# Functionalized galactoglucomannan-based hydrogels for the removal of metal cations from aqueous solutions

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**ABSTRACT:** New types of hydrogels derived from $O$-acetyl galactoglucomannan (AcGGM) hemicellulose have been synthesized and characterized. The objective of this work was to analyze the sorption capacity (S) of three types of hydrogels containing AcGGM derivatives incorporated into the carboxylic groups of the polymer chain in the AA hydrogel, sulfonic groups in the APA hydrogel, and amide groups in the acrylamide (Aam) hydrogel. These hydrogels are capable of interacting and removing ions such as cadmium [Cd(II)], copper [Cu(II)], lead [Pb(II)], nickel [Ni(II)], and zinc [Zn(II)]. The results show that AA and Aam hydrogels had a lower sorption capacity of ions compared to the APA hydrogel, which had a high sorption capacity. The maximal sorption capacity was determined by the successive enrichment method, obtaining Pb(II) amount of 48.3 mg/g of AA hydrogel, 65.8 mg/g of APA hydrogel, and 40.8 mg/g of Aam hydrogel. Hence, Pb(II) ions are greatly retained by the three hydrogels. These results are promising for the development of new materials with potential applications in metal ion removal. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44093.

## INTRODUCTION

Water is one of the most important resources for life and is an essential substance for the well-being and survival of humanity. However, the rapid expansion of urban areas and the establishment of industrial areas where sewage is dumped have limited the availability of clean water, which is now presented as a world threat to human health. For example, water from industries, such as mining, metal coatings, and smelters, are contaminated with various toxic metals, such as lead, zinc, copper, mercury, silver, nickel, cadmium, and arsenic. Due to the development and growth of technologies and processes for the separation of metal ions from various sources, research on separation processes has become important for both industry and academia. The purposes of separation processes may be different throughout the steps of retrieval, analysis, and removal. These separation processes are based on differences in the physicochemical properties among the species of interest and the phase in which they are dispersed. Thus, it is possible to achieve separation by differences in the size, solubility, volatility, density, chemical reactivity, and so on.[1]

Technologies for the purification of water include the utilization of renewable biomaterials with performance properties comparable to petroleum-based synthetic materials. Modified polymers of renewable origins are environmentally friendly compared with those of synthetic origins and can lead to highly cost-effective technologies for enriching or separating metal ions from water systems by binding, adsorption, chelation, membrane processes and ion-exchange processes.[2–8] Hemicelluloses display excellent potential for this type of application.[9–11] Hemicelluloses constitute a complex group of heterogeneous polysaccharides and represent one of the major sources of renewable organic matter in nature.[12] The chemical modification of hemicelluloses presents an alternative for preparing materials with unique properties that can increase the value and utility of these biopolymers.[13] One area of application is superabsorbent hydrogels, which have attracted significant attention in the biomedical area and in wastewater treatment.[14–19]

Galactoglucomannan (GGM) hemicelluloses are the most abundant ones in spruce and coniferous woods, representing up to 25% of their weights.[20] As water-soluble polysaccharides, GGMs are released and accumulated in the process waters during the course of thermomechanical pulp production. $O$-acetyl GGMs (AcGGMs) from softwoods consist of a backbone with β-
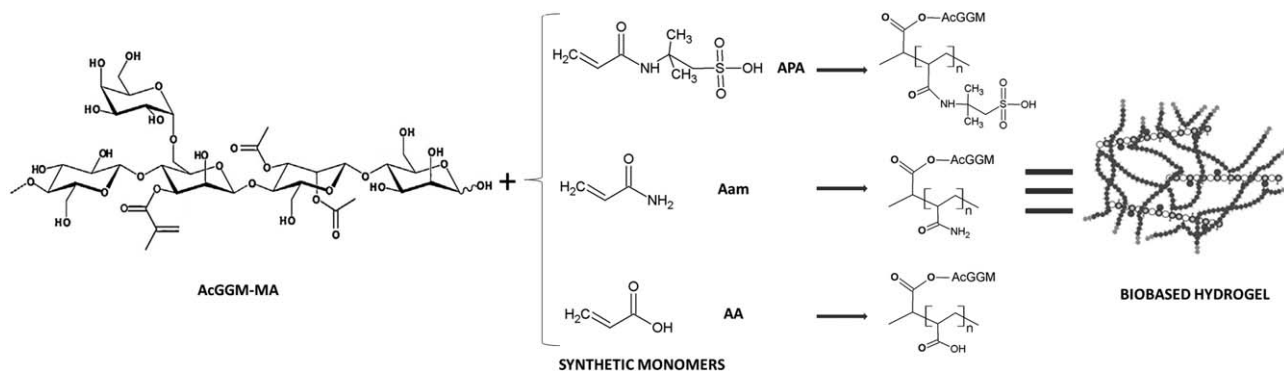
**Scheme 1.** Simplified illustration of hydrogel synthesis.

