Superabsorbent Hydrogel Based on Modified Polysaccharide for Removal of Pb²⁺ and Cu²⁺ from Water with Excellent Performance

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ABSTRACT: This contribution describes the absorption percentage of Pb^{2+} and Cu^{2+} from water by a superabsorbent hydrogel matrix (SH) made from an anionic polysaccharide copolymerized with acrylic acid (AAc) and acrylamide (AAm). Metal-absorption tests, upon sequential pH variation, indicated that the SH has pH-sensitivity for the absorption of both metals from solution, attributed to the functional ionic groups (—COOH) present in the AAc and arabic gum (AG) segments. At the pH 5.0, the SH exhibited good absorption capacity: 73.10% for Pb^{2+}, 81.99% for Cu^{2+} in water and 63.64% for Pb^{2+}, and 76.67% for Cu^{2+} in saline water with 0.1 mol kg^{-1} ionic strength. A replicated 2^2 full factorial design with a central point was built to evaluate the maximum absorption capacity of

the metals into the SH. It was found that both the interaction and main effects of the pH and the initial concentration of metal solution on absorption percentage of the metals were statistically significant. Surface response plots indicated that the absorption capacity of both metals into the SH may be appreciably improved by using the solutions with lower initial concentration of metal and with higher pH values. Metal-absorption results demonstrated that the SH is a convenient material for absorption of Pb^{2+} and Cu^{2+} from pure aqueous and saline aqueous environments. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2903–2909, 2007

Key words: hydrogels; metal-polymer complexes; polysaccharides; swelling; water-soluble polymers

INTRODUCTION

The increasing number of heavy metals discarded into environment has been become a serious factor for contamination of water, soil, flow river, and wastewater.[1] The heavy metals have been discarded in a number of different ways such as coal combustion, sewage wastewaters, automotive emissions, battery industry, mining activities, tanneries, alloy industries, and utilization of fossil fuels.[2] The heavy metals Pb^{2+} and Cu^{2+} can cause serious environmental impacts because their toxicity to many life forms.[3] They may cause mental disturbance, retardation, and semipermanent brain damage, and are clas-

sified as persistent environmental toxic substances.[2,4] Currently, adsorption processes have been used as effective and clean technique for removal of heavy metals and dyes from the wastewaters polluted by industries.[5,6] Affordable materials that exhibit either good absorption or adsorption performance have been increasingly developed in an attempt to minimize environmental impact.[7–11] For example, few fibers have been used for adsorption and diffusion of methylene blue,[12] hydrogel beads having phosphinic acid groups for absorption of lanthanide ions,[13] and bagasse fly ash, a waste byproduct of the sugar industry, for removal and recovery of Pb^{2+} and Cr^{3+} ions from wastewater[14]; Duolite C-433 for removal of Hg^{2+}, Pb^{2+}, and Cd^{2+} [15]; Bagasse Fly Ash for removal of Zn^{2+} [16]; and silkworm chrysalides, chitin, and chitosan for removal of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Al^{3+} from wastewater.[4] Superabsorbent polysaccharide-based hydrogels have been used successfully for removal and separation of methylene blue and orange II from aqueous solutions.[5] Because of the superabsorbent ionic hydrogel (SH) based on polysaccharides to be considered as a biodegradable and affordable absorbent,[5,17] the searching of such a material has been inclined towards the wastewater treatment

applications. SH are formed of three-dimensional polymer networks of flexible chains that carry functional ionic groups.[18] When are immersed in an aqueous environment, superabsorbent ionic polymer networks are not dissolved and have sufficient ability to absorb up to 1000 g of water per 1 g of dry polymer, resulting in considerable changes on its three-dimensional polymer structure.[18] Upon contact with water, the functional ionic groups may be changed into negatively charged groups,[18–20] enabling gel to interact with cationic ions, such as the Pb^{2+} and the Cu^{2+}. With the purpose of finding a potentially biodegradable and affordable material for the removal of heavy metals from wastewaters, we have tested the ability of arabic gum-based SH to remove both the Pb^{2+} and the Cu^{2+} from water at different pH-values.

