

Application of Anionic Acrylamide-Based Hydrogels in the Removal of Heavy Metals from Waste Water

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ABSTRACT: Crosslinked acrylamide (AM) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) homopolymers and copolymers were prepared by free radical solution polymerization using *N,N'*-methylenebisacrylamide as the crosslinker. The chemical structures of hydrogels were characterized by FTIR analysis and the results were consistent with the expected structures. These hydrogels were used for the separation of Cd(II), Cu(II), and Fe(III) ions from their aqueous solutions. The influence of the uptake conditions such as pH, time and initial feed concentration on the metal ion binding capacity of hydro-

gel was also tested. The selectivity of the hydrogel towards the different metal ions tested was Cd(II) > Cu(II) > Fe(III). It was observed that the specific interaction between metal ions and ionic comonomers in the hydrogel affected the metal binding capacity of the hydrogel. The recovery of metal ions was also investigated in acid media. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2500–2510, 2012

Key words: hydrogel; 2-acrylamido-2-methylpropane sulfonic acid; acrylamide; waste water; adsorption; heavy metal

INTRODUCTION

Removal of heavy metal ions, both from waste water and natural waters, has gained importance to minimize the industrial and ecological waste problems. Copolymers having ion-exchange property find applications for removal of heavy metal ions from aqueous solutions.^{1–4} Noncompetitive adsorption is used to describe the behavior of metal ion removal from aqueous solution containing only one type of metal. The amount of metal removed by noncompetitive adsorption is about twice of that can be achieved by competitive adsorption.⁵

Metal ion chelation polymers, called polychelators, 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.⁶ Hydrogels containing amide, amine, carboxylic acid, hydroxyl, and ammonium groups can bind metal ions and be good polychelators for water purification applications.⁷ Acrylamide and its *N*-substituted derivatives are widely used for the synthesis of water soluble polymers and hydrophilic gels which find applications in various fields.^{8–10} Acrylamide monomers can easily copolymerized by classical free radical techniques under mild conditions with vari-

ous functional groups (ionizable, reactive, thermosensitive, etc.). 2-acrylamido-2-methylpropanesulfonic acid (AMPS) is of special interest because it is quite hydrolytically stable and bears a strong acid functionality. Applications of AMPS include its use in various hydrogels where pH-independent swelling behaviour has been observed.^{11,12} In this respect, this study aims to prepare crosslinked copolymers of AMPS with AM in the presence of *N,N'*-methylenebisacrylamide (MBA) crosslinker to remove toxic heavy metal ions from waste water through complexation and ion exchange mechanism.

EXPERIMENTAL

Materials

Acrylamide (AM, Sigma) was crystallized from acetone/ethanol mixture (70/30 by volume) below 30°C. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS, Sigma) was recrystallized twice from a mixture of methanol and 2-propanol or boiling methanol. The crosslinker *N,N'*-methylenebisacrylamide (MBA, Sigma) was recrystallized twice in water. Potassium persulfate (KPS) was recrystallized from deionized water before use. Hydrochloric acid (Merck) was used as a desorption agent. Deionized water of 18.2 MΩ cm, resistivity obtained from a Milli Q-water purification system (Millipore) used for the preparation of all solutions. Buffer solution with ionic strength of 0.2M (citric acid/trisodium citrate) and 0.2M (sodium dihydrogen phosphate/di-sodium hydrogen phosphate) were used to prepare

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buffer solutions ranged from 3 to 6 and 6 to 10, respectively. 0.2M HCl was used to prepare solutions of pH 1–3.

Atomic absorption spectrophotometer standard solutions of 1000 mg/L Cd(II), Cu(II) and Fe(III) were purchased from Merck. Other dilute standard solutions were prepared from these stock solutions.

All other chemicals were Prolabo products and were used as received.

Synthesis of hydrogels

Preparation of crosslinked PAMPS

Crosslinked PAMPS hydrogel was prepared by free radical solution polymerization of AMPS monomer (50 wt %) in the presence of water as solvent. Different weight percentages (1–10 wt %) of MBA crosslinker were added and 0.1 wt % of KPS was used as initiator at 60°C under a nitrogen atmosphere in cylindrical glass tubes. The time of reaction was extended to ensure a complete polymerization of monomer. The amount of the initiator and crosslinker was calculated with respect to the monomers. The procedure of preparation and purification was discussed in the previous work.¹²

Synthesis of crosslinked AM/AMPS

AM/AMPS crosslinked copolymer was carried out in water, as the solvent, at 40°C in the presence of 0.1 mol % with KPS as the initiator. AMPS content of the monomer mixture was varied from 0 to 100 mol%. The crosslinker ratio (mole ratio of the crosslinker MBA to the monomers AM/AMPS) and the total monomer concentrations were fixed at 10 wt % in distilled water solution. The procedure to prepare AM (50 mol %)/AMPS (50 mol %) described as following: AM (2.84 g), AMPS stock aqueous solution (25.0 mL, 8.28 g of AMPS in 16 mL of distilled water), MBA (0.1112 g), and KPS stock solution (3.2 mL) were dissolved in 84 mL of distilled water at 10°C. The solutions bubbled under nitrogen for 20 min, the solution was poured into several glass tubes of 11 or 5.5 mm internal diameters and about 250 mm long. The glass tubes were sealed and immersed in water bath at 40°C, and the polymerization was conducted for predetermined reaction times. The polymer rods were post-cured at 105°C in an air oven for 24 h to ensure complete polymerization. The rods were cut to thin discs that were used for determining the soluble fraction (SF%) and swelling parameters.

Characterization

FTIR spectrum was recorded on Shimadzu 8303 FT-IR Spectrometer.

A Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer (FAAS) equipped

with deuterium lamp for continuous background correction was used.

SEM imaging of the hydrogels was performed on a JSM-5600LV (JEOL, Japan) instrument at 20 kV. The specimens were prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å.