$(1\rightarrow4)$-D-mannopyranosyl and $\beta$-$(1\rightarrow4)$-D-glucopyranosyl units carrying single $\alpha$-D-galactopyranosyl residues that are $1\rightarrow6$-linked to mannose units, and acetyl substituents are attached to the C-2 or C-3 position of mannose.[21] GGMs have attracted growing interests in recent years because of their potential applications in many different areas. For example, GGMs have the potential to become high added-value products with various applications in the food, health, papermaking, textile and cosmetic industries, as well as wastewater treatment.[14,22,23]

In this article, the synthesis of novel hydrogels derived from AcGGM that are able to interact with different metal ions is reported. These hydrogels are composed of AcGGM derivatives incorporated into the carboxylic groups of the polymer chain in the AA hydrogel, sulfonic groups in the APA hydrogel, and amide groups in the acrylamide (Aam) hydrogel. These hydrogels are capable of interacting and removing ions, such as cadmium [Cd(II)], copper [Cu(II)], lead [Pb(II)], nickel [Ni(II)], and zinc [Zn(II)].

## EXPERIMENTAL

### Materials
2-Acrylamido-2-methyl-1-propanesulfonic acid, Aam, acrylic acid (AA), 97% glycidyl methacrylate (GMA) (Aldrich, Chile), ammonium persulfate (Aldrich, Chile), dimethyl sulfoxide (DMSO) (Merck, Chile), acetone (Merck, Chile), 98% 4-(dimethylamino)pyridine (DMAP) (Aldrich, Chile), ethanol (Merck, Chile), NaOH (Merck, Chile), $HNO_3$ (Merck, Chile), $Cu(NO_3)\cdot3H_2O$, $Cd(NO_3)\cdot4H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2\cdot6H_2O$, and $Zn(NO_3)_2\cdot6H_2O$ (Merck, Chile).

### Methods
**Extraction and Purification of AcGGM.** Extracted AcGGM from Norway spruce (*Picea abies*) was provided by the Finnish Forest Research Institute (Metla). The extraction conditions were studied and optimized in a previous study[24] for by researchers at the Finnish Forest Research Institute (Metla), and AcGGM was obtained as a solution with a concentration of 30 wt %. To remove impurities and to narrow down the molar mass distribution [low polydispersity (PDI)], the extract was purified. A total of 330 mL of the concentrated AcGGM solution was diluted with 670 mL water and then precipitated in 9 L of ethanol at room temperature. The obtained colourless solid was filtered and washed successively with ethanol, acetone, and methyl *tert*-butyl ether. The purified AcGGM fraction was

obtained with a weight average molar mass (Mn) of 8.9 kDa (PDI $\sim$ 1.3). The sugar unit ratio of AcGGM was determined by acid methanolysis and gas chromatography and was approximately 4.2:1:0.9 [Man:Glc (Gal + GalA)]. The degree of acetylation[25] ($DS_{AC}$) was $\sim$0.20.

**Modification of AcGGM to Produce Macrocrosslinkers.** The AcGGM macrocrosslinking reagent was synthesized using a previously described method by Dax *et al.*[19] The AcGGM (9 kDa) (2 g, 12 mmol of anhydrous sugar units) was dissolved in 20 mL of dry DMSO at 50 °C. Subsequently, DMAP (0.2 g, 1.637 mmol) and GMA (1.2 g, 8.32 mmol) were added, and the mixture was stirred under nitrogen atmosphere at 50 °C for 16 h. The reaction mixture was then diluted with 20 mL of distilled water and then precipitated in an excess of acetone. After filtration, the solid AcGGM-MA derivative was dissolved in a minimum of distilled water and transferred into a dialysis tube (cutoff of 3.5 kDa) and dialyzed against distilled water for 3 days with daily water exchange. Subsequently, the final product was freeze-dried (1.4 g, 70%).

**Preparation of AcGGM-based Hydrogels.** AcGGM-based hydrogels were prepared using the following reagents: AcGGM-MA derivative, monomers acrylamido-2-methyl-1-propanesulfonic acid (APA), Aam, acrylic acid (AA), deionized water and a redox initiator solution containing ammonium persulfate and sodium metabisulfite. A simplified illustration of the hydrogel synthesis is shown in Scheme 1. The details of the polymerization can be found in Table I, and an example synthesis is described below. AcGGM-MA (0.4 g dissolved in 15.21 mL of deionized water) was mixed with APA (3.6 g, 17.37 mmol) and 0.79 mL (0.35 mmol) of a redox initiator solution containing a mixture of ammonium persulfate and sodium metabisulfite (concentration of 100 mg/mL or 0.44 mmol/mL). The polymerization was completed in an oven at 60 °C for 1 h. The resulting hydrogels were swollen in an excess of deionized water to remove all molecules not linked to the hydrogel network. The mass yields for the synthesized hydrogels were 38, 85, and 36% for AA, APA, and Aam; respectively.