EXPERIMENTAL

Materials

The start materials were used as follows: arabic gum (Company-Sudan), glycidyl methacrylate (GMA, Acros Organics), sodium persulfate (Sigma), dimethyl sulfoxide (DMSO, Labsynt-Brazil), N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma). Both the Pb^{2+} and the Cu^{2+} nitrate solutions (Merck) and all regents used were prepared without further purification.

Chemically modified arabic gum (MAG)

The chemically modified AG with GMA was obtained by using a similar procedure reported in the literature.[21] An appropriate mixture consisting of aqueous-DMSO was prepared to dissolve both the AG and the GMA. The aqueous-DMSO solution to dissolve 1 g AG was prepared by mixing 6 mL distilled-deionized water and 4 mL DMSO. The AG was added into the DMSO–water mixture under constant stirring. Then, 0.13 mmol TEMED (as the accelerator) and 0.1 g GMA were added.

Synthesis of superabsorbent polysaccharide-based hydrogels

A known concentration of potassium hydroxide (KOH) was dissolved in 10 mL distilled-deionized water. Because of the high heat generated by KOH–acrylic acid (AAc) neutralization-reaction, the solution was transferred to a water-thermobath, with temperature controlled to 5°C. With slowly stirring the solution, the AAc was slowly dropped to form a neutral solution. After, known concentrations of acrylamide (AAm), MAG, and 84 μmol sodium persulfate (as the initiator) were introduced. Then the prepared solution was transferred to a cylindrical glass tube and heated to 50°C. The SH was obtained by copolymerization of MAG with AAc and AAm (MAG-*co*-AAc-

co-AAm). The gelation was observed within 20–25 min. The formed hydrogels were taken out from tub and immersed in fresh distilled-deionized water for 24 h. Next, the swollen hydrogels were dried under reduced pressure (0.2 Pa) at 50°C for 24 h. The [1.5/0.5/0.5] label, used to describe hydrogel formulation, indicate composition in grams per 10 mL^{-1} of MAG, AAc, and AAm, respectively.

Equilibrium swelling ratio of the SH

The swelling ratio (SR) of SH swollen to equilibrium was estimated from the following equation:

$$SR = \frac{(W_s - W_d)}{W_d} \quad (1)$$

where W_s is the weight of the hydrogel swollen at a specified time and W_d is the weight of the dried hydrogel.

Scanning electron microscopy for hydrogel morphology assay

The SH morphology assays were obtained by using Shimadzu, model SS 550 scanning electron microscopy (SEM) operating at 12 keV. SEM images of SH surface were obtained in swollen state. Hydrogel swollen to equilibrium was first frozen in liquid nitrogen and lyophilized by freeze-drier (Martin Christ, Freeze Dryer, Alpha 1-2/LD) for 24 h. It was assumed that the original characteristics of hydrogel swollen to equilibrium were preserved after freeze drying.

Metal absorption studies

The hydrogel performance for removal of metals was evaluated by square wave voltammetry. The voltammograms were taken out from an Autolab Pgstat30 potentiostat/galvanostat coupled to a thermobath. Solutions of 100 μg mL^{-1} $Pb(NO_3)_2$ and 100 μg mL^{-1} $Ni(NO_3)_2 \cdot 6H_2O$ were used as storage solutions. A range of dry gel particle size from 300 to 425 μm was used as the absorbent. The solutions used in the metal absorption experiments were prepared by addition of 50 mg dried SH particles to either the 100 mL Pb^{2+} or the 100 mL Cu^{2+} storage solutions. The percentage of metal-absorption A (%) in gel was determined by following equation:

$$A(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the initial and the final concentrations of metal solutions (in mg mL^{-1}) respectively. A (%) was determined by the difference between the initial and the final concentrations of metal solutions.