Sol Fraction

The polymer rods were post-cured at 105°C in an air oven for 24 h to ensure complete polymerization. These rods were cut to thin disks and dried in vacuum at 60°C to a constant weight. Cylindrical hydrogels were cut with a length of 10 mm. The dried xerogel discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with deionized water at 100°C. After extraction for 24 h, the disks were dried under atmospheric pressure for several hours and then dried to a constant weight in a vacuum oven at 60°C. The sol fraction, SF, was expressed as the fractional loss in weight of xerogel, eq. (1):

$$\%SF = [(W_0 - W)/W_0] \times 100 \quad (1)$$

where W_0 and W are the weights of the disk before and after extraction, respectively.

Swelling behavior of the hydrogels

The mass swelling of the hydrogels were measured in deionized water and in various pH mediums ranging from 2 to 12. The hydrogel samples were placed in vials filled with 25 mL of deionized water or different buffer solutions. The vials were placed in a temperature-controlled bath at 25°C. The hydrogel samples were periodically removed from the vials, wiped with filter paper to remove the superficial water or buffer solution, weighed and then placed in the same vials. The equilibrium water content, EWC, and mass swelling of the hydrogels (q) were calculated from the eqs. (2) and (3):

$$EWC(\%) = [(m_t - m_0)/m_0] \times 100 \quad (2)$$

$$q(g/g) = m_t/m_0 \quad (3)$$

where m_0 and m_t are the initial mass of the hydrogel and the mass of the hydrogel at time t , respectively.

Single-component heavy metal adsorption

The adsorption properties of hydrogels for metal ions Cd(II), Cu(II), and Fe(III) were examined in the batch experiments. To investigate the optimum pH for maximum adsorption, the dry gel samples were immersed in 1000 mg/L single ion solutions at pH

from 1.0 to 5.5 at room temperature for 24 h. The effect of the initial heavy metal ion concentration on the adsorption capacity was also studied. In this case, the dry hydrogels were equilibrated for 24 h in 5–5000 mg/L heavy metal ions prepared in buffer solution at pH 5.0 for Cd(II) and Cu(II) and at pH 2.5 for Fe(III). The flasks were stirred magnetically at 200 rpm. After equilibrium was attained, aqueous phases separated from the hydrogels and the concentration of Cd(II), Cu(II), and Fe(III) ions were analyzed using a Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer via applying a deuterium background correction. The instrument response was periodically checked with known heavy metal solution standards.

The amount of metal ion adsorbed (mg/g) were calculated using the eq (4):

$$Q = [(C_0 - C) \times V] / [(m \times 1000)] \quad (4)$$

where C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the adsorption period, respectively (mg/L); V is the volume of the aqueous phase (mL); and m is the amount of dry hydrogel (g).

Multicomponent heavy metal adsorption

Adsorption of heavy metal ions from synthetic wastewater was carried out in a batch system. The concentration of metal ions in synthetic wastewater is 1000 mg/L for each of Fe(III), Zn(II), Co(II), Pb(II), Mn (II), Na(I), Cd(II), and Cu(II). To adjust salinity, 700 ppm of NaCl was added to the synthetic wastewater. A dry hydrogel sample, after removal of SF and drying in vacuum oven, was transferred into 10 mL of synthetic wastewater, stirred and incubated at room temperature (pH 5.0). After adsorption, the concentration of the metal ions in the remaining solution was determined by FAAS as described earlier.

Recovery and reuse

Hydrogels loaded with metal Cd(II), Cu(II), and Fe(III) ions (0.1 g) were stirred with HCl solution (10 mL, 2 N) at room temperature for 2 h to desorb the metal ions. The final metal ion concentration in the aqueous phase was determined using a FAAS. The desorption ratio was calculated by the following equation: Desorption ratio = [(amount of metal ions desorbed into the elution medium)/(amount of metal ions adsorbed onto the hydrogels)] \times 100. Thereafter, the hydrogel was neutralized after recovery with 2N HCl with dilute NaOH, washed with deionized water and again subjected to adsorption processes to determine the reusability of the hydrogels. Adsorption–desorption cycles were repeated

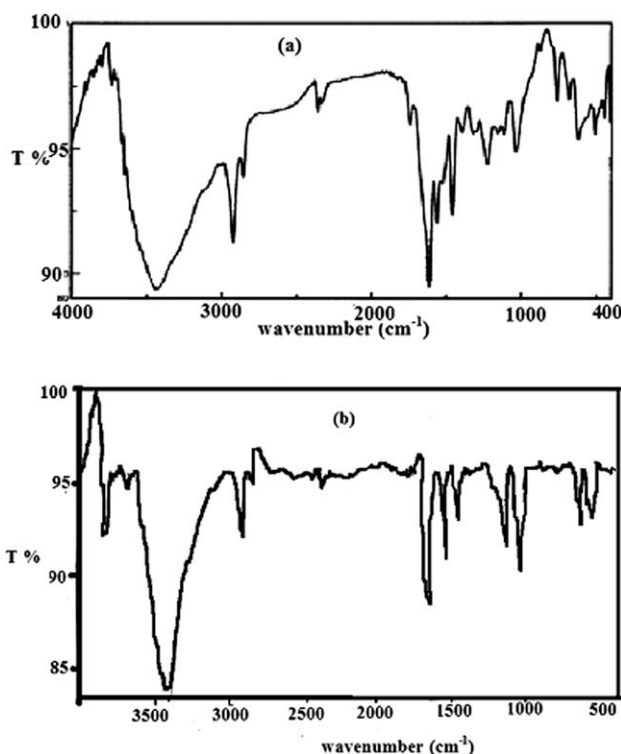


Figure 1 FTIR spectrum of crosslinked (a) PAMPS and (b) AM (50 mol %)/AMPS (50 mol %) crosslinked with 1 wt % of MBA.

five times by using the same hydrogels. Every hydrogel sample was treated before each test as described previously.