### Swelling of the Hydrogels
The degree of swelling was determined by placing 100 mg of dried AcGGM-based hydrogel in a beaker containing 80 mL of deionized water. It was then allowed to stand for 24 h at room temperature, and the hydrogel was subsequently removed from the solution for filtration. Later, the weights of the swollen and

**Table I.** Reaction Conditions for the Polymerization of AcGGM-MA with Monomers

| Monomer | AcGGM-MA (g) | n monomer (mmol) | n initiator (mmol) | V initiator (mL) | $H_2O$ (mL) |
|---|---|---|---|---|---|
| APA | 0.4 | 17.37 | 0.35 | 0.79 | 15.21 |
| Aam | 0.4 | 50.65 | 1.01 | 2.30 | 13.70 |
| AA | 0.4 | 50.65 | 1.01 | 2.30 | 13.70 |

dry hydrogels were determined, and the swelling ratio ($Q$) was calculated using the following equation:

$$Q = (m_t - m_0)/m_0 \qquad (1)$$

where $m_t$ is the weight of the hydrogel at time $t$ and $m_0$ is the initial weight of the dried sample.[26]

**Nuclear Magnetic Resonance (NMR) Spectroscopy**
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, with $D_2O$ as solvent and tetramethylsilane as an internal standard.

**FT-IR Measurements**
FT-IR spectra were obtained to examine the presence of functional groups in the synthesized hydrogels. FT-IR measurements were performed with a Nicolet Magna 550 spectrophotometer with discs of KBr and in the spectral range of 4000–400/cm.

**Scanning Electron Microscopy with X-ray Microanalysis**
Scanning electron microscopy (SEM) with X-ray microanalysis was used to analyze the superficial morphology of the hydrogels. SEM images were recorded using a JEOL microscope (JSH 6380LV model), and an Oxford Instruments INCAx-sight was used for the energy dispersive X-ray spectroscopy measurements.

**Removal of Metal Ions from Aqueous Solutions**
Batch experiments were carried out by stirring fixed masses of dry hydrogels (20 mg) in 10 mL of metal solutions (100 mg/L) at 140 rpm for 60 min at 25 °C. The initial pH values (3 and 5) of the solutions were previously adjusted with diluted $HNO_3$ or NaOH using a pH meter. At the end of the experiment, the mixture was centrifuged, and the supernatant was removed. The metal ion concentrations in the supernatant were determined by atomic absorption spectroscopy (AAS) (Unicam Solaar 5 M series). For the AAS measurements, a flame atomizer with 40% acetylene and 60% oxygen was used, and an electrode discharge lamp was used as the radiation source. The detected wavelengths were 324.7 nm for copper, 228.8 nm for cadmium, 283.3 nm for lead, 232.0 nm for nickel, and 213.9 nm for zinc.

Sorption equilibrium experiments were carried out to determine the swelling rate of the hydrogels, the optimum pH, optimum contact time, maximum sorption capacity, and selectivity. Successive batch experiments using the same hydrogel samples were performed to estimate the maximum sorption capacities of the hydrogels. The studied ions were copper, cadmium, lead, nickel, and zinc. The sorption capacity (S) of the hydrogel was determined by eq. (2), where $S$ is the amount of metal ion sorbed into the hydrogel matrix (mg metal sorbed per g of hydrogel). $C_i$ and $C_f$ (mg/L) are the concentrations of the ions in the solution before and after sorption by the hydrogels, $V$ is the volume

(L) of the aqueous phase, and $m$ is the mass of the dried hydrogel (g).

$$S = \frac{(C_i - C_f) \times V}{m} \qquad (2)$$

## RESULTS AND DISCUSSION

**Characterization of AcGGM-MA Macrocrosslinker and the Hydrogels**
The synthesis of the AcGGM-MA macrocrosslinker was performed with good yields (1.4 g, 70%), and the characterization is in agree with the results presented by Dax et al.[19] ^{1}H NMR (400 MHz, $D_2O$, ppm): δ 1.81–2.00 (s, 3H, $CH_2$=C–$CH_3$), 2.04–2.22 (m, 3H, –CO–$CH_3$), 3.09–5.56 (nonanomeric and anomeric protons of AcGGM), 5.70–5.87 (m, 1H, C=$CH_2$), 6.09–6.33 (m, 1H, C=$CH_2$); ^{13}C NMR (100 MHz, $D_2O$, ppm): 17.47 (C=$CH_2$), 20.27 (–CO–$CH_3$), 59.75–77.48 (nonanomeric AcGGM carbon signals), 98.41–103.3 (anomeric AcGGM carbon signals), 127.47 ($CH_2$=C–$CH_3$). The FT-IR spectra for AcGGM-MA were recorded at room temperature. FT-IR (KBr): 1/cm = 3408 (O—H); 2929, 2890 ($C_{sp^3}$–H); 1734 (C=O); 1639 (C=C).

The AA, Aam, and APA hydrogels are insoluble in common organic solvents; for this reason, the structural determination by NMR was impossible; therefore, the characterization was limited to infrared spectroscopy at room temperature. AA hydrogel: FT-IR (KBr): 1/cm = 3430, 3186 (O—H); 2937 ($C_{sp^3}$–H); 1734 (C=O). Aam hydrogel: FT-IR (KBr): 1/cm = 3406 (O—H); 3196 (N—H); 2935 ($C_{sp^3}$–H); 1667 (C=O). APA hydrogel: FT-IR (KBr): 1/cm = 3437 (O—H); 2930 ($C_{sp^3}$–H); 1647 (C=O); 1224 (–$SO_3H$).