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TABLE I
Factors and Levels Selected to Build the Replicated 2^2 Full Factorial Design with a Central Point for Maximum Absorption Capacity of Pb²⁺ and Cu²⁺ into the SH

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Factor	Unit	Type	(−1.33)	(−1)	(0)	(+1)	(+1.33)
Initial concentration of metal	g mL⁻¹	Numerical	50	100	250	400	450
pH		Numerical	1.5	2	3.5	5	5.5

Surface response methodology for maximum metal absorption

A replicated 2^2 full factorial design, with following codifications −1, −1.33, 0, +1, +1.33, was build to evaluate the maximum absorption capacity of metal into the SH. Both the initial concentration of metal and the pH were selected as the independent variables. The percentage of the absorbed metal was used as response (or dependent variable). The limits of inferior and superior levels were selected as follows: 100 mg L⁻¹ and 400 mg L⁻¹ for initial concentration of metal C_i, 2 and 5 for pH. The data were evaluated by means of Statistica 6.0® software. Table I shows the two-variable and the five-level combinations of data fed into computer.

RESULTS AND DISCUSSIONS

Absorbent characteristics and factors affecting metal absorption

A superabsorbent polymer matrix composed of modified ionic arabic gum copolymerized with AAc and AAm was used as the SH in experiments of metals absorption. The selection of such a SH was made considering its chemical structure, in which the polymer networks are supported on the AG chains. By making the assumption that the polysaccharide is the key constituent, it could be degraded by microorganisms that live in environment in which SH has been applied, and polymer networks of remaining SH could be undone, thus minimizing environmental impact. The chemical characterization of hydrogel based on MAG has been demonstrated in previous works.[5,21] It was found that the monomers AAm and AAc react with the chemical bonds of C=C, from the GMA, coupled to the polymeric structures of MAG. Here, a schema of such a SH structure was represented in Figure 1.

The [1.5/0.5/0.5] SH synthesized here showed high SR and was assigned as a superabsorbent material. This SH swelled up to 325 ± 7 times with respect to its dry weight. Data of SR were calculated as the average over the three SR determinations. Pictures of this nonpowered SH taken after (a) the synthesis and (b) 24 h of water immersion are illustrated in Figure 2. It has highly porous structure, displayed in Figure 3, which was correlated to its high water-absorption efficiency. When the SH is immerged in an aqueous medium, the water molecules easily diffuse into hydrogel through these large pores and interact with functional ionic groups in polymer networks. Upon contact with water, the fixed carboxylic groups (COOH) present in AAc and in AG segments[22] are converted to negatively fixed-charged groups (COO⁻) that cause anion–anion electrostatic repulsion forces, expanding the gel networks.

The choice of the [1.5/0.5/0.5] SH was carried out on basis of its high water-absorption capacity, because it is an essential parameter for further studies of metal removing from solution. The large amount of water in a highly porous structure allows solute diffusion through hydrogel.[23] In metal removing by hydrogels, it is interesting to consider that the absorption of the metals depends on both the amount of available water and the chemical nature of polymer that form the hydrogel, which allow to interact with metal ions. When a superabsorbent anionic gel is immersed in a metal-rich aqueous solution, water molecules penetrate primarily into gel (because of its hydrophilic networks) and dissociate COOH groups to COO⁻ groups,[21] resulting in a dimensional increase
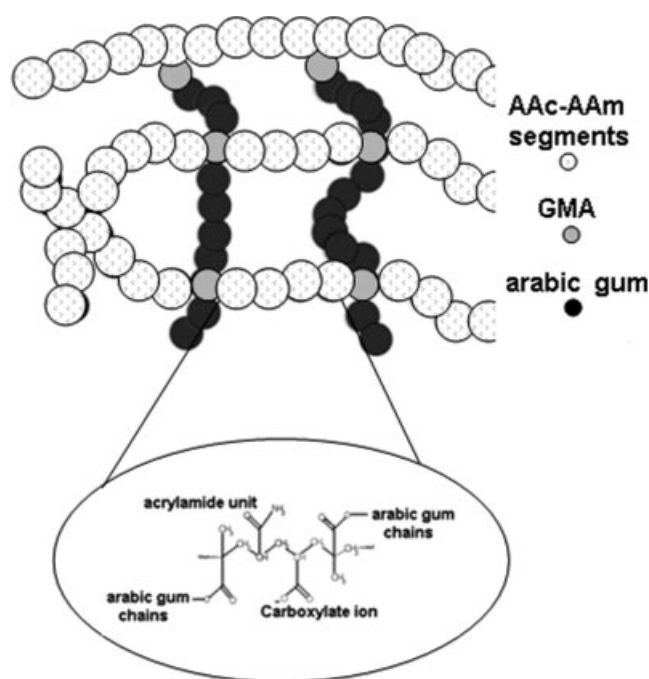

