Artículo de Investigación. Revista Ciencia e Ingeniería. Vol. 39, No. 1 pp. 57-70, diciembre-marzo, 2018.
ISSN 1316-7081. ISSN. Elect. 2244-8780 Universidad de Los Andes (ULA)

Applications of hydrogels in the adsorption of metallic ions

Aplicación de hidrogeles in la adsorción de iones metálicos

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Abstract

Industrial activities generate effluents that in many occasions are discarded to nature without adequate treatment so that, in case of having polluting species, they can reach natural bodies of water (such as lakes, rivers or seas), affecting the ecological balance. Among the polluting species, heavy metals are found, which are mostly highly toxic even at low concentrations because they can accumulate in living beings, causing various disorders and diseases. The hydrogels are crosslinked polymeric materials containing functional groups (carboxylic acids, amines, hydroxyls and sulfonic acids, etc.) can be used as complexing agents for the removal of metal ions from aqueous solutions, sometimes selectively and with the possibility of recovering them, presenting advantages over other techniques for eliminating them. The elimination of metals is a possible solution to the problem of pollution that affects water quality. In this review, different aspects on the application of hydrogels as adsorbent materials of metallic ions are treated

Keywords: Hydrogels, metallic ions, adsorption, desorption.

Resumen

Las actividades industriales generan efluentes que en muchas ocasiones son desechados a la naturaleza sin tratamiento adecuado por lo que, en caso de tener especies contaminantes, éstas pueden llegar hasta cuerpos de aguas naturales (tales como lagos, ríos o mares), afectando el equilibrio ecológico. Entre las especies contaminantes, se encuentran los metales pesados, los cuales en su mayoría son altamente tóxicos aún a bajas concentraciones debido a que pueden acumularse en los seres vivos, causando diversos desordenes y enfermedades. Los hidrogeles son materiales poliméricos reticulados que contienen grupos funcionales (ácidos carboxílicos, aminas, hidroxilos y ácidos sulfónicos, etc.) que pueden usarse como agentes acomplejantes para la eliminación de iones metálicos de soluciones acuosas, a veces selectivamente y con la posibilidad de recuperarlos, presentando ventajas sobre otras técnicas para eliminarlas. La eliminación de metales es una posible solución al problema de la contaminación que afecta la calidad del agua. En esta revisión, se tratan diferentes aspectos sobre la aplicación de hidrogeles como materiales adsorbentes de iones metálicos.

Palabras claves: hidrogeles, iones metálicos, adsorción, desorción.

1 Introduction

Hydrogels are three-dimensional polymeric crosslinked networks having a solid-like appearance that do not dissolve in water but can absorb large volume of water or aqueous solution. Hydrophilic groups present in the polymer chains assist the hydrogel to swell in water. Due to their characteristic properties (high swell ability in water, hydrophilicity, biocompatibility and not toxicity) and to their abilities to respond to a variety of changes in the surrounding medium (pH, temperature, ionic strength, light intensity, electric and magnetic field, and presence and concentration of some chemicals), hydrogels have been utilized in wide range of biological, medical, pharmaceutical, and in solving environmental problems (Bae and col., 1991, Franklin and col., 1993, Rosiak and col., 1995, Qiu and col., 2001, Gupta and col., 2002).

Heavy metal/metal ion pollution is a major environmental problem due to rapid global industrialization. Furthermore ions of toxic heavy metals such as Cu, Co, Cr, Cd, Zn, and Zr are resistant to biological degradation and can accumulate in humans, causing health issues [Jang and col., 2008, Zhou and col., 2009, Zhou and col., 2009]. Many processes and technologies have been developed and applied to remove heavy metal ions from water, including chemical precipitation (Matlock and col., 2002), ion-exchange solvent extraction (Isshiki, 1996), electrode depositions (Grimm and col., 1998), and activated carbon adsorption (Baccar and col., 2009) are well known but expensive. The use of absorbents is an effective method from both economic and technological viewpoints and in the case of hydrogels water retention, network porosity, and elasticity properties enable them applications as adsorbents for various metal ions present in aqueous solution. During the adsorption process, different authors had mentioned formation of metal-hydrogel complex through the functional groups (i.e., –COOH, $–SO_3^{2–}$, $–C=O(NH_2)$, –SH, –COO–, $–NH_2$, and –OH) present in this last (Rifi and col., 1994; Katime and col., 2001, El-Hag Ali and col., 2003, Essawy and Ibrahim, 2004, Ozay and col., 2009).

The use of polymeric crosslinked networks had been reported from the 70 years, specifically that derivative of diethylester, divinylphosphonic acid and acrylic acid show capacity of adsorption of heavy metal ions (Saraidyn and col., 1995). Later, at final of 80 years and at the beginning of 90 years, were synthesized hydrogel using derivatives of amidoximes which used in the recuperation of uranium in residual waters (Hirotsu and col., 1986, Saraidyn and col., 1995). In 1994 Rifi y col. used hydrogels based in poly(sodium acrylate-*co*-acrylic acid) for the extraction of copper, cadmium and other metals. They observed a strong variation in the pH of the solution containing the metal ions upon contact with the hydrogel. Therefore, they indicated that the retention occurred by cation exchange and that an acid-base rearrangement of the hydrogel occurred, but they did not postulate any mechanism of such a process (Rifi and col., 1994).

2 Retention processes of metal ions and possible mechanisms

The chemical structure that forms the hydrogel plays a crucial role in the retention and interaction of metal and even non-metal ions. For example, the Hg^{2+} ion has been found to have a high affinity for compounds containing thiol groups forming complexes (Yetimoglu and col., 2009); while the compounds with ionizable functional groups that promote the adsorption of ammonium ions (NH_4^+) which is an important contaminant that promotes eutrophication (Zheng and col., 2011).

Generally, the types of monomer to be used in the synthesis of hydrogels can be varied depending on the final characteristics required for the material and its possible application. Thus, there are polymeric hydrogels with functional groups such as carboxylic acids, amines, hydroxyls and sulphonic acids, among others, which can be used as complexing agents for the removal of metal ions in aqueous solutions (Moradi and col., 2009, Zhu and col. 2009). In many cases, the adsorption process occurs selectively or with several ions, and with the possibility of recovery and reuse of the hydrogel.

Various types of possible interactions may occur between the interlinked network of the hydrogel and the metal ions that may act in multiple or dynamic ways. For example, if there are sulfonate groups present in the network, electrostatic interactions can be created, whereas complex amine groups may form complexes (García and col., 2010).