By FT-IR studies, it has obtained the following information for the AcGGM-MA macrocrosslinker. The signal at 3408/cm is attributed to the O—H stretch vibration, the signals at 2929 and 2890/cm corresponding to the C–H stretch vibration of the $CH_3$ and $CH_2$ groups, the strong signal to 1734/cm corresponding to the C=O stretching vibration the carboxyl group due to the introduced methacrylate groups and the signal at 1639/cm was assigned to the C=C stretch of the unsaturated carbon atoms. Comparing with the synthesized hydrogels, it is observed that for the AA hydrogel, the signal to 1639/cm (C=C) disappears and appears a signal to 3186/cm, corresponding to the O—H stretch vibration attributed to the carboxylic acid group. For the Aam hydrogel, the absorption bands to 3196/cm (N—H) and 1667/cm (C=O) are observed, corresponding to the insertion of the amide group and for APA hydrogel the bands to 1647 cm$^{-1}$ (C=O) and 1224/cm (—$SO_3H$) are observed, attributed to the amide and sulfonic groups; respectively.
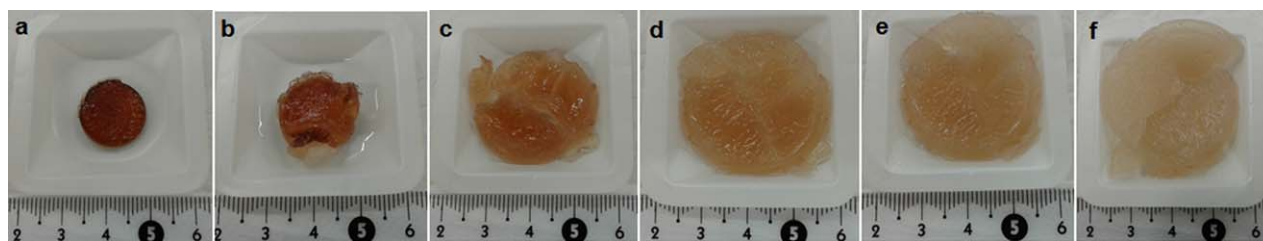
**Figure 1.** Swelling behaviour of the APA hydrogel to (a) $t = 0$ min, (b) $t = 10$ min, (c) $t = 20$ min, (d) $t = 60$ min, (e) $t = 120$ min, and (f) $t = 24$ h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## Swelling Studies

The swelling rate ($Q$) obtained for the AA hydrogel is $Q = 23$, for the APA hydrogel $Q = 35$, and for the Aam hydrogel $Q = 26$. Figure 1 shows a sequence of photographs illustrating the swelling of the hydrogels. At $t = 0$, the hydrogel was free of water after oven drying and showed a brownish colour, which likely was due to the synthetic polymer [Figure 1(a)]. At $t = 10$ min, the hydrogel had already begun to absorb water; therefore, swelling occurred [Figure 1(b)]. After 20 min ($t = 20$ min), the hydrogel was broken into smaller fragments due to greater swelling [Figure 1(c)]. At $t = 60$ and 120 min, it was observed that the brown colour began to fade [see Figure 1(d,e)]. After 24 h, the hydrogel was fully swollen ($Q = 35$), and the brown colour vanished completely [Figure 1(f)].

## Effect of pH on the Sorption of Metal Ions

To estimate the retention capacity of metal ions by the hydrogels as a function of pH, removal experiments were carried out at pH 3 and pH 5. It was not possible to work at a higher pH because at values >7, the ions can precipitate. The results obtained at different pH conditions (after 60 min of polymer metal contact) are shown in Figure 2 in which the hydrogel type, pH, and sorption capacity (S) are comparatively analyzed. The results showed that all hydrogels were capable of retaining ions in different proportions at the different pH values studied.

Hydrogels containing weak acid and amide groups (AA and Aam, respectively) exhibited less affinity to metal ions compared to the hydrogel containing strongly acidic groups (APA). The AA hydrogel containing carboxylate groups was able to form complexes with the metal ions and reach higher retention capacity compared to AAm hydrogel. The retention capacity of all the metal ions studied was higher for AA hydrogel than AAm hydrogel (see Figure 2).