Figure 1 A drawing of the SH networks composed of arabic gum modified with GMA and copolymerized with AAc and AAm.
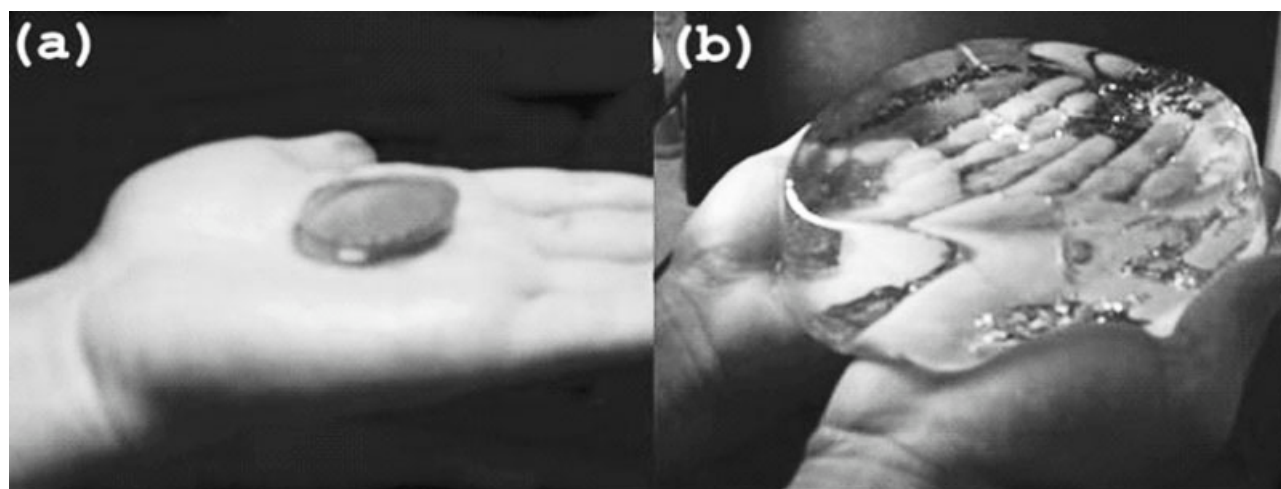
Figure 2 Pictures of nonpowered [1.5/0.5/0.5] SH, composed of MAG, AAc, and AAm, taken after (a) the synthesis and (b) 24 h of water immersion.

of polymer system. After the initial hydration of the polymer networks, concentration gradient of metal ions is formed at gel–water interface, and the diffusion of metal ions into gel is started. Over the additional hydration, there is a movement of water molecules inward that carries metal ions into gel matrix and thereby increases absorption of the metals. At the hydrogel interior, metal ions may or may not be trapped by the polymer networks, depending on factors as chemical nature and ionic size of metal ions.