RESULTS AND DISCUSSION

Low conversion linear AM/AMPS copolymers (<10%) were prepared in the presence of water and reported in the previous work.¹² FTIR was used to determine the reactivity ratios and percentage of the components in AMPS/AM copolymer. The data show that the average values of r_1 and r_2 for AM 1/AMPS 2, obtained by the Fineman-Ross and Kelen-Tudos methods, are 0.95 and 0.27, and 1.530 and 0.105, respectively. The data indicates that the AMPS/AM has random copolymer structure and high AM content.¹² The chemical structure of the crosslinked PAMPS, PAM, and AM/AMPS copolymers were investigated by FTIR spectra. IR spectra of PAMPS and AM (50 mol %)/AMPS (50 mol %) crosslinked with 1 wt % of MBA were selected and represented in Figure 1. Careful inspection of FTIR spectra indicates that the disappearance of bands at 3050, 1600, and 950 cm^{-1} which attributed to =CH stretching, C=C stretching, and =CH (out of-plan-bending), respectively; refers to the complete polymerization of monomers and MBA crosslinker. The absorption bands at 1457 and 2925 cm^{-1} are observed in all spectra that attributed to CH_2

TABLE I
SF Content and Swelling Parameters of Crosslinked PAM, PAMPS, and AM/AMPS
in Aqueous Solution at 25°C

Copolymer compositions (AM/AMPS)	Crosslinker contents (wt %)	SF (%)	Swelling parameters	
			EWC (%)	q (g water/g polymer)
0/100	1.0	29.74	99.9	1449.1
	2.0	19.25	99.9	1199.2
	4.0	15.07	99.9	840.6
	10.0	10.52	99.8	598.4
	20.0	8.10	99.7	362.7
10/90	10	18.99	99.40	165.57
30/70	10	15.19	99.20	125.24
50/50	0.5	19.27	99.24	132.17
	1	18.12	99.05	105.11
	3	17.23	99.02	101.80
	5	15.78	98.94	93.91
	10	14.58	98.82	84.76
70/30	10	12.52	98.74	79.48
90/10	10	10.38	98.26	57.43
100/0	1	11.04	98.66	75.11
	2	9.85	98.58	70.80
	4	8.17	98.43	63.91
	10	5.42	97.56	40.76
	20	3.14	97.14	35.20

asymmetric bending and asymmetric stretching respectively. On the other hand, the absorption bands at 1394 and 2855 cm^{-1} can be referred to CH_3 symmetric bending and symmetric stretching of AMPS monomer. The absorption bands at 618, 1034, and 1040 cm^{-1} appeared in the spectrum are assigned to the S—O stretch, S=O asymmetric stretch, and symmetric stretch of sulfonic acid groups, respectively. The absorption band at 1613 cm^{-1} the so-called amide I mode is mode with contributions of the C=O stretching modes, amide II bands at 1560 cm^{-1} , and the N—H band at about 3431 cm^{-1} , the appearance of these bands indicates the contribution of AMPS in the crosslinked polymers. The characteristic absorption peak of AMPS units is shown at 1040 cm^{-1} due to the SO group. The intensity of this peak was normalized using the C=O stretching peak of both AM and AMPS units at 1660 cm^{-1} . The calculation of the absorbance at 1040 and 1660 cm^{-1} (A1040 and A1660, respectively) was performed using the base-line method.¹³

This work aims to study the affinity of crosslinked PAM, PAMPS, and AM/AMPS copolymers towards MBA crosslinker through measuring soluble fraction contents (SF %). In this respect, SF % was determined by measuring the soluble materials through Soxhlet extraction using water as solvent. SF values of PAM, PAMPS, and AM/AMPS gels were determined and are listed in Table I. It was noted that SF values decrease with increasing amounts of crosslinker concentrations. This can be attributed to the high reactivity of MBA crosslinker towards acrylate

monomers.¹⁴ On the other hand, it was found that the crosslinked PAM have lower SF values than PAMPS and AM/AMPS copolymers. This can be attributed to the high reactivity of the PAM towards acrylate crosslinker.¹⁵ The efficiency of crosslinking was referred to reactivity of MBA crosslinker towards PAM, PAMPS homopolymers, and AM/AMPS copolymers. The data of SF %, Table I, can be used to arrange MBA reactivity toward the present polymers in the order PAM > AM/AMPS > PAMPS. Accordingly, MBA is suitable to use as a crosslinker for AM/AMPS copolymers due to its capability to copolymerize well with AM and AMPS homopolymers and copolymer.

Morphology of the crosslinked polymers

It is now well understood that a phase separation during the network formation process is mainly responsible for the formation of porous structure in dried state. Depending on the synthesis parameters, phase separation takes place on a two cases of macroscale or microscale. In the first case, when the network starts to form crosslinked structure, the network collapses at the critical point for phase separation and becomes a microsphere. The separated liquid phase was remained as continuous phase in the reaction system. As the reaction proceeds, new microspheres are continuously generated due to successive separation of the growing polymers. Agglomeration of microspheres leads to formation of a macroporous network consisting of two

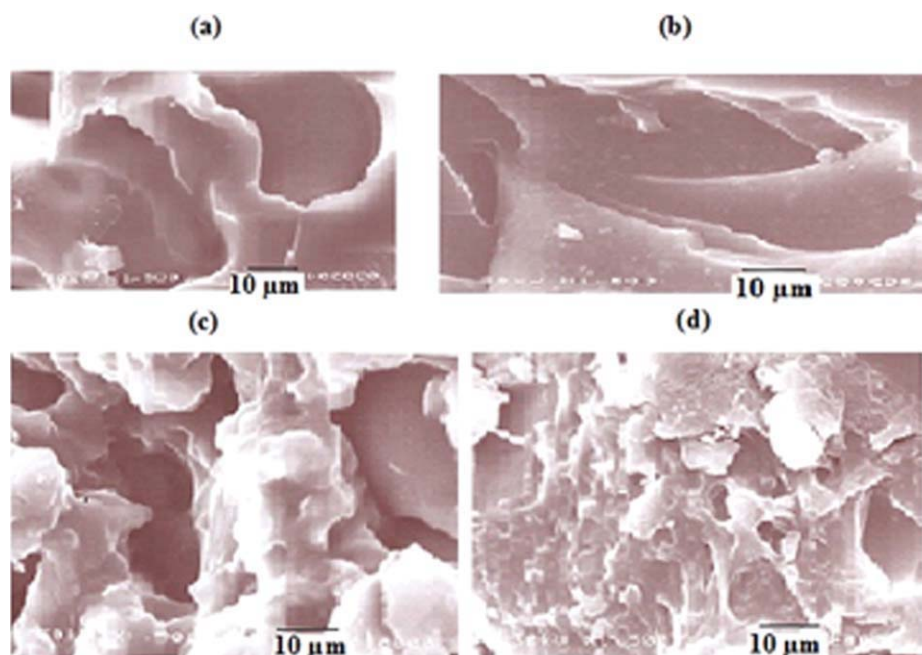


Figure 2 SEM micrographs of crosslinked (a) PAMPS, (b) PAM, (c) AMPS (90 mol %)/AM (10 mol %), and (d) AMPS (10 mol %)/AM (90 mol %) with (10 wt %) of MBA crosslinker. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

