Removal of Heavy Metals from Model Wastewater by Using Carboxymehyl Cellulose/2-Acrylamido-2-methyl Propane Sulfonic Acid Hydrogels

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ABSTRACT: A series of functional copolymer hydrogels composed of carboxymethyl cellulose (CMC) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) were synthesized using γ-radiations-induced copolymerization and crosslinking. Preparation conditions were optimized, and the swelling characteristics were investigated. The ability of the prepared hydrogels to recover some toxic metal ions from their aqueous solutions was studied. The prepared hydrogel showed a great capability to recover metal ions such as: Mn^{+2}, Co^{+2}, Cu^{+2}, and Fe^{+3} from their solutions. The data revealed that the chelating ability of the prepared hydrogels is mainly dependent on their internal composition, in addition to the physical properties of the metal ion solution such as pH and metal ion concentration. The data show that the chelating ability of the prepared hydrogels increases by increasing the AMPS content in the hydrogel as well as the increment in the pH of the solution and the metal ion concentration. The prepared CMC/AMPS copolymer hydrogels are chemically stable enough to be reused for at least five times with the same efficiency. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 763–769, 2012

Key words: radiation; hydrogel; copolymerization; metal ions; removal

INTRODUCTION

The presence of heavy metals in the environment has been of great concern because of their high toxicity and susceptible carcinogenic effect. Water pollution caused by heavy metal ions, such as Cu^{2+}, Pb^{2+}, and Cd^{2+}, is deteriorating the inhabited environment and endangers the human health.[1] Such toxic heavy metals accumulated in living organisms, thus, causing various diseases and disorders even in relatively lower concentrations. Heavy metal contamination of the water streams comes from many industrial effluents such as chemical, plating, mining, tanneries, painting, plumbing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used.[2,3]

The treatment of heavy metal bearing effluent streams to prevent the discharge of pollutants in waterways has become the subject of legislation. Many techniques were developed and used to remove the heavy metal ions from different aqueous solutions. Such techniques involve solvent extraction,[4] ion exchange,[5] coprecipitation,[6] membrane process,[7] and carbon adsorption.[8] However, no satisfactory removal ratio could be achieved by the earlier-mentioned techniques. Moreover, the implementation of these technologies is expensive, and so, their application is limited in an obvious extent. Therefore, the development of a new, cheap, flexible, and environmentally friendly process for treatment of industrial effluents is a major challenge.

Polymers are good candidates as starting materials for the development of new functional materials able to remove toxic metal ions from their solutions. Polychelatogens are functional polymers that contain one or more electron donor atoms such as N, S, O, and P that can form coordinate bonds with most of the toxic heavy metals.[9] Hydrogels containing amide, amine, carboxylic acid, sulfonic acid, and/or ammonium groups can chelate metal ions and be good polychelatogens for the treatment of wastewater.

The objective of this work is to synthesis a good polychelatogen composed of 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and carboxymethyl cellulose (CMC) using ionizing radiation as for initiation and copolymerization. Either AMPS or CMC used to be a counterpart in several polymeric chelating materials.[10–13] The factors governing the complete copolymerization process will be optimized and the prepared hydrogel will be characterized. The chelating ability of the prepared hydrogels will be estimated by studying their affinity toward different metal ions, and the parameters affecting their efficiency will be investigated.

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EXPERIMENTAL

Materials

2-Acrylamido-2-methyl propane sulfonic acid (AMPS) of purity 99.9% (Merck, Germany) and carboxymethyl cellulose (CMC) (El-Nasr Co. for Chemical Industries, Egypt) were used as received. Other reagents, namely metal chlorides and the components of the citrate and phosphate buffers, were analytical grade and purchased from El-Nasr Co. for Chemical Industries (Egypt) and used as received without further purification.

Preparation of CMC/AMPS copolymer hydrogels

CMC/AMPS gels were obtained by radiation-induced homo/copolymerization of mixtures of different compositions using ^{60}Co gamma rays at a dose rate 10.28 kGy/h using Canadian gamma cell, Nordion 2.2 established by National Center for Radiation Research and Technology, NCRRT, Atomic Energy Authority, AEA (Cairo, Egypt). All samples were washed in excess water to remove the unreacted component then air dried at room temperature.