Thus, the hydrogels polyelectrolytes have attracted a lot of attention due to the high swelling rates reached when they come into contact with water, but in addition they have worked very well in the adsorption of metal ions (Katime and col., 2001, Milosavljevic and col., 2010, El-Hag Ali and col., 2003, Yetimoglu and col., 2009).

The study of the type of mechanism that involves the adsorption and complexation of the metal ions with the interlinked structure of the hydrogel has attracted much attention in the last decade, since it is a very interesting and important fact to be able to describe the behavior of these polymeric materials with metal ions, especially with those of greater toxicity.

The techniques to study the interaction of the metal ion with the functional groups of the hydrogel goes from infrared spectroscopy, thermogravimetric analysis (TGA), electron microscopy, kinetic parameters, to the use of X-rays. Each of them brings different results, which together can generate a complete study of the type of metal-hydrogel interaction.

Rojas de Gascue and col. (2007) synthesized hydrogels with different monomers whose structures contain amine groups (acrylamide, AAm), carboxylic acid groups (maleic acid, AM and acrylic, AAc) and carboxylic acid-ester groups (octyl monoitaconate, MI-8), to study the ability of each hydrogel in the adsorption of Cu^{2+} ions. With regard to swelling in water, the authors found that as the ratio of crosslinking agent to octyl monoitaconate increases for a specific series of hydrogels, swelling decreases, while as the acid concentration in each increases of the samples, the swelling increases. This behavior is well known for this type of material (Katime and col., 2004).

However, when the hydrogel pellets (0.1g each pellet) were brought into contact with a $CuSO_4$ solution of 63.52 ppm for 20 hours and with constant agitation, they observed that for all cases the initial concentration of Cu^{2+} greatly decreased especially for samples containing a higher proportion of maleic and acrylic acid. However, when the proportion of crosslinking agent was increased, the adsorption of the ions decreased considerably so that obviously not only the monomer type plays a crucial role in the adsorption of ions, but also the stiffness of the crosslinked structure. This means that a higher degree of crosslinking in the hydrogel structure results in a lower free volume, which hinders the interaction between the functional groups present in the hydrogel (amino groups and carboxylic acid groups) and metal ions.

On the other hand, they observed that in the case of the AAm/Am and AAc/MI-8 hydrogels, the amount of Cu^{2+} ions adsorbed varied very little with the proportions of the comonomer units in the polymer material. In both types of hydrogels, each comonomeric unit has carboxylic acid groups in its structure, however, even though the MI-8 monomer has a longer chain, it may be rearranged in such a way that it does not so much damage the interaction of Cu^{2+} with the related functional groups. Other authors reported the use of hydrogels of N-[3-(dimethylamino) propyl]metaacrilamide, which has an amide group and an amino group, the latter being in a long chain that possibly acts as a spacer arm facilitating the capture of said metal ions (García and col., 2010).

The authors also found a color change in the hydrogel during the adsorption process, from colorless to light blue which is characteristic of the $CuSO_4$ salt. This was previously reported for both hydrogels in contact with Cu^{2+} salts and with other salts (Katime and col., 2001, Saraidyn and col., 1995). For example, Ozgur Ozay and col. (2009) report a red-orange color for Fe (II) -Fe (III) -hydrogel interaction with a hydrogel based on 2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) (see Figure 1). Also, García and col., (2010) found that hydrogels formed by amino and amide groups changed color during the adsorption processes of transparent to celestial with Cu^{2+} and to whites (opaque) when they interacted with Pb^{2+}.

In agreement with García and col., El Halah and col. (2011), observed an intense blue coloration for acrylamide/monomethoxymethylitaconate hydrogels (AAm/IME) when they were brought into contact with a concentrated Cu^{2+} solution, and such staining intensified as the ratio of IME in hydrogels was increased (Figure 2).

However, the change in coloration is not only observed in the hydrogels, but also the color tone of the solution, as it was reported by Ozay and col. (2011), For poly (4-vinyl pyridine-*co*-2-hydroxyethylmetacrylate) magnetic hydrogels (P(4-VP-*co*-HEMA)) used for the adsorption of UO_2^{+2} and Th^{4+} ions, which are shown in Figure 3.

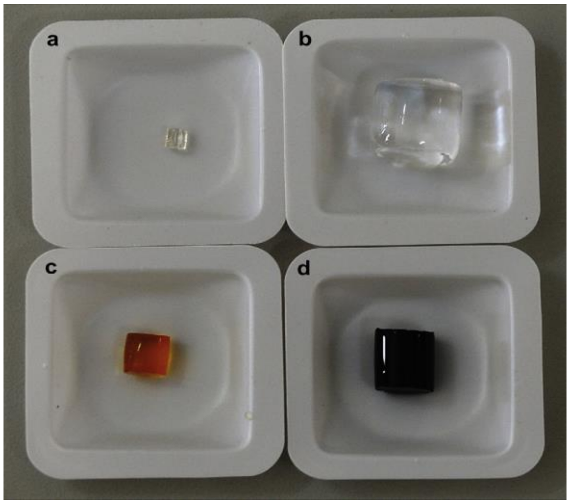

Figure 1. Photographs taken from Ozay and col. 2009, where the hydrogel of PAMPS is a) dry b) swollen, c) Fe^{2+} and Fe^{3+} adsorbed and d) magnetic composite.

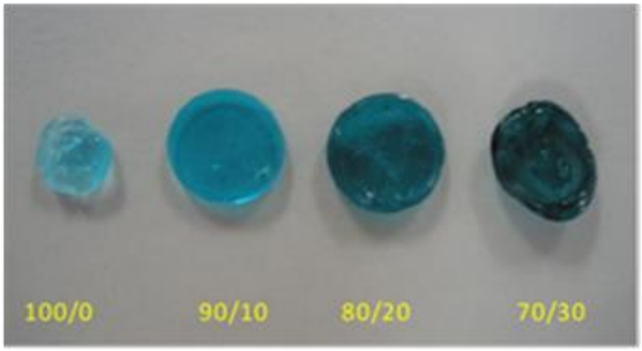

Figure 2. Photograph of dry AAm / IME hydrogels with different molar proportions, and loaded with Cu^{2+} ions (El Halah and col., 2011).