continuous phases. In the second state, phase separation results in the formation of a dispersion in the reaction system. Thus, the liquid phase during the gel formation process separates in the form of the small droplets inside the gel and become discontinuous. Because of slowness of the volume change of the gel sample, the initiator of the sample is initially under constant volume condition; further polymerization and crosslinking reactions fix the two phase structure in the final material. The structural morphology of PAMPS, different AM /AMPS copolymers and PAM, was studied by SEM and represented in Figure 2. The SEM micrographs of the hydrogels revealed a porous internal structure. The porosity confirmed the three-dimensional structure of the hydrogels. SEM micrographs clearly illustrated the dependence of hydrogels morphology on the AMPS and AM contents. It was observed that PAMPS displays a more open and porous channel structure than PAM. The hydrogels morphology can be correlated with data of SF% values that obtained from Soxhlet extraction and represented in Table I. Large pores were formed with increasing AMPS content in copolymers in the presence of MBA, while microspores were formed when AM content was increased in the crosslinked copolymers. This can be attributed to the high affinity of copolymer having high content of AM towards crosslinking which agree with data of SF% values. Accordingly, the formation of heterogeneous and microsphere of

AM/AMPS networks can be proposed. When the polymerization is initiated by the decomposition of KPS initiator, the primary radicals formed start to grow by adding the monomers of AMPS and AM and the crosslinker. Initially, the primary molecules contain AM/AMPS, AMPS, AM units and MBA units with two pendant vinyl groups involved in cycles. As the reaction time proceeds, more primary molecules are formed so that the intermolecular crosslinking reactions between the primary molecules may be occurred during the polymerization. The importance of cyclization reactions in free radical crosslinking copolymerization was indicated in previous studies.^{16,17} Thus, cyclization clearly dominates over the intermolecular crosslinking reactions. Since every cycle reduces the coil dimension of the molecule as well as the solvent content inside the coil, the structure of the formed polymers is rather compact and can be considered as clusters. The microspheres are nonporous and constitute the highly crosslinked region of the network. The agglomeration of the microspheres during crosslinking polymerization through their peripheral pendant vinyl groups and radical ends leads to the formation of large, unshaped, discrete agglomerates, which are further agglomerated to form the final network. Macropores constitute the interstices between the microspheres while the voids between the agglomerates build the large pores in the network.

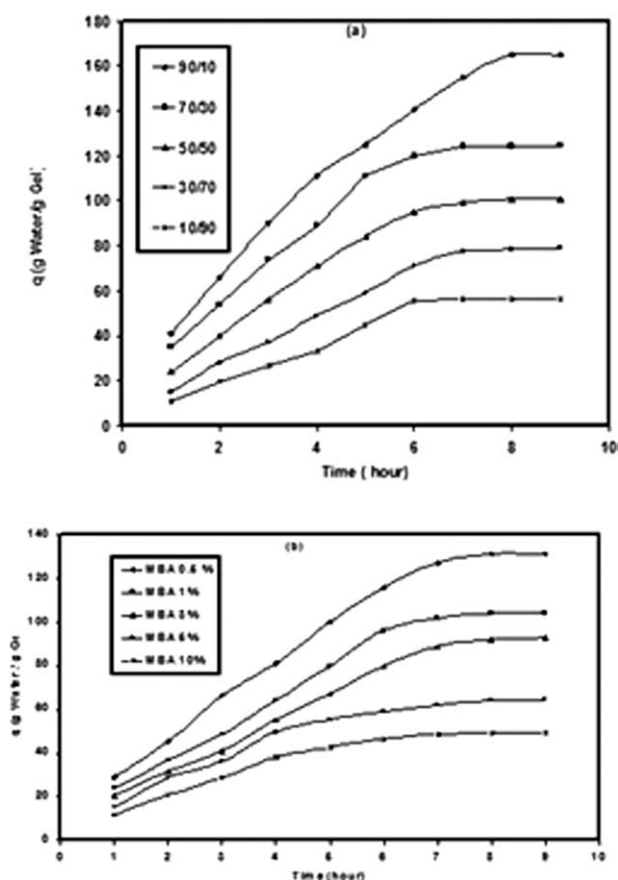


Figure 3 Swelling ratios versus time for crosslinked AM/AMPS copolymers (a) having different AMPS contents and (b) AM (50 mol %)/AMPS (50 mol %) crosslinked with different wt % of MBA at 25°C.

Swelling parameters of AM/AMPS

EWC and swelling ratios (q) in water were calculated and listed in Table I. Figure 3 shows the relation between q and the swelling time. The relation between q and AMPS content was illustrated in Figure 4. The data show how the swelling ratios (q) of the hydrogels varied with their AMPS content. Figure 4 illustrates that, contrary to the classical theory of swelling equilibrium,¹⁶ the equilibrium degree of swelling is not a monotonically increasing function of the ionic group content of the hydrogels. The dependence of the gel swelling on the charge density illustrated in the three stage curves. First, the degree of swelling increased sharply with increasing ionic group content of the hydrogels until a plateau is reached at about 30 mol% AMPS. Second, between 30 and 50 mol% AMPS, the equilibrium gel swelling in water (Fig. 4) is independent of the ionic group content of the hydrogels. Third, further increase in the AMPS content beyond this value increases the gel swelling continuously up to 100 mol % (Table I). Increasing degree of equilibrium swelling with increasing ionic group content of the hydrogels is

