazzese, D. *Anal. Bioanal. Chem.* **2013**, *405*, 881.
11. Vakili, M.; Rafatullah, M.; Salamatinia, B.; Abdullah, A. Z.; Ibrahim, M. H.; Tan, K. B.; Gholami, Z.; Amouzgar, P. *Carbohydr. Polym.* **2014**, *113*, 115.
12. Abreu, F. O. M. S.; Bianchini, C.; Forte, M. M. C.; Kist, T. B. L. *Carbohydr. Polym.* **2008**, *74*, 283.
13. Castro, C.; Morales, A.; Koschella, A.; Heinze, T. *Macromol. Symp.* **2010**, *296*, 429.
14. Castro, C.; Morales, A.; Kharissova, A.; Koschella, A.; Heinze, T. *Macromol. Symp.* **2010**, *294*, 58.
15. Das, R.; Panda, A. B.; Pal, S. *Cellulose* **2012**, *19*, 933.
16. Das, R.; Pal, S. *Colloids Surf. B* **2013**, *110*, 236.
17. Dubolazov, A. V.; Nurkeeva, G. A.; Mun, V. V.; Khutoryanskiy, V. V. *Biomacromolecules* **2006**, *7*, 1637.
18. Oladipo, A. A.; Gazi, M. *Toxicol. Env. Chem.* **2014**, *96*, 837.
19. Oladipo, A. A.; Gazi, M. *J. Water Process Eng.* **2014**, *2*, 43.
20. Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1980**, *13*, 69.
21. Hasani, M.; Cranston, E. D.; Westman, G.; Gray, D. G. *Soft Matter* **2008**, *4*, 2238.
22. Habibi, Y.; Chanzi, H.; Vignon, M. R. *Cellulose* **2006**, *13*, 679.
23. Araki, J.; Wada, M.; Kuga, S. *Langmuir* **2001**, *17*, 21.
24. Castro–Guerrero, C. F.; Gray, D. G. *Cellulose* **2014**, *21*, 2567.
25. Roman, M.; Gray, D. G. *Langmuir* **2005**, *21*, 5555.
26. Katime, I.; Katime, O.; Katime, D. In *Los Materiales Inteligentes de Este Milenio: los Hidrogeles Macromoleculares, Síntesis, Propiedades y Aplicaciones*; Servicio Editorial del País Vasco: Bilbao, **2004**.
27. Katime, I.; Katime, O.; Katime, D. *An. R. Soc. Esp. Quim.* **2005**, *4*, 35.
28. Zhang, X. R. B. *J. Colloid Interface Sci.* **2003**, *264*, 30.
29. Paulino, A. T.; Guilherme, M. R.; Reis, A. V.; Tambourgi, E. B.; Nozaki, J.; Muniz, E. C. *J. Hazard. Mater.* **2007**, *14*, 139.
30. Morales–Cepeda, A. B.; Martínez–Vázquez, N.; Antonio–Cruz, R. C.; Álvarez–Castillo, A.; Mendoza–Martínez, A. M. *Rev. Mex. Ing. Quim.* **2007**, *6*, 337.
31. Nesrinne, S.; Djamel, A. *Arab. J. Chem.* **2013**, DOI: 10.1016/j.arabjc.2013.11.027, to appear.
32. Aberkane–Mechebbek, L.; Larbi–Youcef, S. F.; Mahlous, M. *Mater. Sci. Forum* **2009**, *609*, 255.
33. Ulusoy, U.; Şimşek, S. *J. Hazard. Mater.* **2005**, *127*, 163.
34. Oladipo, A. A.; Gazi, M.; Saber–Samandari, S. *J. Taiwan Inst. Chem. Eng.* **2013**, *45*, 653.
35. Moulay, S.; Bensacia, N.; Garin, F.; Fechete, I.; Boos, A. C. *R. Chim.* **2014**, *17*, 849.
36. Minamisawa, H.; Arai, N.; Okutani, T. *Anal. Chim. Acta* **1999**, *378*, 279.
37. Minamisawa, H.; Arai, N.; Okutani, T. *Anal. Chim. Acta* **1999**, 2289.
38. Minamisawa, M.; Minamisawa, H.; Yoshida, H.; Takai, N. *J. Agric. Food Chem.* **2004**, *52*, 5606.
39. Chang, R. In *Química*; Seventh ed.; McGraw-Hill: Mexico City, **2003**.
40. Brunton, L. L.; Lazo, J. S.; Parker, K. L. In *The Pharmacological Bases of Therapeutics*; Goodman, L. S.; Gilman, A., Eds.; McGraw–Hill: San Diego, **2010**.
41. Wan Ngah, W. S.; Teong, L. C.; Hnafiah, M. A. K. M. *Carbohydr. Polym.* **2011**, *83*, 1446.
42. Kumar, M.; Tripathi, B. P.; Shahi, V. K. *J. Hazard. Mater.* **2009**, *172*, 1041.
43. Ren, Y.; Abbod, H. A.; He, F.; Peng, H.; Huang, K. *Chem. Eng. J.* **2013**, *226*, 300.
44. Abdel–Halim, E. S.; Al–Deyab, S. S. *Carbohydr. Polym.* **2012**, *87*, 1863.
45. Samuels, R. J. *J. Polym. Sci. Part A–2: Polym. Phys.* **1969**, *7*, 1197.