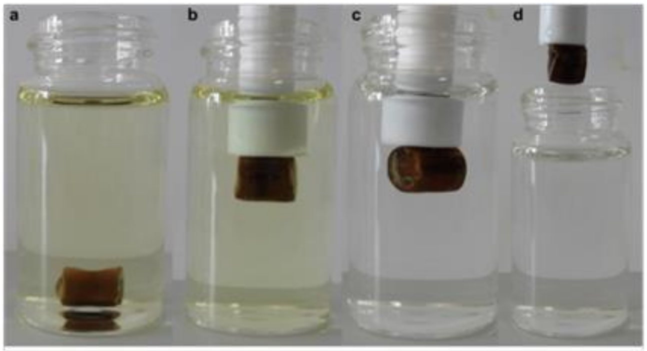

Figure 3. Use of P(4-VP-c-HEMA) magnetic hydrogels to remove UO_2^{+2} ions from an aqueous solution. (a) magnetic hydrogel in solution of UO_2^{+2}, (b) application of the magnetic field, before (c) and after (d) removal of UO_2^{+2} ions (Ozay and col 2011).

Dai and col. (2001), Performed the synthesis of pearl type chitosan hydrogels for the adsorption of Cu^{2+} ions and phosphates. They analyzed the hydrogel charged with Cu^{2+}

by infrared spectroscopy (FTIR) and comparing the spectra found that the characteristic peaks around 1649 and 1064 cm^{-1} assigned to the voltage vibrations for the $-NH_2$ and -OH groups, respectively, shift slightly at shorter wavelengths and the intensity of the two peaks becomes stronger. Therefore, the authors propose that the Cu^{2+} ion are coordinated with these functional groups.

A similar study was carried out by Milosavljevic and col. (2010), where they also report the FTIR spectrum for hydrogels of chitosan, itaconic acid and methacrylic acid (Ch/IA/MAA) before and after the adsorption of Cd^{2+} ions (see Figure 4).

Figure 4.a shows that the peak at 3435 cm^{-1} corresponding to the symmetric stretching vibration of the N-H bond tend to overlap with the stretching of the hydroxyl group (CO-H), in addition it is noticed that the intensity of this peak decreases and moves (from 3435 cm^{-1} to 3431 cm^{-1}) when the hydrogel is charged with the Cd^{2+} ion (Figure 4.b). A similar behavior was observed by Dai and col. (2001).

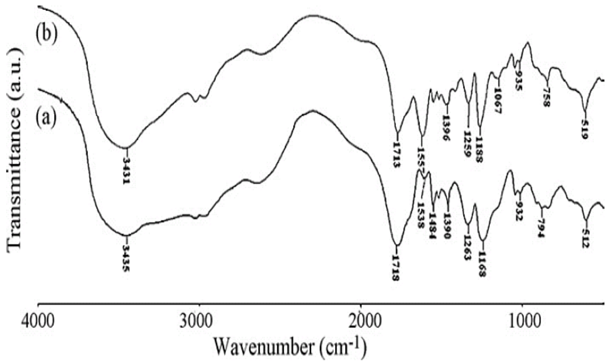

Figure 4. FTIR spectrum of the hydrogel Ch/IA /MAA: a) before and b) after the adsorption of Cd^{2+} ions. Figure taken from Milosavljevic and col., 2010.

On the other hand, the absorption band at 1718 cm^{-1} (Figure 4.a) assigned to the stretching vibrations of the carboxyl group (C=O) too undergoes displacement towards smaller wavelengths, 1713 cm^{-1}, when loaded with Cd^{2+} (Figure 4.b). In contrast, the peak observed at 1538 cm^{-1} (assigned to the ionic interaction between chitosan and acid groups) and the peak at 1168 cm^{-1} characteristic of the deformation of the -OH groups, both signals are shifted to longer lengths (Figure 4a). These results allowed Milosavljevic and col. to conclude that effectively the $-NH_2$, -OH and -COOH groups are responsible for the uptake of Cd^{2+} ions. Milosavljevic and col. also performed scanning electron microscopy (SEM) on the Cd^{2+} charged hydrogel (see Figure 5).

It can be clearly seen in Figure 5 the structural changes that the hydrogel undergoes after interacting with the Cd^{2+} ion. It is noted in detail that Figure 5a has a highly porous hydrogel whereas in Figure 5b practically the pores disappear or become much smaller. Evidently this confirms that the Cd^{2+} ions were retained by the hydrogel structure.

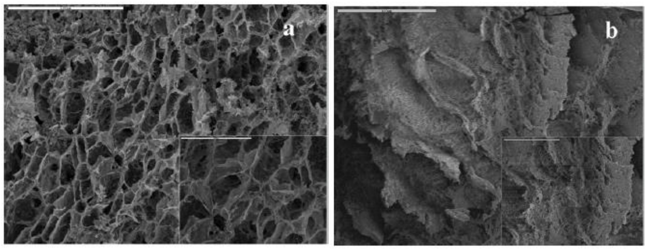

Figure 5. SEM (a) micrographs with a barrier of 500µm, 90x; and with zoom between 200µm, 300x of the Ch /IA/MAA hydrogel without ion charge and (b) SEM between 100µm, 400x; with zoom between 50µm, 1000x of the Ch/IA/MAA hydrogel after loading with Cd^{+2}. Image taken from Milosavljevic and col., 2010.

Carvalho and col. (2010) carried out the extraction of a natural hydrogel contained in the covering of a seed of the tree Magonia pubescens very abundant in the Brazilian plant species, which is constituted mainly by polysaccharides. They studied their behavior to absorb Na^+, Mg^{2+}, K^+, Ca^{2+}, Cr^{3+}, Fe^{3+} and Zn^{2+} ions and demonstrated that the polysaccharide structure of the seed coating has a high retention capacity of ions analyzed in aqueous solution. The authors performed the structural analysis and the adsorption mechanism using differential scanning calorimetry (DSC), thermogravimetry (TG) and X-ray.

The thermal studies were carried out with the pure hydrogel and charged with Zn^{2+} and Ba^{2+} ions, both 1M. The authors chose these cations because of their differences in ionic radius and polarizability. Figure 6 shows the results obtained for both DSC and TG.

In Figures 6a and 6b changes are observed when comparing the dried polymer with each of the samples loaded with the different cations. This is in agreement with what has been reported in the literature, since it has been found that the thermal behavior of the polymer matrix is influenced by the metal cations that may contain them in the form of complexes (Prado and Airoldi, 2003, Lima and Airoldi, 2004, Carvalho and col., 2010).