Figure 2(a) shows that for all of the metal ions studied, Pb(II) was higher sorbed by the AA hydrogel at pH 5 (18.2 mg/g). The metal sorption capacity of the AA hydrogel was different depending on the nature of the metal ion, speciation, and capacity to form a complex. In general, metal ions were more retained in the AA hydrogel at pH 5 than at pH 3. This was probably because at pH 5, the AA group was less protonated than at pH 3 and can form a complex with the metal. However, in the cases of Cu(II) and Zn(II), the behaviour was the opposite. In the case of Cu(II) at pH 5, the ion was in equilibrium with its non-soluble copper species; therefore, the sorption decreased. A similar behaviour was observed in the case of Zn(II) sorption. According to the speciation of copper and zinc

in aqueous media, at pH 5 and concentration around $4 \times 10^{-4}$ mol/L (our experimental conditions), the $Cu(OH)_2$ or $Zn(OH)_2$ are formed and exist in equilibrium with Cu(II) and Zn(II), respectively.[27] The formation of these species can explain the slight decreasing of retention capacity of copper and
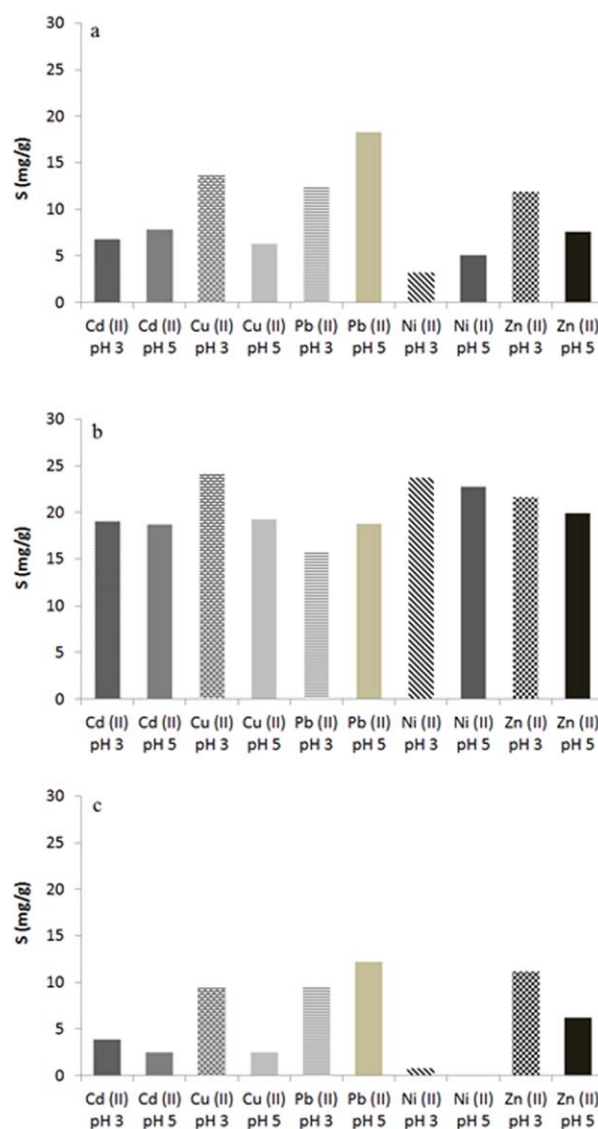


**Figure 2.** Sorption of metal ions by (a) AA hydrogel, (b) APA hydrogel, and (c) Aam hydrogel at different pH conditions and 60 min of polymer–metal contact. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

zinc at pH 5. This behaviour is observed for AA, APA, and Aam hydrogels.

Figure 2(b) shows the metal sorption capacities of the APA hydrogel. Similar sorption capacities toward all of the metal ions studied were observed. This can be explained by the nature of the sulfonic acid group, which can allow for cation exchange between the proton of this strong acid and the metal cations in solution. Using this APA hydrogel, the highest sorption capacities were obtained (between 20 and 25 mg/g) but were not selective for certain metal ions. In the case of Cd(II) and Ni(II), the retention capacity decreased slightly at pH 5 compared with pH 3. At pH 3, the retention capacities were 19.0 and 23.7 mg/g for Cd(II) and Ni(II), respectively, while at pH 5, the retention capacities were 18.7 and 22.7 mg/g for the same ions. At both pH conditions, the species are present as divalent cations. The formation of $Cd(OH)_2$ and $Ni(OH)_2$ begins at pH 10 and pH 7, respectively.[28]

At pH 3, the retention capacities were 19.0 and 23.7 mg/g for Cd(II) and Ni(II), respectively, while at pH 5, the retention capacities were 18.7 and 22.7 mg/g for the same ions. At both conditions, the species are present as divalent cations, since the formation of Cd(OH)2 and Ni(OH)2 begin at pH 10 and pH 7, respectively.[28]

Figure 2(c) shows the results for the Aam hydrogel. Similar adsorption behaviours as that observed in AA hydrogels were obtained. However, the Aam hydrogel removed a smaller amount of metal ions per gram of hydrogel. In this case, it was possible to highlight the selectivity of this hydrogel for Pb(II) at both pH conditions and for Cu(II) and Zn(II) at pH 3.

### Effect of Time on Metal Ions Removal

The aim of this research is to study the capabilities of AcGGM-based hydrogels for the treatment of wastewater. Here, sorption experiments were carried out at different times at pH 5 for the three hydrogels. These hydrogels were contacted at different times with different ions. A total of 20 mg of dry hydrogel was added to 10 mL of metal ion solution (100 mg/L), and the mixture was stirred continuously for 30, 60, and 180 min (see Figure 3).