Gel determination

The dried hydrogel polymer networks were soaked in water for 24 h at 80°C to extract the insoluble part. The gelled parts were taken out, then dried, and weighed. This extraction cycle was repeated till the weight became constant. The gel percent in the hydrogel was determined from the following equation:

$$Gel(\%) = \frac{W_e}{W_d} \times 100,$$

where W_d and W_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

Swelling study

The prepared crosslinked gels were soaked in buffer solutions of different pHs, ranged from 1 to 7 at 37°C. The swelling percent (S%) was determined from the following equation:

$$S(\%) = \frac{W_s - W_o}{W_o} \times 100,$$

where W_s and W_o are the weights of the swollen and the dry hydrogel, respectively.

Metal uptake measurement

A fixed weight of the prepared hydrogel was immersed in the metal feed solution of definite concentration (1000 ppm). Merck atomic absorption standard solutions of these metals were used for the calibration process. The pH and temperature of metal feed solutions were adjusted before applying the hydrogels for treatment processes. The remaining metal ions in its feed solution were determined by an atomic absorption instrument (Unicam Model Solaar 929).

The metal uptake (E) was calculated as follows:

$$E(mmol/g) = \frac{C_i - C_f}{W \times A \times 10},$$

where W is the weight of the dry hydrogel (g), A is the atomic weight of metal ion, and C_i and C_f are the initial and remaining concentrations of metal ions in mg/L (ppm). The total uncertainty for all experiments ranged from 3% to 5%.

RESULTS AND DISCUSSIONS

For any particular application, the prepared copolymer hydrogel must be synthesized at a considerable crosslinking level that can stand against its dissolution. In this respect, CMC/AMPS copolymer hydrogels were synthesized by means of γ-irradiation as a high-energy source for copolymerization and crosslinking. The preparation conditions will be optimized to ensure the production of insoluble polymeric material with good physical properties that can be used for the removal of metal ions from their aqueous solutions.

Preparation of CMC/AMPS hydrogel

Table I summarizes the effect of the preparation conditions, namely the composition and concentration of the reactants in the reaction medium and total irradiation dose on the gelation process of CMC/AMPS copolymer hydrogel. The data presented in the table show that at the same reactants concentration and irradiation dose, the increase in the AMPS content in the reaction medium increases the gelation degree. It is also clear that the increase in the reactants concentration results in a significant improvement in the degree of gelation. On the other hand, the increase in the irradiation dose from 10 to 20 kGy improves the gelation process, whereas the further increment has slight negative influence on the gelation degree.

It is well known that there is a difference in the chemical nature of the materials used; CMC is a derivative of a natural polymer. CMC is known to be radiation degradable polymer, which undergoes random main chain session on exposure to ionizing radiations, whereas AMPS is a synthetic monomer with a vinyl group. The presence of the vinyl group

TABLE I
Effect of Preparation Conditions on the Gelation Process and the Swelling of CMC/AMPS Copolymer Hydrogel

Sample code	AMPS content (wt %)	Total concn. (wt %)	Irradiation dose (kGy)	Gel content (wt %)	Swelling (%)
CAM1	10	10	10	0	0
CAM 2	25			52	173
CAM 3	50			73	330
CAM 4	10	20	10	92	581
CAM 5	25			96	617
CAM 6	50			99	690
CAM7	50	20	20	97	722
CAM8	50		30	94	743

in AMPS assists its radiation polymerization and crosslinking. On these bases, it is possible to understand that the increase of AMPS concentration in the reaction medium would result in the increment of homo, copolymerization and crosslinking. Meanwhile, the increase in the gelation degree as a result of the increase in the reactants concentration could be referred to the increase in the viscosity of reaction medium as well as the increase in the number of the radiation reactive vinyl groups. Such condition reduces the mobility of CMC segments and as a result increases the probability of the recombination of the degraded CMC chains as well as crosslinking and self-bridging of the PAMPS, which allow the production of much perfect network of higher crosslinking density. In the same manner, increasing the irradiation dose from 10 to 20 kGy would result in the increment in the number and life time of the formed free radical, which in turn increase the probability of recombination and enhance the degree of crosslinking. Further increase in the irradiation dose may result in the degradation of the already crosslinked CMC, and a slight reduction in the degree of gelation is observed.

Table I also shows the effect of preparation conditions on the swelling degree as a characteristic property of the prepared hydrogel. In general, it is clear that the increase in AMPS content, reaction medium concentration, as well as the irradiation dose increases the swelling ability of the prepared hydrogel.