Effect of pH on the absorption of Pb^{2+} and Cu^{2+} into the SH

The SH, used in this work, is an ionic polymer matrix and its water absorption process is essentially affected by changing the pH-values. Figure 4 shows
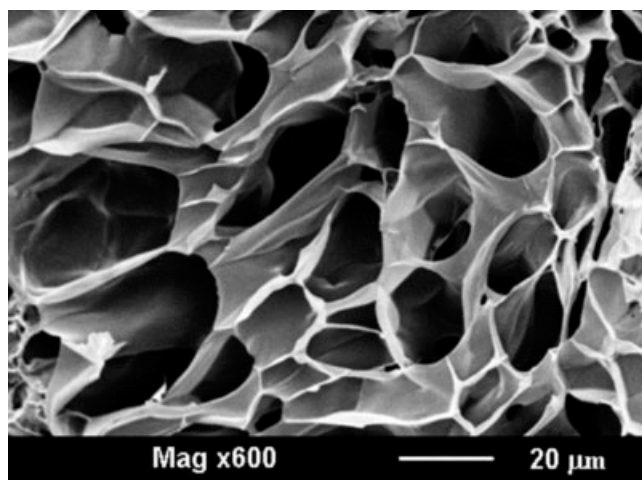
the effect of sequential pH variation on the Pb^{2+} and the Cu^{2+} absorptions into the SH. The SH exhibited sigmoidal-like curves by plotting the metal adsorption percentage versus pH, because it has pH-sensitivity for the absorption of both metal ions from solution. This effect was attributed to the ionization of the carboxylic groups present in the AAc, and the AG segments at pH-values higher than pK_a-value of SH ($\sim$ 4.0).[5] It is important to report that above the pK_a-value, the most of the carboxylic groups are in ionized form. At the lower pH-values, it was observed that the absorption of both metals decreased appreciably. With decreasing pH, the carboxylate anions present in polymer networks are converted to protanated form, which hardly enables SH to inter-

Figure 3 Scanning electron microscopy (SEM) of the (1.5/0.5/0.5) SH composed of MAG, AAc, and AAm. Micrograph of the SH surface freeze dried after equilibrium swelling.
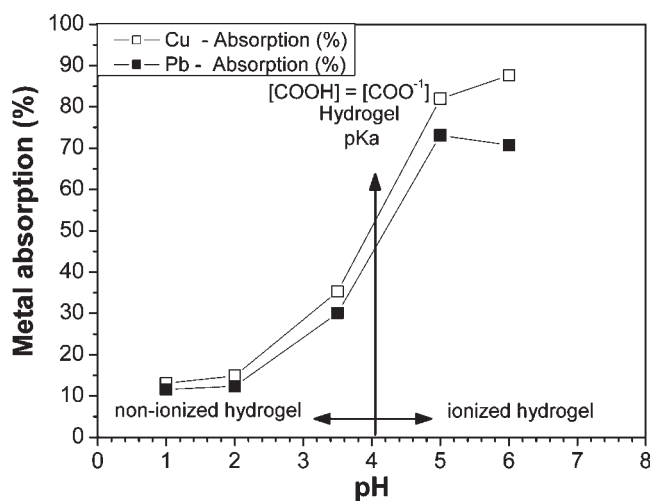

Figure 4 pH-dependent absorption percentages of Pb^{2+} and Cu^{2+} into the SH. Experimental parameters: 50 mg dried hydrogel, particles size between 300 and 425 μm, volume of 100 mL solution, and initial concentration of 100 mg L^{-1} metal.
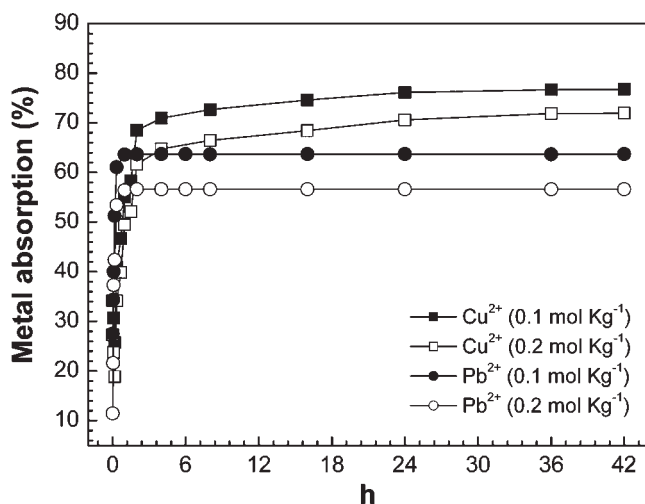
Figure 5 Time-dependent absorption percentages of Pb^{2+} and Cu^{2+} into the SH from metal solutions with different strength ionic. Experimental parameters: 50 mg dried hydrogel, particles size between 300 and 425 μm, initial concentration of 100 mg L^{-1} metal, volume of 100 mL solution, and pH 5.