The AA-hydrogel had a high affinity for the Pb(II) ion and was capable of absorbing this ion at very short contact times; the sorption capacity at all times studied (between 30 and 180 min) was 18 mg/g. For the other ions, the interaction was lower, and the sorption capacity varied between 7 and 8 mg/g for Cd(II) and Z(II) and was 8 mg/g for Cu(II) and 5 mg/g for Ni(II).

The APA hydrogel presented very high sorption capacities for all ions studied [Figure 3(b)]; therefore, this compound exhibited very good properties for the remediation of contaminated water ions. The sorption capacities for Cd(II), Cu(II), Pb(II), and Zn(II) ions varied between 18 and 19 mg/g, and the sorption capacity for the Ni(II) ion was 19 mg/g.

For the Aam hydrogel, the sorption capacities [see Figure 3(c)] obtained were lower compared with the results of the AA and APA hydrogels. This may be due to the lower contribution of the amide group in the coordination with the different ions,
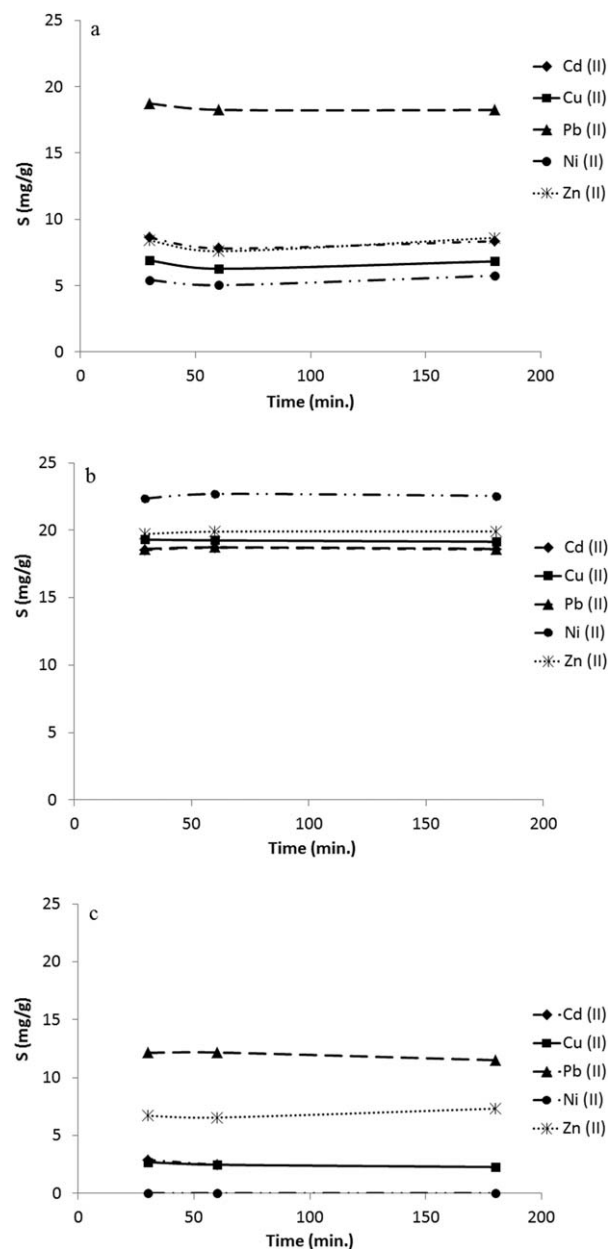


**Figure 3.** Sorption of different metal ions by (a) AA hydrogel, (b) APA hydrogel, and (c) Aam hydrogel at pH 5.

that is, steric factor had an important role in reducing the coordinating capacity. However, the sorption capacity for the Pb(II) ion was high with a value of 12 mg/g, followed by the Zn(II) ion with a value of 6.7 mg/g. The sorption capacities for the Cd(II) and Cu(II) ions were 2.5 mg/g, and the sorption capacity for the Ni(II) ion was zero.