In Figure 6 it is also observed that there is shift in water evaporation temperature of about 19 ºC for seed coat containing Zn^{2+} ions, whereas the curves of the hydrogel-Ba remain the same as the of the dried polymer. The change in the thermal behavior of the hydrogel matrix in the presence of the Zn^{2+} cation, according to Carvalho and col., can be attributed to the fact that Zn^{2+} is a hard Lewis acid; therefore this cation can induce bigger dipole interaction with water molecules than Ba^{2+}. As a consequence, this polarization effect (Zn^{2+}-H_2O) increases the energy required to evaporate the water absorbed by the natural hydrogel.

Another important result of the thermogravimetric curves obtained by the authors is that (Figure 6b) a large reduction, above 70 °C, is observed in the decomposition temperature of the Zn^{2+}-linked polysaccharide when compared with the pure polysaccharide. No changes are observed at 250 °C for the hydrogel with Ba^{2+}. Again, this fact is related to the polarization caused by Zn^{2+}, so the energy required for the decomposition of the reaction is reduced (Carvalho and col., 2010). If one compares the shapes of the curves above 250 °C, of the natural hydrogel with those of the same hydrogel but with the charged metals, a great difference is observed that is attributed mainly to the formation of degradation products containing metals, such as oxalates and carbamates, prior to the complete oxidation of the organic structure.

To continue investigating the possible mechanism of adsorption of Zn^{2+} and Ba^{2+} in the polysaccharide matrix, the authors analyzed the samples by X-ray photoelectron spectroscopy (see Figure 7). They found in the analysis of the X-ray spectrum (Figure 7a) three species with which Zn^{2+} may be bound in the sample.

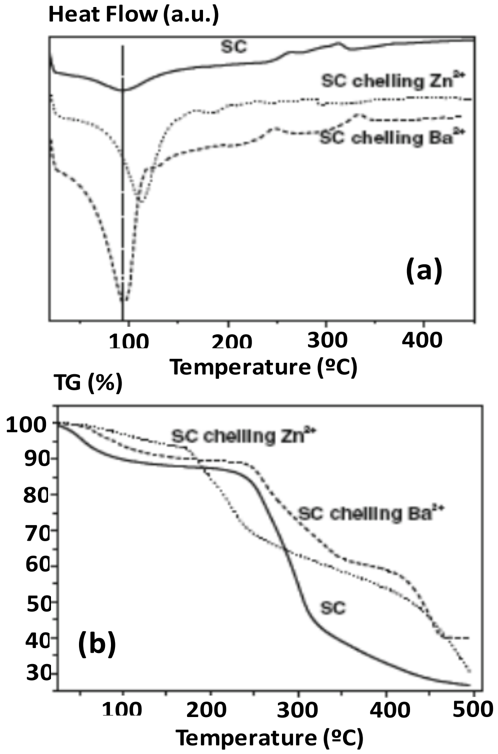

Figure 6. a) DSC for the dry hydrogel (SC), with Zn^{2+} and Ba^{2+} and b) TG for the dry hydrogel (SC) with Zn^{2+} and Ba^{2+} respectively. (Figure taken from Carvalho and col., 2010).

The component at 1023.3 eV corresponds to the species $ZnCl_2$ (38% of the total Zn present in the sample). This structure is related to the experimental process in which a 0.2M solution of $ZnCl_2$ is used, which remains in the polymer matrix after the adsorption process.

The component at 1022.7 eV was attributed to the $Zn(OH)_2$ group (44%). Since the hydrogel matrix consists of polysaccharides (mainly glucose and xylose), the Zn^{2+} ions are probably chelated with the solitary electronic torque of the OH groups. The authors support this based on a spectrum (not shown) in which an oxygen component bound to Zinc at 530.6 eV is observed. The third component at 1020.5 eV corresponds to metal Zn coordinated with 6 carbon atoms, Zn-C6 (18%), due to the reduction to metal Zn by the OH groups present in the hydrogel matrix.

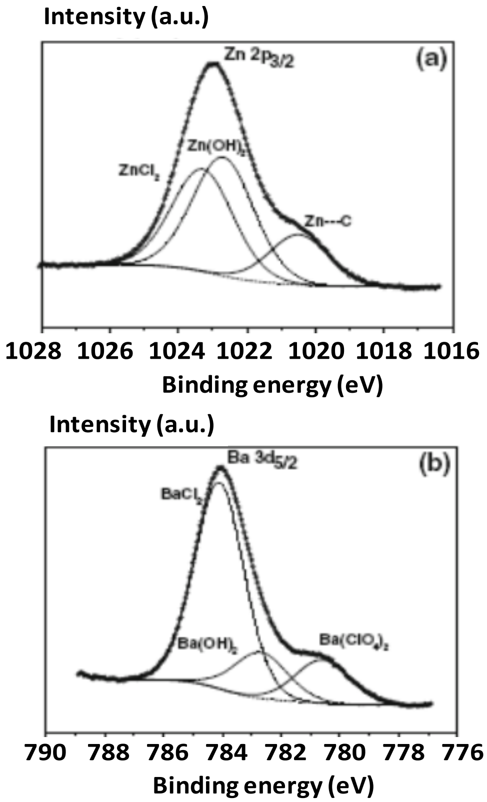

Figure 7. X-ray spectrum of the hydrogel after adsorption of (a) Zn^{2+} and (b) Ba^{2+}. Figure taken from Carvalho and col., 2010.

For the study of the adsorption of Ba^{2+} ions in the polysaccharide matrix, the authors report the following composition: 73% carbon, 18.3% oxygen, 5.6% chlorine and 3.1% barium. Figure 7.b shows a central component at 782.3 eV which is attributed to the interaction between Ba^{2+} and OH groups (16%). The major component at 784.1 eV corresponds to a possibly barium peak which is not clearly identified, but is probably related to the $BaCl_2$ species; and the third component at 780.6 eV (0.5%) can be attributed to the $Ba(ClO_4)_2$ species. Although the presence of $Ba(ClO_4)_2$ was not clear or well defined in the hydrogel matrix, the important point is that there are three types of species bound to Ba in the hydrogel matrix.