The increase in the AMPS content in the reaction medium would increase the hydrophilicity of the prepared hydrogel expressed by increasing its swelling ability because of its high hydrophilic character. In addition, the increase in AMPS content results in the formation of much perfect crosslinking structure that is able to absorb and retain water. On the other hand, the increase in the irradiation dose increases the probability of CMC chain scission even after the formation of the network, which leads to the formation of looser network. These results come in good agreement with that obtained from studying the effect of irradiation dose on the gelation of CMC/AMPS copolymer.

Effect of hydrogel composition

The chelation of CMC/AMPS hydrogels of different compositions was investigated toward Cu^{2+}, Co^{2+}, Fe^{3+}, and Mn^{2+} by the batch equilibration method. The results show a clear dependence of metal ion uptake on the copolymer hydrogel composition. The amounts of metal ions chelated by the different hydrogels are given in Table II. From the table, the amount of metal ion uptake increases with increasing AMPS content. It is also clear that all of the hydrogels under investigation have hydrogels toward the metal ions of interest was in the following order $Fe^{3+}>Cu^{2+}>Co^{2+}>Mn^{2+}$. These results are in a very good agreement with relative size and crystal field radii of these hexacoordinated metal ions.[14]

Effect of the medium pH

It is well known that the pH is a critical parameter that can affect the chelating ability of the prepared hydrogel by influencing its swelling ability, formation of metal ions, as well as the interaction between the hydrogel and the metal ions. Figure 1 shows the effect of pH value of the swelling medium on the equilibrium swelling behavior of CMC/AMPS copolymer hydrogel. The data show a typical behavior of a pH-sensitive copolymer hydrogel. The pH sensitivity of such hydrogel is fully dependent on its composition. All of the investigated copolymer hydrogels possess abrupt change in the swelling degree at pH value around pH 2, which is the *pKa* value of AMPS.[15] At pH values lower than the *pKa* value, the sulfonic groups are associated, collapsed, and possess relatively low swelling degree. At pH values

TABLE II
Effect of CMC/AMPS Copolymers Composition on their Affinity to Selected Metal Ions

	Amount of metal ion recovered (mg/g)			
Sample code	Co^{2+}	Cu^{2+}	Fe^{3+}	Mn^{2+}
CAM 4	16.3	27.4	25.3	7.1
CAM 5	43.1	52.7	56.8	18.6
CAM 6	60.6	75.3	80.4	46.8

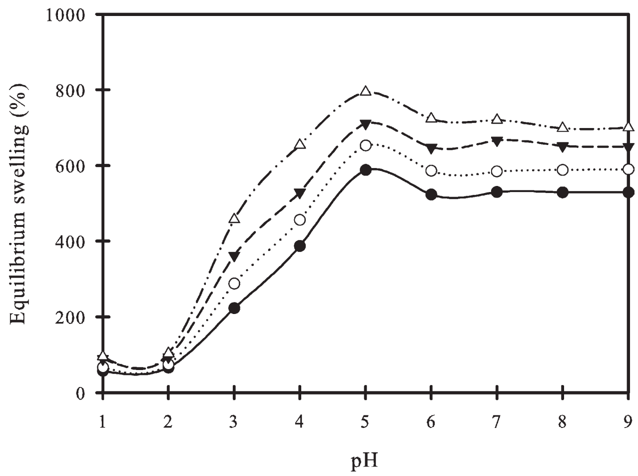

Figure 1 Effect of the swelling medium pH on the equilibrium swelling of CMC/AMPS copolymer prepared at different composition and irradiation doses. (•) CAM4, (○) CAM5, (▾) CAM6, and (Δ) CAM8.

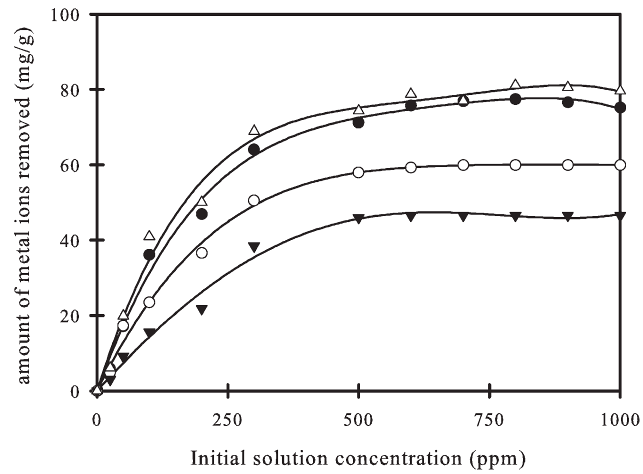

Figure 3 Effect of the metal ions initial concentration on the chelating ability of CAP6 hydrogel. (•) Cu, (○) Co, (▾) Mn, and (Δ) Fe.

higher than the *pKa* value, the swelling degree increased because of the dissociation of the sulfonic groups and broken the hydrogen bonding. The increase in the AMPS content in the hydrogel leads to the increment in the dissociated groups and consequently increases the electrostatic repulsion, which results in the expansion of the network structure.