The retention capacity obtained at 60 min of polymer–metal contact time (see Figure 2) is similar with the results obtained at 30 and 180 min of polymer–metal contact time (see Figure 3). The results showed that all hydrogels are capable of retaining ions in different proportions and at very short contact times, and this retention capacity apparently does not change in the time, which is an advantage for potential application.
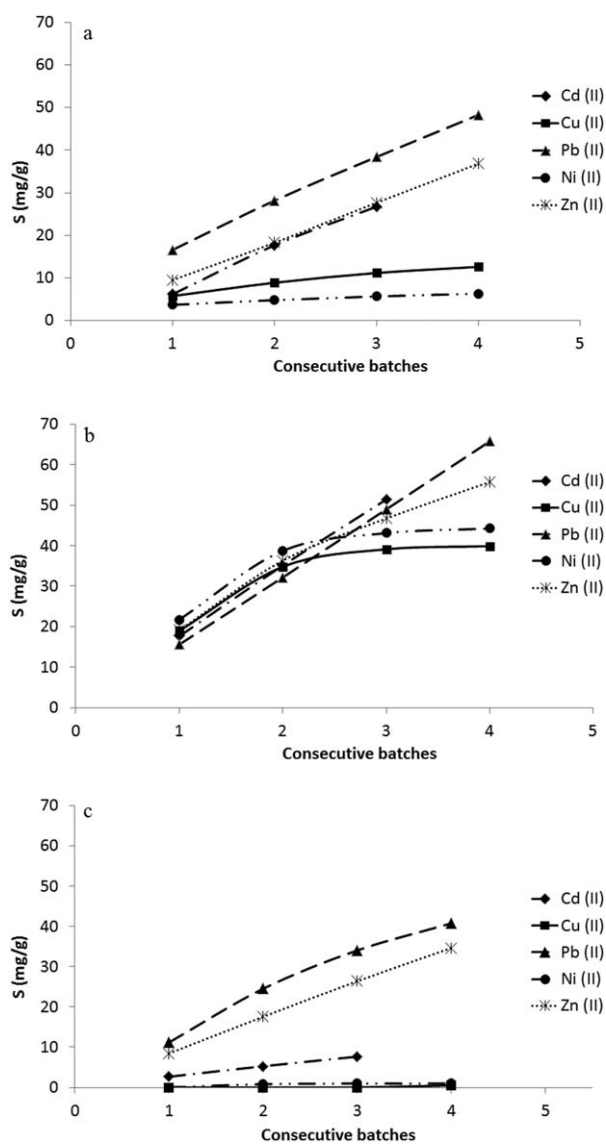
**Figure 4.** Sorption capacity of hydrogels for metal ions as a function of successive batches for (a) AA hydrogel, (b) APA hydrogel, and (c) Aam hydrogel at pH 5.

## Sorption Capacity of Hydrogels for Metal Ions in Successive Batches

To examine the maximum sorption capacity, the three hydrogels were loaded with different ions in successive batches using the conditions described in the Experimental section. The results for the three hydrogels are varied and depended of the ion under study.

The results for the AA hydrogel showed clear differences in the sorption behaviours depending on the nature of the metal ion as a function of the number of consecutive batches [see Figure 4(a)]. These results were in accordance with the previous results for the AA hydrogel. The maximum sorption capacity in the consecutives batches was the highest for Pb(II), followed by Zn(II) and Cd(II). In our experimental conditions, the AA hydrogel did not reach saturation for those metal ions. However, the sorption capacities of Cu(II) and Ni(II) were very small.

For the APA hydrogel after the first batch with Pb(II), a $S_1$ value of 15.6 mg/g was obtained; for the second batch, $S_2$ was equal to 32.2 mg/g; for the third batch, $S_3$ was 48.9 mg/g; and for the fourth batch, $S_4$ was 65.8 mg/g [Figure 4(b)]. After four successive contacts, it was observed that the APA hydrogel was not saturated and was capable of retaining a greater amount of Pb(II) ions. On the other hand, the APA hydrogel reached saturation on the third batch when it was in contact with Ni(II) and Cu(II). These behaviours indicated the maximum retention capacities of the hydrogel.

It can be concluded that the AA and APA hydrogels interacting with Cd(II), Pb(II), and Zn(II) ions did not reach saturation of the active groups and were capable of retaining greater amounts of these ions. Notably, out of these two hydrogels, APA had the highest absorption capacity for all ions studied. The maximum
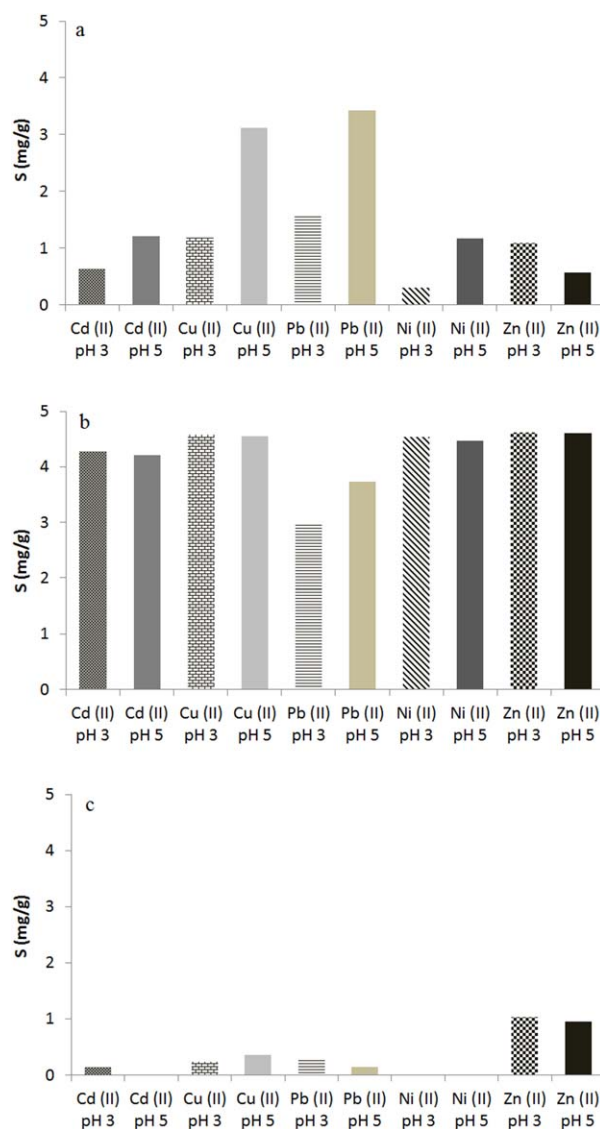