When they performed theoretical studies (whose mathematical treatment will not be discussed in this work) combined with the discussion previously made for Zinc-bound groups, there is evidence that these metal ions were absorbed through coordination bonds with the polysaccharide hydroxyl groups, which also allowed them to represent the most stable structure possible with which Zn^{2+} coordinates with related hydrogel groups (see figure 8).

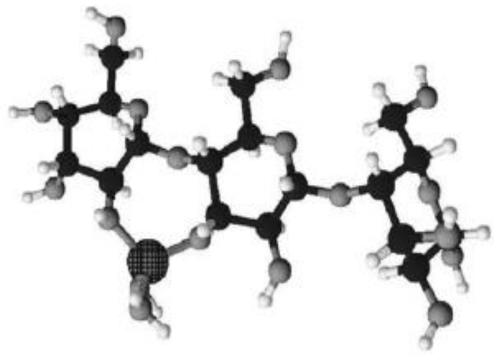

Figure 8. More stable structure obtained by mathematical and X-ray calculations for the adsorption of Zn^{2+} coordinated with the oligosaccharide structure present in the natural hydrogel. Coordination occurs with two hydroxyl groups and two water molecules. The structure includes atoms of carbon (black), oxygen (gray), hydrogen (white) and zinc (II) (grated) (Carvalho and col., 2010).

3 Effect of pH on the adsorption of metal ions by polymer hydrogels. Influence of concentrations of metal ions on solutions

The pH plays a fundamental role in the adsorption of metal ions from polymer hydrogels, since it controls many properties of the latter, especially if electrolytic polymers are used and from the point of view of the metal is also a relevant fact that the pH must be controlled to avoid precipitation. For example, the chloride salts of Mn^{2+} and Cu^{2+} in solutions with a pH above 6 precipitate while for Fe^{3+} chloride solutions a pH below 3 should be chosen (El-Hag Ali and col., 2003).

El-Hag Ali and col. in 2003, studies of the change and influence of pH on poly (vinylpyrrolidone-*co*-acrylic acid) hydrogels (VP/AAc hydrogels) and studied its application in the removal of Fe^{3+}, Cu^{2+} and Mn^{2+} ions. They found that in all cases Fe^{3+} is mostly adsorbed, followed by Cu^{2+} and finally the Mn^{2+} ion. Also, the authors first analyzed the influence of pH on the swelling of hydrogel in water and observed abrupt changes in the degree of swelling at pH values around 4, which coincides with the pKa value of acrylic acid (Kostum and col. 1961). This behavior is due to pH values higher than the pKa value of acrylic acid, dissociation of the carboxyl groups occurs, giving rise to the formation of carboxylate groups and consequently increases electrostatic repulsion between them, resulting in expansion of the network, therefore the entrance of water is favored (El-Hag Ali and col., 2003).

After analyzing the hydrogel separately and having a background of behavior at different pH, the authors proceeded to study the adsorption of the metal ions. For this purpose the dry hydrogel samples (0.5 g) were placed with 50 mL of a solution of 500 mg/L of the respective ion. The pH is adjusted by adding dilute volumes of HNO_3 or NaOH solutions as the case may be. Samples were shaken for 24 h at 25 ° C. For the Mn (II) and Cu (II) solutions they used pH values below 6 and for the iron solution the pH value was below 3. This method is used by several researchers when analyzing the influence of the pH in the adsorption of metal ions, since it is simply a matter of standardizing the solutions, temperature and pH values according to the required (Katime and col., 2001; Yetimoglu and col., 2009, Peñaranda and Sabino, 2010, Wang and col 2011). In Figure 9, the variation of pH with respect to swelling for VP/AAc hydrogels is shown.

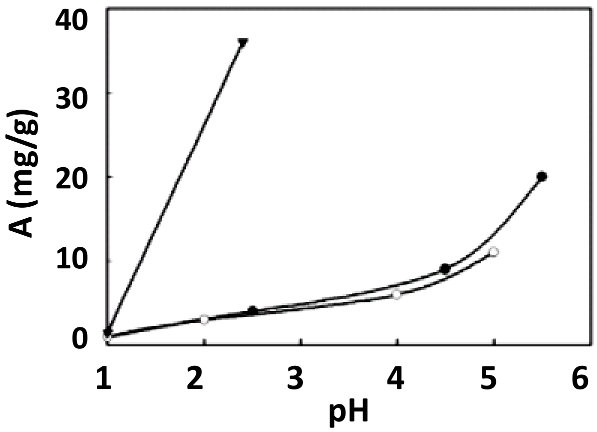

Figure 9. Behavior in the uptake of ions (▼) Fe (III), (○) Mn (II) and (●) Cu (II) by VP/AAc hydrogel at different pH (El-Hag Ali and col., 2003).

It is noted in Figure 9 that the adsorption of the metal ions is increased with increasing pH. This increase in metal uptake may be due to the degree of swelling of the hydrogel also increasing, which favors the diffusion of the metal ion within the crosslinked network of the hydrogel and its interaction with the chelating groups. It can also be observed that the maximum adsorption pH was 2.4 for Fe^{3+}, 5.0 for Mn^{2+} and 5.5 for Cu^{2+}.

El-Hag Ali and col. also conducted studies of the effect of the initial cation feed concentration on the solution in order to determine the hydrogel efficiency expressed in terms of percent adsorbed metal. To carry out such studies, a fixed amount of hydrogel is equilibrated with a series of solutions of the respective ions whose concentration must gradually increase (from 5 to 1000 ppm for this case). Thus the adsorption capacity is given by the maximum amount of metal ion removed from the solution when the chelating sites of the absorbent, which in this case is the hydrogel, are saturated.

The amounts of ions adsorbed by the hydrogel and their respective percentages are shown in Figures 10a and b, and these results are specified in Table 1. The concentrations of the metal ions in the post-adsorption solution were determined by the elemental analysis technique Optical Emission Spectrometry with Inductively Coupled Plasma (ICP-OES). This technique allows determining traces of different types of metals present in a solution, and is very used for this type of experiments. Then the amount of adsorbed ion (A) is determined by the following equation:

$$A = \frac{[V(C_1 - C_2)]}{W} \quad (1)$$

Where V is the volume of the solution (L), W is the weight of the hydrogel (g), C1 and C2 are the concentrations of the metal ion before and after adsorption, respectively (mg / L).

It can be clearly seen in Figure 10a that as the initial concentration of the solution of each respective ion increases, the amount of metal ion adsorbed in terms of ppm increases to a maximum. Therefore there is a proportional tendency between the increase of the initial concentration of the solution and the adsorption of each ion.