On the other hand, Figure 2 shows the adsorption capacities of the prepared CMC/AMPS copolymer hydrogel toward Co^{2+}, Cu^{2+}, Fe^{3+}, and Mn^{2+} ions as the function of hydrogen ion concentration in the pH range of 1–5, with the initial metal concentration of 1000 ppm. It is clear that there is an obvious increase in metal adsorption amount when pH was raised from 1 to 5 except for Fe, which reach its maximum at pH 2. These adsorption trends could probably be affected by the competitive interaction between metal and hydrogen ions with the active sites located within the prepared hydrogel.[16,17] At lower pH, an excess of hydrogen ions can compete effectively with metal ions for binding sites, resulting in a lower level of metal uptake. It is well known that at the pH value higher than 6, the metal ions might precipitate, the presence of alkaline ions help to form the hydroxyl complexes.[18]

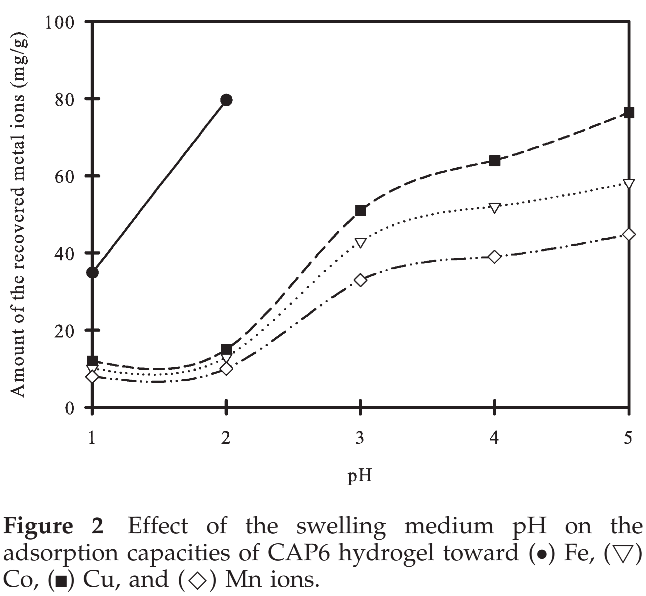

Figure 2 Effect of the swelling medium pH on the adsorption capacities of CAP6 hydrogel toward (•) Fe, (▽) Co, (■) Cu, and (◇) Mn ions.

Effect of initial solution concentration

Investigating the effect of the metal ions concentration on the chelating ability of the prepared hydrogels is an important experiment to estimate the efficiency of the hydrogel as a chelating material at low pollution levels. Figure 3 shows a sharp increase in adsorption capacity at low initial concentrations up to 300 ppm then it tends to level off at higher concentrations. At initial step, the adsorption capacity increases 10 folds as the solution concentration increases from 25 to 200 ppm whereas less than 50% increment in the adsorption capacity as the feed solution concentration increased to 1000 ppm. Such difference in the adsorption trend reveals the variety in the adsorption interactions that involves physical and chemical mechanisms.[19] The prepared hydrogel shows higher chelating ability at low metal ions concentrations, which indicate that the adsorption takes place by the electrostatic attraction (physical adsorption). On the other hand, at higher metal ion concentrations, the adsorption is relatively lower, which indicates that the adsorption takes place by the chelating interaction (chemical adsorption).