**Figure 5.** Sorption of metal ions by (a) AA hydrogel, (b) APA hydrogel, and (c) Aam hydrogel at pH 3 and pH 5 from a metallic mixture solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
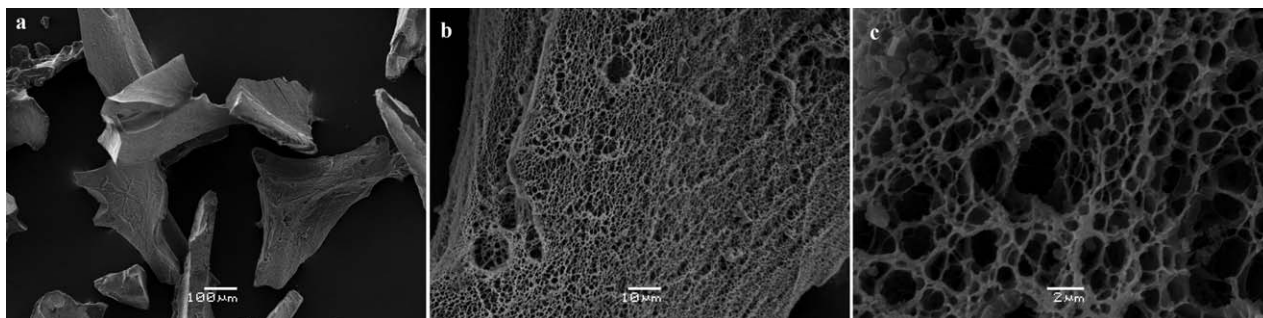
**Figure 6.** SEM images of the APA hydrogel.

sorption capacity of metal ions for the Aam hydrogel was very low and tended to saturate in the first batch for Cd(II), Cu(II), and Ni(II) [Figure 4(c)]; only Zn(II) and Pb(II) showed better results because at the fourth batch, the Aam hydrogel had the ability to absorb more of these ions.

### Selectivity Study on the Sorption of Metal Ions

Selectivity studies were performed with three types of hydrogels using a mixture solution of five metal ions to analyze the recoverability of these ions from aqueous solutions. Mixtures were prepared with Cd(II), Cu(II), Pb(II), Ni(II), and Zn(II) ions at pH 3 and pH 5, and these were contacted separately with different hydrogels. The results are shown in Figure 5.

The AA hydrogel [see Figure 5(a)] had a certain tendency to bind Cu, Pb, and Zn ions at a pH 3 and generally exhibited a sorption capacity of 1 mg/g for these ions. At pH 5, a greater selectivity for the Cu and Pb ions was observed, capturing these ions with sorption capacities of 3 mg/g.

Figure 5(b) presents the results obtained for the APA hydrogel, where selectivity was not shown for any specific ion. This hydrogel was capable of capturing all ions present in the solution at high retention rates. The sorption capacities varied between 3.0 and 4.6 mg/g with the highest value found for the Zn ion and the lowest value found for the Pb ion.

For the Aam hydrogel, a relatively high affinity was observed for Zn ions, having a sorption capacity of 1 mg/g; however, there was little or no interaction with the other ions [Figure 5(c)].

### Analyses of the Morphology of the Hydrogels

SEM was used to examine the morphology of the completely swollen and the subsequently freeze-dried APA hydrogel. Figure 6 shows the micrographs of the microporous surface of this hydrogel. Figure 6(a) shows an overview of the sample and a highly porous structure was observed at a medium magnification [see Figure 6(b)]. APA hydrogel exhibited a microporous structure with high pore density under high magnification [see Figure 6(c)].

### CONCLUSIONS

AcGGM hemicelluloses were modified by a reaction with GMA to produce the macromonomer AcGGM-MA. Subsequent reaction of AcGGM-MA with different monomers, that is, acrylic acid, 2-acrylamide-2-methyl-1-propane sulfonic acid, and Aam,

produced three different hydrogels with different swelling capabilities and interactions with metal ions, such as Cd(II), Cu(II), Pb(II), Ni(II), and Zn(II).

The results obtained from the studies of the effect of time on the sorption capacity showed that all hydrogels were capable of retaining ions in different proportions and at very short contact times. At a contact time of 30 min, the hydrogels were able to remove large amounts of ions, and the sorption capabilities were similar at contact times between 30 and 180 min.

Maximum sorption capacities were analyzed for the three hydrogels, showing that these hydrogels were capable of adsorbing ions in different proportions, with the APA-hydrogel presenting a higher sorption capacity for the different ions. The maximum sorption capacity for all three hydrogels was the highest for the Pb(II) ion, retaining 48.3, 65.8, and 40.8 mg of Pb(II)/g of AA hydrogel, APA hydrogel, and Aam hydrogel, respectively.

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