In terms of hydrogel efficiency, it is also dependent on the initial concentration as well as the behavior of the metal ion (Figure 10b). As the initial concentration of each solution increases, the efficiency decreases, ie there is a relation between efficiency and initial concentration with an inversely proportional behavior.

According to the results obtained by El-Hag Ali and col., it is postulated that the VP/AAc hydrogel has a high efficiency in the range of 5-100 ppm where are removed 60 % of the ions Fe (III) and Cu (II) of the solution and about 25% for Mn (II) ions.

It is interesting to note in Table 1 that the adsorption of all the ions by the VP/AAc hydrogel reaches a peak or saturation point above 500 ppm, so it can be assumed that all functional groups of the hydrogel that can interacting with the ions are already occupied by them and that for concentrations greater than 500 ppm no adsorption will occur.

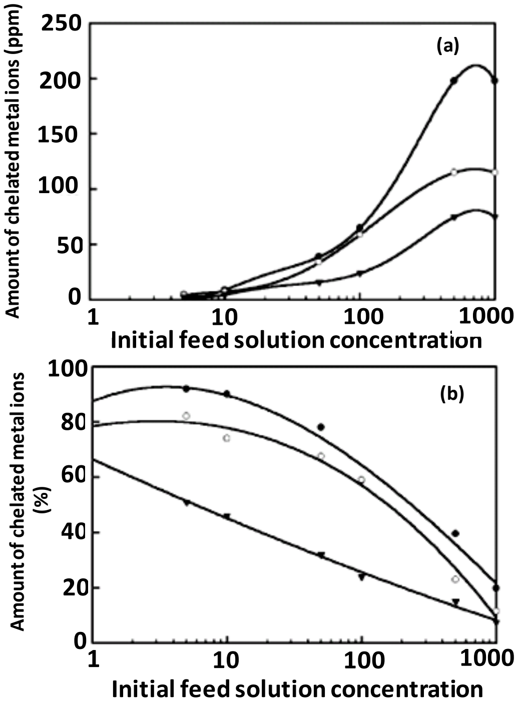

Figure 10. Profile of Adsorption of VP/AAc hydrogels for different initial concentrations of (●) Fe (III), (▼) Mn (II) and (○) Cu (II). Concentration: a) in ppm and b) in percentage. Image taken from El-Hag Ali and col 2003.

Table 1. Adsorption profile of VP/AAc hydrogels for Fe (III), Cu (II) and Mn (II) ions with different initial concentrations. Data taken from El-Hag Ali and col. 2003

Initial Concentration (ppm)	Quantity of chelated metal ion (ppm)					
	Fe (III)		Cu (II)		Mn (II)	
	ppm	%	ppm	%	ppm	%
5	4.6	92	4.1	82	2.55	51
10	9	90	7.4	74	4.6	46
50	39	78	33.8	67.6	16	32
100	58.8	58.8	59	59	24	24
500	198	39.6	115	23	75	15
1000	198	19.8	115	11.5	75	7.5

Similar results have been found by other authors such as Yetimoglu and col. in 2009 with a hydrogel based on sulfathiazole, where they analyzed the effect of the initial concentration for Hg^{2+} ions finding that above 1000 ppm there was already saturation. Milosavljevic and col. in 2010 analyzed this effect with Ch/IA/MAA hydrogels for Cd^{2+} uptake and found that for times greater than 25 h there was no change in the concentration of Cd^{2+} adsorbed per gram of hydrogel. Wang and col. in 2011 also observed that the adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions by interpenetrated hydrogels composed of poly(ethylene glycol diacrylate) and poly(methacrylic acid) reached a maximum saturating above 15 minutes of adsorption.

Continuing the pH effect on the hydrogel, Katime and col. in 2001 studied the adsorption of Cu^{2+} and Zn^{2+} ions from hydrogels composed of acrylic acid/itaconic acid. The concentrations of the ions in the remaining solutions were determined by atomic absorption spectrophotometry. They found that the presence of the carboxylic groups are responsible for the adsorption of the metal ion from the aqueous solution and postulated that the adsorption of Cu^{2+} occurs as a cation exchange between the Cu^{2+} present in the external solution and the H^+ ions from the groups acids of the polymer chain, whereas the carboxyl groups in the hydrogel are bound to the metal ion due to electrical exchange. This was checked with the initial and final pH changes of the different Cu^{2+} solutions as shown in Table 2.

Table 2. Adsorption of Cu^{2+} from aqueous solutions with different initial concentrations by poly(acrylic acid-*co*-itaconic acid) hydrogels in the ratio 80/20. Data taken from Katime and col. 2001.

$C(Cu^{2+})_i$ (M)	$pH_{initial}$	pH_{final}	mg Cu/$g_{xerogel}$
10^{-5}	5.2	4.2	0.5
10^{-4}	5.1	3.6	4.5
10^{-3}	5.0	3.1	18.0
10^{-2}	4.9	2.9	49.3
10^{-1}	4.7	2.8	99.0

On the other hand, the same authors investigated the adsorption of metal ions by varying the pH of the solution whose results are specified in Table 3. In Table 3 a strong dependence of the adsorption of the Cu^{2+} and Zn^{2+} ions with respect to the pH can be observed. That is, as the pH in the solution of the metal ions increases, the pressure of the ionic swelling becomes larger due to the increase in the production of free ions by the dissociation of the -COOH groups in the hydrogel.

Table 3. Adsorption of the metal ion with the variation of the pH and the concentration of the metal in the solution for poly(acrylic acid-*co*-itaconic acid) 80/20 hydrogels. Data taken from Katime and col., 2001.

mg M^{2+}/g xerogel						
	pH=4.7		pH=6.0		pH = 9.0	
$C(M)^{2+}$ (M)	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
10^{-5}	0.4	0.5	0.4	0.5	0.5	0.5
10^{-4}	2.8	3.0	3.1	3.3	4.6	5.8
10^{-3}	23.7	27.4	29.5	30.5	32.2	36.9
10^{-2}	72.7	145.0	96.0	176.0	163.0	198.0
10^{-1}	96.4	303.8	147.0	328.0	320.0	343.2

Kasgoz and col. (2001) using acrylamide based hydrogels, which were chemically modified to increase the proportion of chelating groups in their crosslinked structure, observed that Cu^{2+} ion uptake increases as pH increases. The results obtained indicate that at pH ~ 5.5, it is the optimum adsorption value where the Cu^{2+} ions interact perfectly with the deprotonated amine groups belonging to the hydrogel crosslinked network.