expected. This is a consequence of the osmotic pressure exerted by counter ions of the AMPS units in the network chains. The osmotic pressure increased as the concentration difference of the counter ions between the inside and outside the gel phase increased. Accordingly, the swelling behavior of the hydrogels prepared at low and high concentration of AMPS is expected. The relation between swelling ratio q versus AMPS mol %, shown in Figure 4 by the solid curve, gives a scaling relation q is directly proportional to AMPS mol % (0.63). This means that the scaling parameter is 0.63 and the relation between q and AMPS mol % does not linear. This stands in contrast to that predicted by the Flory–Rehner theory, if applied to highly swollen hydrogels,¹⁸ $q \propto \text{AMPS mol\%}^{1.5}$. Results obtained with poly(acrylic acid) (PAAc) hydrogels¹⁹ as well as with AMPS/*N,N*-dimethylacrylamide based hydrogels²⁰ gave a scaling parameter 0.6, which is close to the value found in this work. We believe that the deviation between the theory and experiment originates from the existence of “wasted” counter ions in the hydrogels.²¹ As seen in Figure 4, the hydrogels prepared between 30 and 50 mol % AMPS exhibit the same degree of swelling. In weak electrolyte hydrogels, the appearance of a plateau region in the swelling curve was observed previously. Silberberg et al.¹⁹ reported that the equilibrium swelling degree of PAAc hydrogels first increases when the ionization degree (ID) of AAc units increases from 0 to 0.35; then, the gel swelling reaches a plateau up to ID = 1. For the same hydrogels, Tong and Liu²² reported that the gel swelling is independent of a between ID = 0.2 and 0.6. Konak and Bansil²³ observed a broad minimum in the swelling curve of poly(methacrylic acid) hydrogels between ID = 0.1 and 0.2, whereas the degree of swelling begins to decrease for ID = 0.2. This feature of the hydrogels may be related to the “counter ion condensation” or to the limited

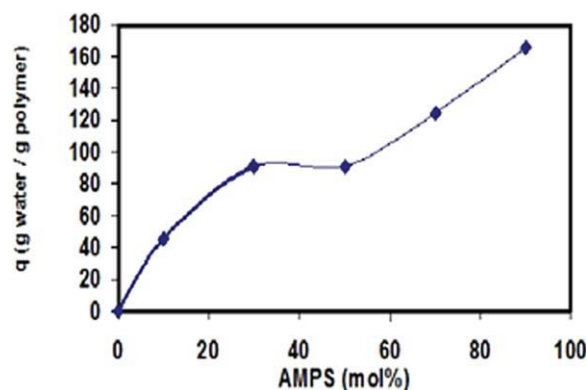


Figure 4 The swelling ratio of the AM/AMPS hydrogels as a function of their AMPS contents at 25°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

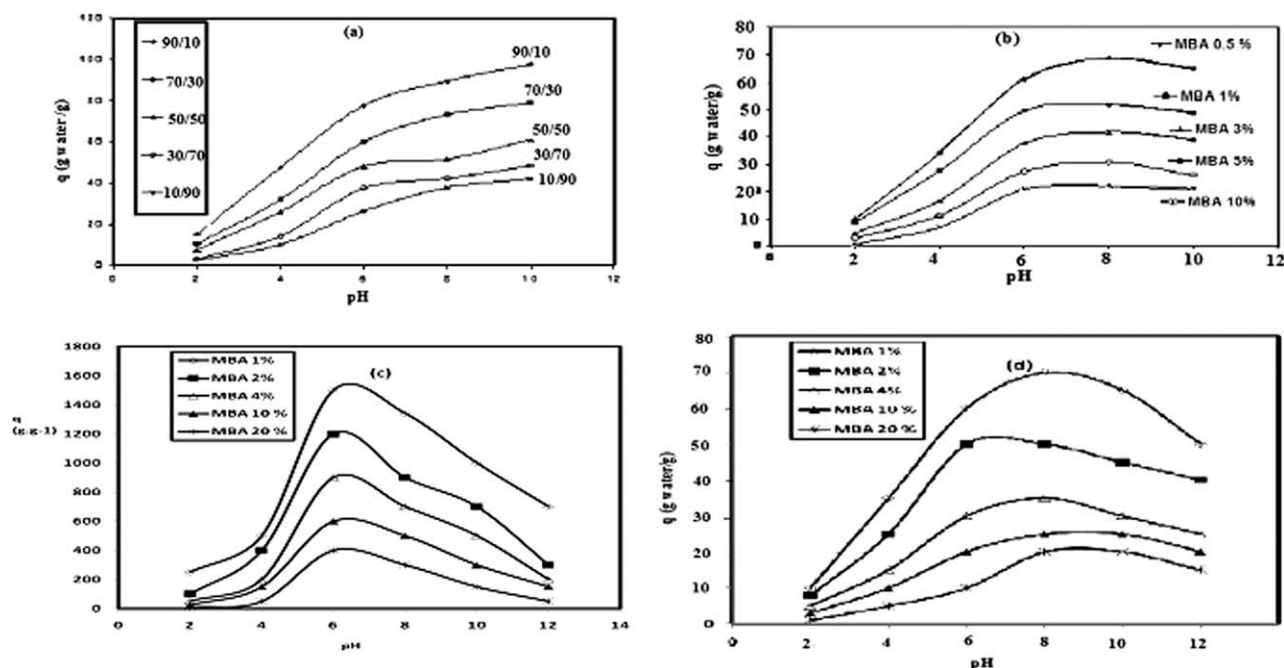


Figure 5 Swelling ratios and pH dependent of (a) AM/AMPS, (b) AM (50 mol %)/AMPS (50 mol %), (c) PAMPS, and (d) PAM crosslinked with different wt % of MBA at 25°C.

extensibility of the network chains.²⁴ On the other hand, the hydrophobic interactions between the alkyl groups of the AMPS units lead to the formation of aggregates; the counterions in these aggregates may condensed and lead to a decrease in the osmotic pressure. Gel heterogeneities may also be responsible for this phenomenon.²⁵ The counter ions in the highly crosslinked (less swollen) regions of the gel may condensed on the network chains and become passive in the gel swelling.

