Radiation Synthesis and Characterization of Poly(*N*-vinyl-2-pyrrolidone/acrylic acid) and Poly(*N*-vinyl-2-pyrrolidone/acrylamide) Hydrogels for Some Metal-Ion Separation

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ABSTRACT: Two different hydrogels, prepared from *N*-vinyl-2-pyrrolidone/acrylic acid (NVP/AAc) and *N*-vinyl-2-pyrrolidone/acrylamide (NVP/AAm), were studied for the separation and extraction of some heavy-metal ions from wastewater. The hydrogels were prepared by the γ-radiation-induced copolymerization of the aforementioned binary monomer mixtures. Further modification was carried out for the NVP/AAc copolymer through an alkaline treatment to improve the swelling behavior by the conversion of the carboxylic acid groups into its sodium salts. The thermal stability and swelling properties were also investigated as functions of the *N*-vinyl-2-pyrrolidone content. The charac-

terization and some selected properties of the prepared hydrogels were studied, and the possibility of their practical use in wastewater treatment for heavy metals such as Cu, Ni, Co, and Cr was investigated. The maximum uptake for a given metal was higher for a treated NVP/AAc hydrogel than for an untreated NVP/AAc hydrogel and was higher for an untreated NVP/AAc hydrogel than for an NVP/AAm hydrogel. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2642–2652, 2004

Key words: hydrogels; radiation; copolymerization; waste

INTRODUCTION

The release of toxic substances and their dispersal in the environment can have tragic effects. The discharge of industrial wastewater without adequate treatment has increased significantly in the last decade as a result of wide industrial expansion.[1] The presence of metals such as lead and nickel is known to cause severe health problems in animals and human beings.[2]

These substances are more easily controlled when they are generated than after they are dispersed. Therefore, our aim of minimizing adverse effects depends largely on the development of processes that isolate and remove the contaminants at their sources.

The ability of certain polymers to form polymer–metal complexes may be applied to several areas, such as hydrometallurgy[3] and biochemistry.[4] In recent years, there has been a great deal of interest in the applicability of polymers for the removal, separation, and purification of metal ions from heavy-metal-contaminated water and solid waste.[5–7] The chemical nature of the functional groups containing atoms able to form donor–acceptor bonds, representing the basis of

the polymer–metal complexes, is very different and generally complicated.[8]

Hydrogels can be defined as three-dimensional networks of polymers, which can swell several hundred times with respect to the dry network mass when in contact with water or aqueous solutions. Polymeric hydrogels have a series of particular characteristics: they are hydrophilic, insoluble in water, soft, and elastic, and they swell with water, keeping their shapes but increasing in volume until reaching a physical chemical equilibrium. The hydrogel properties depend strongly on the (1) the degree of crosslinking, (2) the chemical composition of the polymer chains, and (3) the interactions of the network and surrounding liquid. The properties of the hydrogels as adsorbent materials can be changed with the pH and temperature.[9–11]

This study was designed to investigate the efficiency of prepared hydrogels such as *N*-vinyl-2-pyrrolidone/acrylic acid (NVP/AAc) and *N*-vinyl-2-pyrrolidone/acrylamide (NVP/AAm) copolymers in the removal of cupper, nickel, cobalt, and chrome from their wastes.

EXPERIMENTAL

Materials

Acrylic acid (AAc), acrylamide (AAm), and *N*-vinyl-2-pyrrolidone (NVP; Merck, Germany) with a purity of 99% were used without further purification.

Preparation of the hydrogels

Different comonomer compositions were prepared and subjected to γ irradiation at different doses at a fixed dose rate of 1.43 Gy/s. Distilled water and water/methanol mixtures were used as diluents for the copolymerization processes. The prepared copolymer hydrogels were then dried at room temperature and weighed.

Alkaline treatment of the hydrogels

The alkaline treatment of a synthesized NVP/AAc hydrogel was carried out through refluxing with a 3 wt % aqueous solution of NaOH for 6 h. The hydrogel was then washed with hot distilled water for the removal of occluded NaOH in the hydrogel and then dried in an oven at 40–50°C.

Swelling measurements

A clean, dried hydrogel of a known weight was immersed in distilled water at room temperature. The hydrogel was removed from the water after various time intervals, and the excess water on the surface was removed, blotted with absorbent paper, quickly weighed, and then returned to the distilled water until equilibrium was reached (24 h in most cases). The water uptake (swelling percentage) was calculated as follows:

$$\text{Water uptake (\%)} = [(w_s - w_d)/w_d] \times 100$$

where w_d and w_s represent the weights of the dry and wet hydrogels, respectively.