Another curious fact was also reported by Katime and col. for the adsorption in a concentrated initial solution of Cu^{2+} ions. They performed the swelling in water for a certain time, and after that they put the swollen hydrogel in contact with a solution of $CuSO_4$ $1x10^{-2}$ M, and observed that the hydrogel rapidly deflates until reaching a physicochemical equilibrium (see Figure 11). The authors report that for diluted concentrations of the salt, the swelling curves remain horizontal, whereas for concentrated solutions the hydrogels present a phenomenon of deflagration as seen in Figure 11.

They attributed this phenomenon to the fact that increasing the concentration of the ion in the solution increases the electrostatic repulsion between the charged groups on the network and a concentration gradient inside and outside the hydrogel governed by the Donnan potential. On the other hand, it is also possible that is occurred the displacement of water molecules by the Cu^{2+} ions that are directed into the polymer matrix.

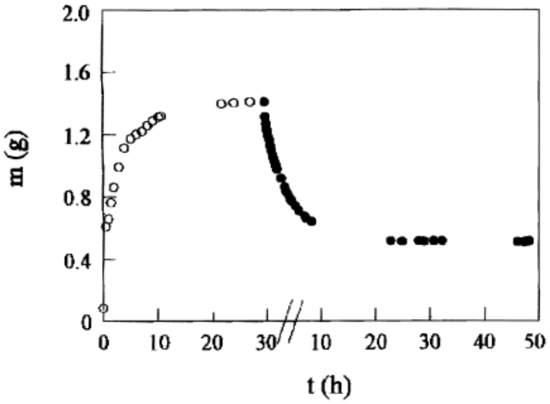

Figure 11. Variation of the mass of the hydrogel (acrylic acid / itaconic acid 80/20) correlated with the adsorption of Cu^{2+} ions: (○) swollen in water, (●) deflated in a solution of Cu^{2+} $1x10^{-2}$ M. (Katime and col., 2001)

4 Isotherms of adsorption

Interactions with water or metal ions occur frequently on the surface of the hydrogel, in order to explain the interaction between the adsorbate and the adsorbent, adsorption isotherms have been widely used which are decisive in the optimal use of adsorbents.

The most used models that describe the interaction between the surface of the solid (the hydrogel in this case) and the metal ions present in the solution are those postulated by Freundlich and Langmuir. Several authors have used both models to determine adsorption isotherms for different types of hydrogels and adsorbed metal cations (Ozay and col., 2011, Wasikiewicz and col., 2005, Ozkahraman and col., 2011, Dai and col., 2011).

The ideal Langmuir model postulates that: the surface has a fixed number of identical and defined active centers;

the adsorption is in monolayers, uniform, on a homogeneous surface, without lateral interaction between the adsorbent molecules and that all the active centers have the same enthalpy of adsorption (García and col., 2010). Whereas, the Freundlich model describes an isotherm originated purely of empirical character and applies for experimental data that do not follow the Langmuir isotherm (Izquierdo and col., 2004). Both models represent the adsorption capacity (X) as a function of the concentration of the equilibrium metal ion in the solution (C). It should be noted that in this section, the mathematical treatment from which the isotherms derive is not included, only its application in the adsorption processes of metal ions by polymeric hydrogels will be briefly described.

The Langmuir model is described by the following equation:

$$\frac{\mathbf{C}}{\mathbf{X}} = \frac{\mathbf{C}}{\mathbf{X_{max}}} + \frac{\mathbf{1}}{\mathbf{X_{max}}}.\mathbf{b} \quad (2)$$

In this equation, Xmax is the maximum amount of metal ions adsorbed in the monolayer (mg/g) and b is the adsorption constant at the Langmuir equilibrium (mL/mg), related to the affinity of binding sites and energy of adsorption. C is expressed in ppm and X in mg of adsorbed metal in the equilibrium per gram of dry hydrogel (mg/g) (García and col., 2010). If the C/X graph is plotted as a function of C, through the experimental data, adjusted linearly and followed by linear regression, it can be obtained the parameters Xmax and b, which correspond to the slope and ordinate in the origin , respectively (see Equation 2).

The Freundlich model is represented by the following equation:

$$\boldsymbol{logX = logk_F + \frac{1}{nlogC}} \quad (3)$$

where, X (mg/g) is the adsorption capacity at equilibrium, C (mg/L) is the equilibrium concentration of the saline solutions, kF and n are the physical constants of the Freundlich adsorption isotherm, the latter two constants indicate the adsorption capacity and the adsorption intensity, respectively.

García and col. determined the X values and performed the Langmuir adsorption isotherms by applying equation (2) for poly(N-[3- (dimethylamino) propyl] methacrylamide) hydrogels (the proportions of the hydrogels are specified in Table 4) for the retention of Cu^{2+} and Zn^{2+} whose results are shown in Table 5.

According to the results shown in Table 5 and taking into account the values of the correlation coefficients (R^2), which are between 0.95 and 0.99, the authors conclude that the results conform to the Langmuir model. It was generally observed that the adsorption values are high and increase with increasing pore size of the matrix, pore volume and water content.

Table 4. Synthesis conditions for DMAPMA hydrogels (García and col., 2010

Hydrogel	DMAPMA^a (molx10^{-3})	BIS^b (molx10^{-3})	APS^c (molx10^{-5})	H_2O (mL)
F18	5,6	1,1	5,6	4
F19	5,6	1,4	5,6	4
F20	5,6	1,7	5,6	4

Table 5. Parameters obtained by García and col., 2010 using the ideal Langmuir model.

Retention of Cu^{2+}				
	R^2	X_{max} (mg/g)	X_{max} (mmol/g)	b (L/mg)
F18	0.962	119.2	1.87	0.044
F19	0.988	91.8	1.44	0.093
F20	0.987	63.5	1.00	0.116
Rentention of Pb^{2+}				
	R^2	X_{max} (mg/g)	X_{max} (mmol/g)	b (L/mg)
F18	0.860	204.1	0.99	0.039
F19	0.986	90.9	0.44	0.201
F20	0.981	90.1	0.43	0.073

This behavior is attributed to the fact that having a lower density of crosslinking in the matrix, there is a greater possibility of diffusion, higher density of adsorption sites and adsorption volumetric capacity and that the functional groups capable of complexing the metal, can be rearranged more easily (García and col., 2010).