act with cationic ions. Conversely, at the higher pH-values, it was verified that the absorption of the metals prominently increased, because at the basic media the formed carboxilate anions throughout the polymer structure of SH allow it to form ionic bonds with metal ions.

Higher metal-absorption percentages into the SH were 73.10% for Pb^{2+} and 81.99% for Cu^{2+} at the pH 5.0. The lower Pb^{2+} absorption was assigned to following factors: (a) larger Pb^{2+} ionic size which hinders its diffusion to inside the polymer networks and (b) lower electroposivity of the Pb atom (with respect to Cu atom) that leads to a weaker ionic bond between the cation and the anion carboxylate.

Effect of strength ionic

Figure 5 shows the percentages of the time-dependent absorption of Pb^{2+} and Cu^{2+} into the SH for metal solutions with strength ionic adjusted upon addition of sodium chloride. The performance of removing for both metal ions into the SH decreases when the ionic strength of the surrounding liquid increases, attributed to the larger counterion concentration that neutralizes the negatively fixed-charged groups and thereby disable SH to interact with the cationic ions.

In spite of the increased ionic strength of solution lead to a metal-absorption decreasing, SH had good capacity for metal absorption from saline water, 63.64% for Pb^{2+} and 76.67% for Cu^{2+} at 0.1 mol L^{-1} ionic strength, enabling it as a potentially viable absorbent for absorption of Pb^{2+} and Cu^2 from saline environments.

Statistical treatment

The replicated 2^2 full factorial design with a central point consisting of 20 runs with included a center point and a replication was built from data summarized in Table II. The analyses of variance (ANOVA model) for absorption data of Pb^{2+} and Cu^{2+} are described in Tables III and IV, respectively. It was found that the P-values for a confidence interval of 95% are lesser than 0.05 for both metals. This means that the interaction and the main effects of both the pH and the C_i on absorption of the metals were statistically significant. The lower P-values found for the lack of fit are indicative of the adjustment quadratic model. This may be verified through square of the multiple regression coefficients R^2, which was 0.9856 for the Pb^{2+} and 0.9916 for the Cu^{2+}. By considering the number of freedom degrees, corrections for the R^2 were made to R^2 adjusted (or R^2_{adi}), thus resulting in 0.9790 for Pb^{2+} and 0.9877 for Cu^{2+}. The ANOVA data indicated that the quadratic polynomial model significantly explains experimental metal-absorption data. The equations generated from the quadratic model for metal absorptions are described as follows:

$$Pb^{2+}(\%) = 6.7864 - 3.5173pH$$
$$+ 3.7808pH^2 + 0.0274C_i + 12 \times 10^{-5}C_i^2$$
$$- 4.09 \times 10^{-2}pH \times C_i - 0.1065 \quad (3)$$