Gel determination in the prepared hydrogels

A dried hydrogel was extracted with water for 48 h at 100°C to extract the insoluble parts of the hydrogel. The insoluble parts, that is, the gelled parts, were taken out and washed with hot water for the removal of the soluble parts and then were dried and weighed. This extraction cycle was repeated until the weight became constant. The gel fraction yield in the hydrogel was determined was follows:

$$\text{Gel (\%)} = (w_e/w_d) \times 100$$

where w_d and w_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

FTIR spectroscopy

The dry hydrogels were ground and pressed with KBr and then were measured with FTIR spectroscopy (Mattson 1000, Unicam, England) from 400 to 4000 cm^{-1}.

pH measurements

The pHs of the used metal solutions in the treatment were determined with a Jenway 3310 pH meter.

X-ray diffraction (XRD)

XRD patterns were obtained with a Shimadzu XD-DI series apparatus with a nickel-filtered Cu Kα target. This technique was performed to clarify the changes in the morphological structure caused by the copolymerizations of different comonomer compositions.

Thermogravimetric analysis (TGA)

A Shimadzu TGA-50 system in a nitrogen atmosphere (20 mL/min) was used. The temperature range was from the ambient temperature to 500°C at a heating rate of 10°C/min.

Scanning electron microscopy (SEM)

Scanning electron micrographs were taken with a JEOL JSM 5400 scanning electron microscope (Japan).

Metal uptake measurement

The fixed weight of the prepared hydrogel was immersed in a metal feed solution of a definite concentration (100 ppm). Merck atomic absorption standard solutions of these metals were used for the calibration process. The pH and temperature of the metal feed solutions were adjusted before the hydrogels were applied for treatment processes. The remaining metal ions in the feed solution were determined with a Unicam Solaar 929 atomic absorption instrument.

The metal uptake (E) was calculated as follows:

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

where W is the weight of the dry hydrogel (g) and A is the atomic weight of the metal ion. C_i and C_f are the initial and remaining concentrations of metal ions (mg/L; ppm). Metal-ion solutions of 100 mL, instead of 1 L, were used, so we divided by 10. The total uncertainly for all the experiments ranged from 3 to 5%.
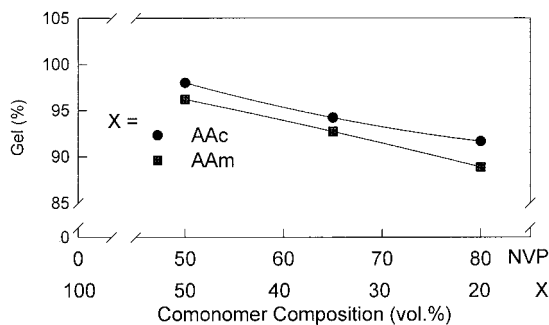
Figure 1 Effect of the NVP content on the gel percentage for the NVP/AAc copolymer hydrogel in H₂O/MeOH and for the NVP/AAm copolymer hydrogel in H₂O. The dose was 15 kGy.

Figure 2 Effect of the dose on the gel percentage for the NVP/AAc copolymer hydrogel in 80/20 (v/v) H₂O/MeOH at different NVP/AAc compositions. The comonomer concentration was 80 vol %.

RESULTS AND DISCUSSION

Preparation of the hydrogels by radiation copolymerization

The hydrogels were prepared by the γ-radiation-induced copolymerization of binary monomer mixtures, NVP/AAc and NVP/AAm. Such a radiation process is generally considered a clean technique, not requiring any extra chemicals or leaving some unwanted residue. It can be applied at any temperature and dose rate. Extensive work has been performed on methods for optimizing yields when monomers are irradiated with ionizing radiation such as γ-rays.[12]

Effect of the comonomer composition

The influence of the NVP/AAc and NVP/AAm compositions on the gel fraction yields formed in the respective copolymers is shown in Figure 1. As the NVP content increases, the gel fraction yield decreases. This behavior has been observed for both binary monomer systems, although the gel content is higher for the NVP/AAc system at a given composition. This is due to the higher affinity of AAc to crosslinking through the formation of hydrogen bonding via —COOH groups.

Effect of the irradiation dose

In the direct radiation method, the total dose determines the number of initiated sites able to be copolymerized. The effect of the radiation dose on the conversion yield in the NVP/AAc and NVP/AAm systems is shown in Figures 2 and 3, respectively. The higher the dose is, the higher the gel fraction yield is at a given comonomer composition. The results also indicate that the crosslinking process in the prepared hydrogels is enhanced at higher doses. Meanwhile, the higher the NVP content is in the comonomer composition, the higher the gel fraction yield is. This be-
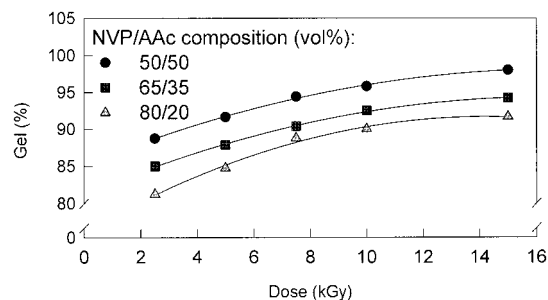
havior has been observed for both NVP/AAc and NVP/AAm systems.