Effect of pH on the swelling parameters

Polyelectrolyte hydrogels are based on charged networks that contain ionized groups. Negatively or positively charged hydrogels usually exhibit different degrees of equilibrium swelling at different pH values depending on the ionic composition of the polymers. Conventional pH-sensitive polymers are mostly based on those containing ionizable groups of a base (amino group). In AM/AMPS copolymers there are different ionic contents such as SO_3H , and weak base amide and it is expected that the ionic content will change their swelling equilibrium at different pH media. AMPS received attention in the last few years due to its strongly ionizable sulfonate group; AMPS dissociates completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH independent swelling behavior. Effect of pH on the swelling ratios of the crosslinked AM/AMPS and PAMPS hydrogels is shown in Figure 5(a–c). The swelling measurements were carried

out using buffer solution as described in the Experimental section. As we can see, the swelling ratios of AM/AMPS and PAMPS gels crosslinked with 10 wt % of MBA crosslinker attain a maximum value at pH 7. Three different pH swelling dependant were observed for crosslinked PAMPS and AM/AMPS copolymers. It was observed that the swelling ratios increased with increasing pH of solution up to 12. On the other hand, the q values were reduced with increment of MBA content above 3 wt % as represented for crosslinked AM (50 mol %)/AMPS (50 mol %) copolymers [Fig. 5(b)]. The swelling ratios q values for crosslinked PAMPS were decreased with increasing pH of solution above 7. This result can be explained on the basis that the presence of SO_3H groups have low tendency to dissociate at low pH aqueous solution due to the presence of strong hydrogen bonds between SO_3H and amide groups of AM. Increasing the pH of the external solution increases the ion dissociations of SO_3H and, consequently, the charges on the polymeric chains increased. Since PAMPS is a strong organic acid and is in the molecular state at $\text{pH} < \text{p}K_a = 3$,²⁶ there is a strong hydrogen bonding between the SO_3H group of the PAMPS and $-\text{CONH}$ group of the AM. This increases the gel expansions and, consequently, the swelling capacities of the gel were gradually increased. Finally, in a high alkaline environment ($\text{pH} > 10$), the Na salt screens ionic interaction and the gel behaves as if it was uncharged. Hence, the swelling ratio of the gel decreases rapidly under this condition. It was reported that²⁷ the linear polymers

with sulfonate groups derived from AMPS exhibit extensive coil expansion in aqueous solutions; even in a 5M NaCl solution, the expansion of polymer coils due to charge repulsion cannot be totally screened. The stepwise gel expansion of AM/AMPS copolymers having different AMPS contents [Fig. 5(a)] is probably due to the delayed acid dissociation of the pendant SO_3H groups.²⁸ The delayed acid dissociation of AM/AMPS gels is explained on the basis that the first dissociation of few acids SO_3H affects the pK_a of the remaining pendant acids by shielding of the residual acid units of the same polymer. Therefore, the charged $-\text{SO}_3^-$ groups formed during the acid dissociation process may have a greater shielding effect on the remaining pendant acid groups. It is well known that the delayed acid dissociation occurs for flexible chains.²⁹ It is believed that AM/AMPS copolymers having low MBA contents are more flexible than those crosslinked in the presence of high MBA crosslinker contents. The presence of sulfonate groups causes a modification of the physico-chemical properties as well as flexibility of the polymer chain.³⁰

Application of AM/AMPS copolymers for heavy metal adsorption

Metal ion uptake on hydrogels can be affected by hydrophilic-hydrophobic balance, the nature of monomer and the extent of crosslinking of macromolecular supports. In this study, AM/AMPS resins were selected due to hydrophilicity to determine the metal ion uptakes. It is well known that the pH is a critical parameter that can affect the hydrogel performance and influence its swelling and ion uptake capability. In this study, metal ion uptake for AM/AMPS hydrogels was examined at different pH ranged between 3.0 and 5.5 for Cd(II) and Cu(II) metal ions and from 1 to 3 for Fe(III) ion at concentration of 1000 mg/L. The curves were not represented here for brevity. The data indicated that the rapid interaction of metal ions with the adsorbent is very favorable for the feasible processes. Moreover, it was noted that the adsorption capacity of the AM/AMPS hydrogels was increased with increasing pH. The results also show that the maximum adsorption values of the metal ions were obtained at pH 5.0 for Cd(II) and Cu(II), and 2.5 for Fe(III). For Fe(III), adsorption experiment could not be performed at $\text{pH} > 3$ due to the insolubility of the metal hydroxide. An increase in pH decreases the competition of H^+ ions for the resin sites and the complex formation of the metal ion is favored. The maximum binding of all the metal ions occurred within the first 3 h and remained uniform throughout the 24 h. The adsorption rate of Cd(II) is higher when compared with Cu(II) and Fe(III) ions. More-

over, the adsorption capacity of the hydrogel was increased with increasing pH. The amide groups of AM and $-\text{SO}_3\text{H}$ groups of AMPS comonomer in the hydrogel structure are primarily responsible for the specific binding of metal due to the coordination between metal ions and $-\text{CONH}-$, $-\text{CONH}_2$, and $-\text{SO}_3\text{H}$ groups. The dependence of adsorption capacity of the hydrogel onto the initial concentrations of metal ions was determined by equilibrating the fixed amount of the hydrogel with a series of metal ion solutions of gradually increasing concentration. Adsorption capability of the hydrogel towards Cd(II), Co(II), and Fe(III) ions with different initial ion solution concentrations varying from 5 to 3000 mg/L was measured and represented in Figure 6. All measurements were performed at optimum pH as illustrated in the previous section. As