Langmuir isotherm is one of the most commonly used isotherms to evaluate the sorption capacity of the chelating material. From the linear form of this isotherm, equations can be written as follows:

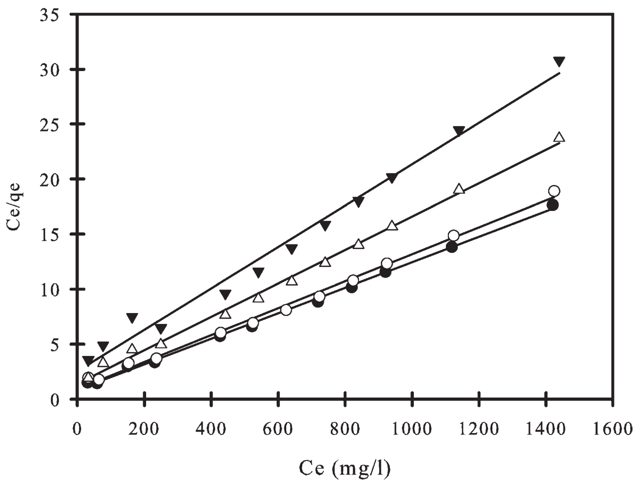

Figure 4 Plot of (C_e/q_e) against C_e for CAP6 hydrogel toward (•) Fe, (○) Cu, (▾) Mn, and (Δ) Co.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left[\frac{a_L}{K_L}\right] C_e,$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), and K_L and a_L are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. The linear plot of (C_e/q_e) against C_e (Fig. 4) for the metal ions under investigation shows that the adsorption data are well fitted by Langmuir isotherm model ($r^2 > 0.99$). The Langmuir constants were evaluated and reported in Table III. The ratio $[K_L/a_L]$ from the table is known as the capacity factor, which is the maximum adsorption capacity of the hydrogel toward particular metal ion.

Adsorption kinetics

The rapid interaction of metal ions with the adsorbent is very favorable for the feasible processes. The effect of contact time on the adsorption capacity of the prepared CMC/AMPS copolymer hydrogel toward Co, Cu, Fe, and Mn ions was shown in Figure 4. The amount of the absorbed metal ions increased sharply during the first 45 min and then slows down. Numerous researchers thought that the decrease of free chelating site resulted from polymer chains shrinkage that takes place as a result of the adsorption occurring at the polymer surface. So the cations were difficult to diffuse toward the adsorption sites located in the bulk of the hydrogel. In other words, at the beginning of the process, the adsorption occurs on the polymer surface, and so, a fast adsorption rate was found.[20,21] After that, the adsorption takes place at the inner surface of the polymer, and so, the adsorption rate was slow because of the pore diffusion of metal ions into the polymer matrix, i.e., intraparticular diffusion or chemical reaction (chelating or ion-exchange) would be the rate limiting step of sorption kinetics.

To interpret the mechanisms of metal adsorption processes, the adsorption data for heavy metals under investigation were analyzed by a regression

TABLE III
Langmuir Model

	Langmuir equation			Langmuir parameters		
	Slop	Intercept	r^2	K_L	a_L	K_L/a_L
Fe	0.011	0.85	0.998	1.176	0.013	90.91
Cu	0.012	0.94	0.995	1.064	0.013	81.97
Mn	0.019	2.50	0.990	0.400	0.008	52.63
Co	0.015	1.39	0.996	0.719	0.011	66.67

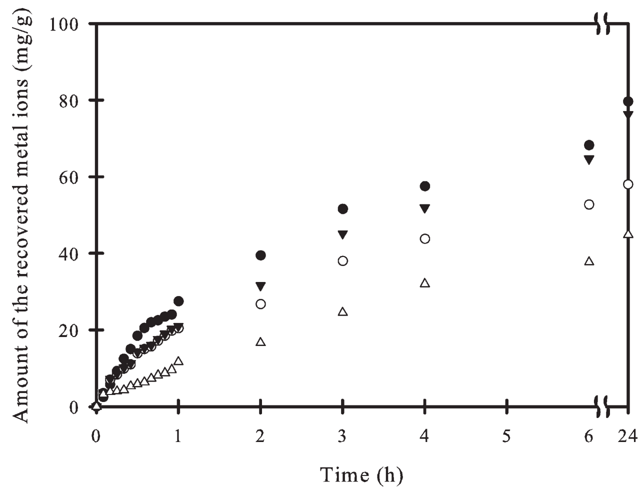

Figure 5 Effect of contact time on the adsorption capacity of the prepared CAP6 hydrogel toward (•) Fe, (○) Co, (▾) Cu, and (Δ) Mn.