TABLE II
Metal-Absorption Percentages into the SH Obtained for the Replicated 2^2 Full Factorial Design with a Central Point

| Runs | Factors | | Responses | |
	pH	C_i (mg L^{-1})	Pb^{2+} absorption (%)	Cu^{2+} absorption (%)
01	2.0 (−1)	100 (−1)	12.35	15.15
02	2.0 (−1)	400 (+1)	9.32	13.25
03	5.0 (+1)	100 (−1)	73.51	85.03
04	5.0 (+1)	400 (+1)	34.08	37.28
05	1.5 (−1.33)	250 (0)	10.85	12.32
06	5.5 (+1.33)	250 (0)	60.43	69.03
07	3.5 (0)	50 (−1.33)	32.80	36.84
08	3.5 (0)	450 (+1.33)	17.18	12.35
09 (C)	3.5 (0)	250 (0)	20.65	22.46
10 (C)	3.5 (0)	250 (0)	20.56	22.65
11	2.0 (−1)	100 (−1)	12.42	15.23
12	2.0 (−1)	400 (+1)	9.92	13.23
13	5.0 (+1)	100 (−1)	73.64	85.36
14	5.0 (+1)	400 (+1)	33.87	37.05
15	1.5 (−1.33)	250 (0)	10.52	11.92
16	5.5 (+1.33)	250 (0)	59.52	69.85
17	3.5 (0)	50 (−1.33)	32.15	37.76
18	3.5 (0)	450 (+1.33)	16.45	12.32
19 (C)	3.5 (0)	250 (0)	20.15	22.89
20 (C)	3.5 (0)	250 (0)	20.96	22.23

TABLE III
ANOVA Data of Pb^{2+} for the Replicated 2^2 Full Factorial Design with a Central Point

Source	Sum of square (SS)	Degree of freedom	Mean squares	F value	P value
pH	6,056.76	1	6,056.76	36,475.53	<0.0001
pH^2	603.71	1	603.71	3,635.72	0.00027
C_i	1,058.80	1	1,058.80	6,376.42	0.00016
C_i^2	57.98	1	57.98	349.19	0.00285
pH by C_i	678.40	1	678.40	4,085.57	0.00024
Lack of fit	121.70	11	121.70	66.63	0.01488
Pure error	0.33	2	11.06		
Total (SS)	1,691.13	19			

TABLE IV
ANOVA Data of Cu^{2+} for the Replicated 2^2 Full Factorial Design with a Central Point

Source	Sum of square (SS)	Degree of freedom	Mean squares	F value	P value
pH	7,682.13	1	7,682.13	65,144.23	<0.0001
pH^2	1,046.82	1	1,046.82	8,876.98	0.00011
C_i	1,835.30	1	1,835.30	15,563.24	0.00001
C_i^2	49.34	1	49.34	418.26	0.00230
pH by C_i	1,061.68	1	1,061.68	9,003.04	0.00110
Lack of fit	98.25	11	98.25	75.74	0.01310
Pure error	0.24	2	8.93		
Total (SS)	1,691.13	19			

$$Cu^{2+}(\%) = 12.4776 - 7.8488\text{pH}$$
$$+ 5.0971\text{pH}^2 + 0.0504C_i + 11.06 \times 10^{-4}C_i^2$$
$$- 5.12 \times 10^{-2}\text{pH} \times C_i - 0.074 \quad (4)$$