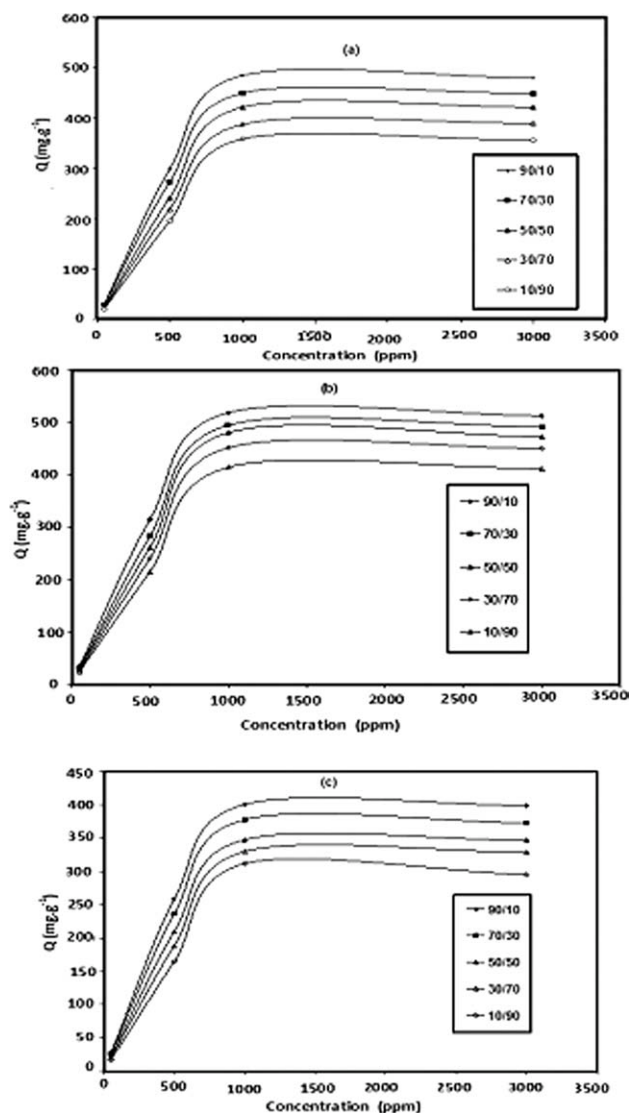


Figure 6 Metal ion uptakes of crosslinked AM/AMPS at different concentrations of (a) Cd (II) of pH 5, (b) Cu (II) of pH 5, and (c) Fe(III) of pH 2.5 at 25°C.

expected the maximum metal ion uptake was achieved by using AM (10 mol %)/AMPS (90 mol %) hydrogel, which possesses the highest AMPS content. The AMPS comonomer in the hydrogel structure is primarily responsible for the specific binding of the metals due to the coordination between metal ions and the sulfonic acid groups. Moreover, increasing of AMPS content caused increment in the cation exchange capacity of the synthesized resins. At lower pH values the sulfonic group is protonated and metal ions must compete with the proton.³¹ On the other hand at higher pHs, sulfonic acid groups of hydrogel are ionized, therefore, formation of specific interaction with metal ions is more pronounced. Figure 6 indicated that the metal uptake increased rapidly with increasing initial metal ion concentration up to 1000 mg/L. From these plateau values, the maximum load capacities were measured as 510.8, 480.5, and 400.2 mg/g dry hydrogel for Cd(II), Cu(II) and Fe(III) ions, respectively. The data indicated that the synthesized hydrogel exhibits the strongest affinity for Cd(II). The affinity order of metal ions is Cd(II) > Cu(II) > Fe(III), which is mainly dependent on polarity, electronic configuration, ionic radius, etc., and also on the nature of interaction with the functional groups of the hydrogel.^{32,33} By comparing the metal adsorption capacities of AM/AMPS with the data reported on *N*-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid (NVP/AAC/AMPS)-based hydrogels,³⁴ it was found that the same selectivity of the hydrogel towards the different metal ions tested was Cd(II) > Cu(II) > Fe(III). While, the removal of Fe(III), Cu(II), and Mn(II) from aqueous solution by the prepared poly(vinylpyrrolidone/acrylic acid) (PVP/AAC) copolymer/PVP/AAC chelating hydrogel was examined by batch equilibration technique.³⁵ The results show that the removal of the metal ion followed the following order: Fe(III) > Cu(II) > Mn(II). The amounts of the removed metal ions increased with treatment time and pH of the medium. These results are in a very good agreement with relative size and crystal field radii of these hexa-coordinated metal ions.³⁶ The adsorption capacities of the NVP/AAC/AMPS hydrogels³⁴ at optimum pH are 74.12 mg/g for Cd(II), 62.74 mg/g for Cu(II) and 25.28 mg/g for Fe(III). It appears that the synthesized hydrogel exhibits the strongest affinity for Cd(II). In the present system of AM/AMPS hydrogels show high metal adsorption capacity than the reported systems. This can be attributed to morphology of the prepared AM/AMPS hydrogels, which indicated that large pores were formed with increasing AMPS content in copolymers in the presence of MBA (as described in the previous section). Hence, the size of hydrated metal ions also becomes an important factor.³⁷ Hence, hydrated Cd (II) ions

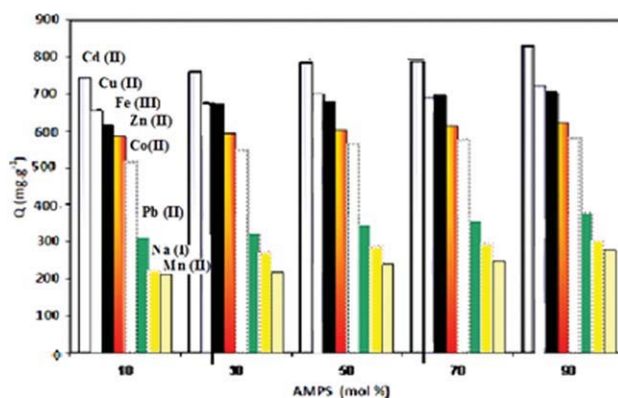


Figure 7 Effect of multimetal ion concentration on metal uptake capacity of AM/AMPS hydrogels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

being smaller are sorbed more in the smaller pores of hydrogels as compared to the larger hydrated Cu (II).