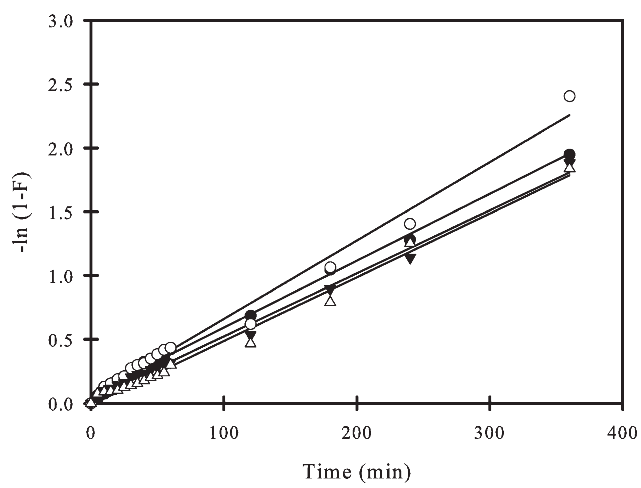

Figure 6 Adsorption rate curves of the prepared CAP6 hydrogel toward (•) Fe, (○) Co, (▾) Cu, and (Δ) Mn.

analysis to fit Langmuir and Freundlich models.[22,23] The linear form of these two isotherms, and its equations can be written as follows:

$$-\ln(1-F) = Kt + C),$$

where K is the equilibrium constant, and

$$F(t) = \frac{C_o - C_t}{C_o - C_e},$$

where C_o, C_t, and C_e (all in mg/L) represent the concentration of metal ions initially, in aqueous solution, at time t and at equilibrium, respectively. The experimental results of Figure 5 can be converted into the plots of $-\ln(1-F)$ versus t as shown in Figure 6, and the adsorption rate constants, rate of sorption (K_s), and rate of desorption (K_d) of the chelating hydrogel can be calculated from the slopes and intercepts of the plots as follows:

$$K_d = k\left(\frac{C_e}{C_o}\right) \text{ and } K_s = K - K_d.$$

Table IV shows the values of K_s and K_d, from which the following can be observed; the highest sorption rates (K_s) were found in case of the reaction with Fe and Cu revealing the high affinity of the chelating hydrogel for the adsorption of these metal ions.

Regeneration of CMC/AMPS copolymer

Currently, emphasis is given on recovery of the adsorbed metal ion rather than simple adsorption and disposal. Regeneration of the chelating hydrogels after metal sorption process without damaging or reducing their absorption capacity is a very important factor for the success of sorption technology development. Recovery of different metal ions adsorbed on CMC/AMPS copolymer hydrogel was carried out by 0.1M HNO_3 for 2 h, at room temperature. The regeneration stability was tested by applying the adsorption and desorption processes several times. The test shows that almost insignificant decrease in the sorption capacity on regeneration as shown in Table V.

TABLE IV
Adsorption Rate Constant of Different Metals on CAP6 Hydrogel

	K ($\times 10^{-3}$ s^{-1})	(C_e/C_0)	r^2	K_d (s^{-1})	K_s (s^{-1})
Fe	5.24	0.842	0.994	1.176	0.013
Cu	6.14	0.884	0.986	1.064	0.013
Mn	4.94	0.847	0.994	0.400	0.008
Co	4.99	0.910	0.989	0.719	0.011

TABLE V
Effect of Regeneration on the Efficiency of CAP6 Toward Different Metal Ions

	Amount of metal ion recovered (mg/g)			
Regeneration cycle	Co^{2+}	Cu^{2+}	Fe^{3+}	Mn^{2+}
1	60.6	75.3	80.4	46.8
2	60.4	75.2	80.1	46.5
3	59.9	75.0	79.8	46.0
4	59.3	74.7	79.1	45.8
5	59.1	74.2	78.9	45.6

CONCLUSIONS

CMC and AMPS were used to prepare chelating polymeric hydrogels by means of γ-rays-induced copolymerization and crosslinking. Characteristics and some properties of the prepared grafted polymers were investigated. The possibility of their applications in the removal of some heavy metals was studied. From the obtained results, it can be concluded that AMPS content is the main effective parameter for the affinity of the copolymer toward different metal ions such as Mn^{+2}, Co^{+2}, Cu^{+2}, and Fe^{+3} from their solutions. The data show that the affinity of the prepared hydrogels increases by increasing the AMPS content in the hydrogel as well as the increment in the pH of the solution and the metal ion concentration. The prepared CMC/AMPS copolymer hydrogels were also chemically stable enough to be reused for at least five times with the same efficiency.

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