Figure 6 shows generated response surface plots on (a) Pb^{2+} and (b) Cu^{2+} absorption percentages. The circular open points indicate experimental metal-absorption data. The capacity absorption of both metals into the SH may be appreciably improved by using the solutions with lower initial concentration of metal and with increasing pH-values. This means that excellent-performance for metal absorption may be achieved when the number of negatively fixed-charged groups
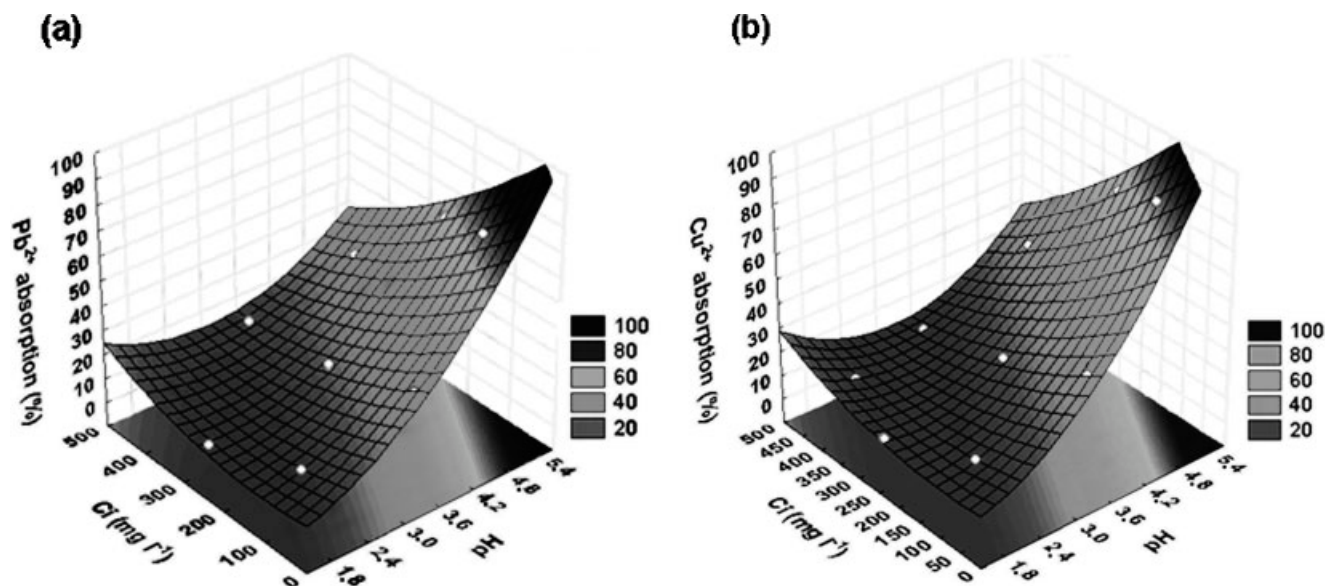

Figure 6 Response surface plots on (a) Pb^{2+} and (b) Cu^{2+} absorption percentages. Experimental parameters: 50 mg dried hydrogel and particles size between 300 and 425 µm and volume of 100 mL solution.

present in gel is equivalent to the number of cations in surrounding liquid. Thus, the decrease in metal-absorption percentage in metal-richer solutions, in response surface plots, was assigned to the remaining number of cations in surrounding liquid that can not be absorbed and retained by the metal-sutured SH. In this logic, the absorption capacity of metal is mainly governed by the number of negatively fixed-charged groups in polymer networks that are highly dependent on pH of solution.

CONCLUSIONS

The SH, composed of MAG, AAc, and AAm, exhibited high equilibrium swelling ratio and porous structure, and was assigned as a water-superabsorbent material. Metal-absorption tests, upon sequential pH variation, indicated that the SH has pH-sensitivity for the absorption of both the Pb^{2+} and the Cu^{2+} ions from solution, attributed to the functional ionic groups (—COOH) present in AAc and in AG segments. At pH 5.0, the SH exhibited good capacity for metal absorption: 73.10% for Pb^{2+}, 81.99% for Cu^{2+} in water and 63.64% for Pb^{2+}, 76.67% for Cu^{2+} in saline water with 0.1 mol kg^{-1} ionic strength. It may be considered that at the pH-values above at the pK_a-value of SH, the most of the carboxylic groups are in form carboxylate anions (COO^{-}), enabling SH to form ionic bonds with cations. The interaction and main effects of both the pH and the C_i on absorption percentage of the metals were statistically significant. Surface response plots indicated that the maximum-performance removal for both metals may be achieved in solutions with lower initial concentration of metal and with higher pH-values. Metal-absorption results demonstrated that the SH is a convenient material for absorption of Pb^{2+} and Cu^{2+} from both aqueous and saline aqueous environments. Because of its anionic character, the SH is also able to absorb other metal ions from water.

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