In addition, García and col. determined the Langmuir constant (b), with which they were able to calculate the separation factor R_L, which corresponds to the adsorption intensity and which is based on the Langmuir equation. The mathematical expression of R_L is:

$$\boldsymbol{R_L = \frac{1}{(1+b.C_0)}} \quad (4)$$

This value predicts whether the adsorption system is irreversible (R_L=0), favorable (0<R_L <1) or unfavorable (R_L>1). With the value of b one can also determine the ΔG of the metal-hydrogel junction for each of the matrices, according to the equation given below:

$$\boldsymbol{\Delta G = -RTlnb} \quad (5)$$

The parameter b is used in units of L/mol.

The results found by García and col. are shown in the following tables.

In Table 6 it can be clearly seen that retention in all matrices corresponds to favorable adsorption systems, mainly where C_0 are low and that the values of ΔG obtained are high (see Table 6) and suggest strong interactions between the ion and the amino functional group (García and col., 2010).

Table 6. R_L and ΔG values for Cu^{+2} and adsorption systems (García and col., 2010)

C_0 of Cu^{2+} (ppm)	R_L (F18)	R_L (F19)	R_L (F20)
39.0	0.370	0.210	0.180
213.0	0.096	0.048	0.039
335.5	0.063	0.031	0.025
546.5	0.040	0.019	0.016
ΔG (Kj/mol) for Cu^{+2}	-19,062	-20,859	-21,390
ΔG (Kj/mol) for Pb^{+2}	-21,593	-25,531	-23,100

Ozgur Ozay and col. in 2009 studied the adsorption of Pb^{2+} by hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS hydrogels), using the Langmuir and Freundlich models applying equations (2) and (3). Figure 12a and 12b shows the graphs obtained by the authors when applying both models. In the graphs of Figure 12, it can be observed that the linearity is followed for both methods; however the authors report that the data are better with the Langmuir isotherm, so the adsorption is in monolayers, with a homogeneous surface structure and whose adsorption sites are identical.

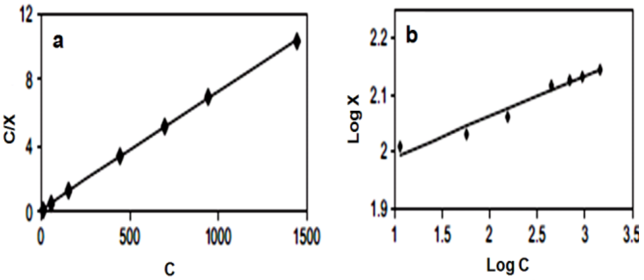

Figure 12. Curves applied to: a) Langmuir model y b) Freundlich model, for the adsorption of Pb^{2+} by magnetic AMPS hydrogels. Figures taken from Ozay and col. 2009.

5 Studies of desorption. Recovery of the hydrogel

One of the most attractive advantages that hydrogels offer unlike traditional methods of absorbing heavy metal ions from aqueous solutions or contaminated water is the fact that, apart from being inexpensive, they are easily retrievable and reusable. These two advantages have attracted a lot of attention to various researchers, since the fact that the material can be reused encourages environmental decontamination and cost reduction in materials and synthesis, and in addition biodegradable and biocompatible polymers can be used.

The most commonly used desorption method is to expose the hydrogel charged with the metal ion to several desorption cycles in an acidic, basic solution or a salt, depending on the metal adsorbed and the type of hydrogel.

Tang and col. (2011) performed studies of regeneration of the Cr^{6+} charged hydrogel. To this end, 0.1 g of the hydrogel was subjected to adsorption cycles of 40 mL of a 100 ppm solution of Cr^{6+}. The solutions were quickly filtered and the charged hydrogel was collected. The Cr^{6+} adsorbed by the hydrogel was recovered by introducing the hydrogel with 40 mL of a 0.5 M solution of NaCl. After each adsorption/desorption cycle, the hydrogels were used in successive adsorption cycles, finding that more than 80 % of the hydrogel is recovered, and besides the regeneration is not affected by the number of cycles, since practically in the first cycle an almost complete recovery is achieved.

On the other hand, Wang and col. (2011) performed recovery studies of interpenetrated hydrogels that had adsorbed Cu (II), Cd (II) and Pb (II) ions. The studies were carried out by immersing the hydrogel in a solution of HCl 1 M. After this process, the hydrogels were washed with distilled water and a sodium bicarbonate solution to remove excess acid.These studies suggested that the interpenetrated hydrogels composed of poly(polyethylene glycol diacrylate) and poly(methacrylic acid) have a high recovery capacity and reuse, in addition the metal desorption and recovery of the hydrogel do not change significantly with the repetitive applications compared with the first run (Wang and col., 2011).

Ozay and col. in 2009, they studied a wider range of metal ion recovery from AMPS magnetic hydrogels. They employed a solution 0.1 M of HNO_3 in which the charged hydrogel was immersed with the respective ions and allowed to stir for 24 h and finally determined the concentrations of the metal ions in the solution using the ICP-OES technique. The results found for the desorption of Co (II), Cr (III), Pb (II), Fe (II), Ni (II), Cd (II) and Cu (II) Figure 13.

Figure 13a shows that more than 80% of the adsorbed ions are recovered and this occurs for all cases. And in Figure 13b, in concordance with the results obtained by Tang and col. and Wang and col., in the first cycle practically all the metal ion is recovered and there are no significant changes with respect to the subsequent cycles.

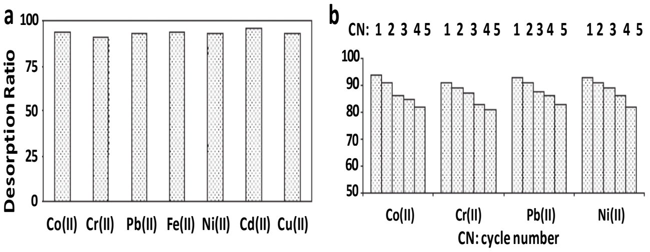

Figure 13. (a) Studies of release of various metals adsorbed by AMPS magnetic hydrogels; b) consecutive adsorption/desorption cycles (performed in 500 mL of HNO3, 0.1M). Figure taken from Ozay and col. 2009.

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Recibido: *08 de abril de 2016*

Aceptado: *04 de junio de 2017*

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