These results showed that the AM/AMPS hydrogels can be used to remove such metals from wastewater. Since various ions are present in the wastewater, it is essential to investigate the competitive binding affinity of these ions towards hydrogel. The results show that the binding capacities of all ions were decreased under the competitive conditions. Since various ions are present in the wastewater, it is essential to investigate the competitive binding affinity of these ions towards hydrogel. It was reported that, different factors, such as hydrogel structure, metal combination, level of metal concentration, uptake time, and experimental conditions affects the interaction between the metal ion and the reactive sites at hydrogel.³⁸ In the present system, AM/AMPS hydrogels were used to investigate the competitive binding affinity of ions in the waste water. The data were collected and represented in Figure 7. The results show that the binding capacities were 730–800 mg/g for Cd(II), 650–720 mg/g for Cu(II), and 610–700 mg/g for Fe(III). In this case, the hydrogel also adsorbed other metal ions Zn(II), Mn (II), Co(II), Pb(II), and Na(I), the binding capacities were 580–620, 610–680, 500–581, 300–350, and 200–280 mg/g, respectively. The selectivity of the metal adsorption capacities of AM/AMPS hydrogels can be arranged in the following order Cd (II) > Cu(II) > Fe(III) > Zn(II) > Mn (II) > Co(II) > Pb(II) > Na(I). These trends can be explained based on the electrochemical series activity. In this context, Cu(II) is beneath hydrogen in the direction of increasing strength of oxidation with standard reduction potential of +0.337 V. Therefore, the H atom of SO₃H of AMPS is easily replaced by Cu(II) effectively. However, Co(II) metal is above hydrogen in the electrochemical series activity in the direction of increasing

strength of reduction with standard reduction potentials of -0.28 V. Also, both metal ions are beneath sodium in the series with standard reduction potential of -2.764 V. Thus, sodium is effectively replaceable by other metal ions than the H atom of SO_3H of AMPS. From a mechanistic view point, the order of increasing binding capacities does not exhibit classical ion-exchange behavior, where the affinity is proportional to ionic charge only. The copolymer does however exhibit an order of affinity in accordance with the increasing acidity and polarizability of the divalent metal ions measured, similar to that described by the Irving-Williams series.³⁹ The monovalent alkali metal ions have a higher capacity than the divalent alkaline earth metal ions due to the influence of ion-exchange behavior and the greater concentrations required to balance the charge with the copolymer hydrogel. It is likely that Cd and Cu also have increased affinity due to coordination (formation of inner sphere complexes) with the carboxylic acid groups.⁴⁰ Previous studies⁴¹ have shown that the amide group in polyacrylamide does not interact significantly with metal ions. The amide groups may play a secondary role in the complexation of the transition metals alongside the carboxylic acid groups however. Consequently, the adsorption capacity of metal ions is based on the composition of the prepared AM/AMPS hydrogels and on the binding capacities of the metal ions towards amide group and SO_3H of AM/AMPS resins.

From the pH profile experiments, which are not represented here for brevity, it is clear that metal ion uptake drops significantly at low pHs. All metal ions were desorped using 2N of HCl aqueous solution. Therefore, it is assumed that the metal ions can be recovered by decreasing the pH. The AM/AMPS hydrogels were completely saturated with the metal at the optimum pH and time. Then, all adsorbed metal ions were desorped by using 2N HCl. The recoveries of Cd(II), Cu(II), and Fe(III) using AM (50 mol %)/AMPS (50 mol %) crosslinked with 10% of MBA were found to be 98.5%, 93%, and 94%, respectively. To obtain the reusability of the AM/AMPS hydrogel, adsorption-desorption cycles were repeated three times by using the same hydrogel without loss of adsorption capacity (Fig. 8). In this respect, the Cd (II) ions recovery was selected as representative samples. The data indicated that the prepared AM/AMPS hydrogels were eluted in a strong acid (2N HCl) to ensure that the strong acid medium did not degrade the chemical structure of the prepared resins. It was determined that, the reusability depends on the copolymer compositions. It was found that, the resins have AMPS mol % resist the degradation and hydrolysis. This observation can be attributed to the hydrolysis of the AM

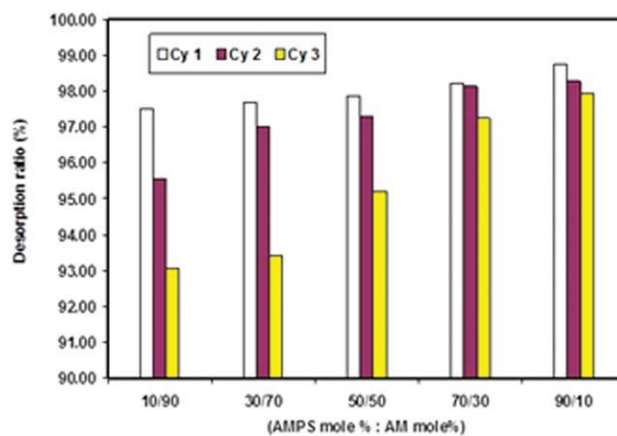


Figure 8 Adsorption amount of Cd (II) heavy metals after repeated adsorption-desorption cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups at higher mol % of AM. The regeneration efficiency was increased in case of highly crosslinked resin than that of lower crosslinked resin.

CONCLUSIONS

The following conclusions can be summarized from the previous results:

1. Crosslinked AM/AMPS copolymer was prepared using free radical solution polymerization at 40°C .
2. The equilibrium degree of swelling of the final hydrogels increased with increasing ionic group content of the hydrogels until a plateau is reached at about 10 mol % AMPS. Between 10 and 30 mol % AMPS, the equilibrium gel swelling in water was independent of the ionic group content of the hydrogels. Further increase in the AMPS content beyond this value increased the gel swelling continuously up to 100 mol %.
3. It has been found that the adsorption capacity of hydrogels increased with increasing AMPS content in the gel structure. This has been explained as the result of the incorporation of more specific acid groups into the network, which consequently leads to the higher swelling capacity of the gels.
4. The adsorption studies also showed that pH and initial metal ion concentration are the basic parameters affecting the maximum metal uptake capacity of the hydrogels. Maximum uptake can be reached at pH 5 within the first 3 h.
5. It was concluded that these hydrogels showed higher selectivity towards Cd(II) and Cu(II),

and more than 90% recovery was attained after three repeated usage.

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