The use of 50/50 (w/w) NVP/AAm at 15 kGy resulted in a 97% gelled hydrogel. However, from a practical point of view, the hydrogel should possess some suitable porosity and hydrophilicity for the purpose of adsorption. Therefore, a 65/35 (w/w) composition has been selected to be the best condition for the preparation of hydrogels that can meet the requirements of metal adsorption from their wastes. At this NVP/AAm composition, the prepared hydrogel possesses about 92% gel; that is, the crosslinking content is less than that obtained with 50% NVP. The former hydrogel is expected to possess higher hydrophilicity and allow water to diffuse. As a result, the amount of metals sorbing will be higher.

Characterization and some selected properties of the hydrogels

To determine the possibility of practical uses for the prepared copolymer hydrogels, we thoroughly investigated some of their selected properties. These included the swelling behavior, the characterization of the thermal properties, and the crystallinity of the prepared hydrogels.
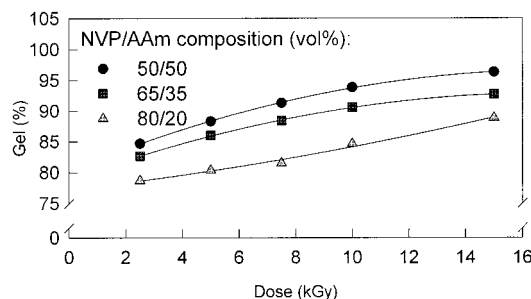

Figure 3 Effect of the dose on the gel percentage for the NVP/AAm copolymer hydrogel in H₂O at different NVP/AAm compositions. The comonomer concentration was 80 vol %.
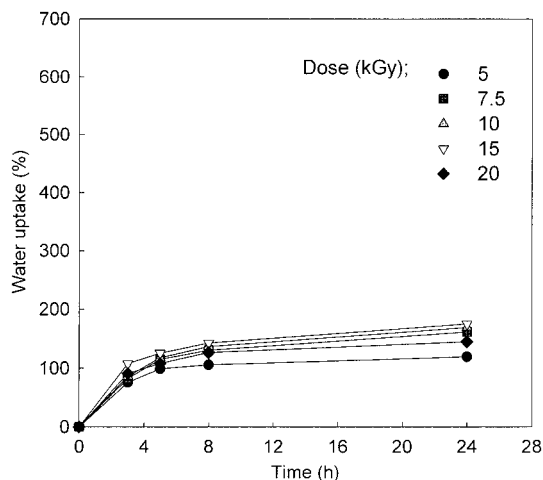
Figure 4 Effect of the swelling time on the water uptake percentage for 80/20 (v/v) NVP/AAc copolymer hydrogels at different doses.

Swelling behavior

Swelling is one of the most important parameters affecting the characteristic properties of hydrogels and, therefore, determining their applicability for practical use. The influence of the swelling time on the water uptake was investigated for NVP/AAc and NVP/AAm hydrogels prepared at different irradiation doses, as shown in Figures 4 and 5, respectively. The water uptake percentage increases as the swelling time increases, reaching a certain limiting value after almost 8–10 h, which is called the maximum swelling at equilibrium (S_{max}). This behavior was observed for all the hydrogels prepared at different doses, which ranged from 5 to 15 kGy. Meanwhile, S_{max} increases as the irradiation dose increases up to 15 kGy, and there-
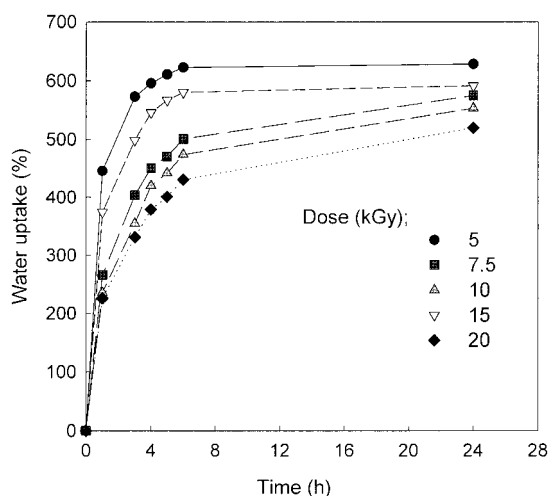
TABLE I
Effect of the Comonomer Composition and Dose (kGy) on the Water Uptake (%)

| Dose (kGy) | Water uptake (%) | | | | | |
| | NVP/AAm (vol %) | | | NVP/AAc (vol %) | | |
	50/50	65/35	80/20	50/50	65/35	80/20
2.5	381	520	487	46	76	119
5	396	556	542	53	81	157
7.5	405	578	553	62	98	169
10	427	638	570	79	120	172
15	456	592	594	95	125	180
20	354	562	561	85	116	150

Swelling time = 6 h.

after it decreases. This is due to the enhancement of the crosslinking process at higher doses, and as a result, the diffusion and swelling properties are hindered by the formation of the network structure. This is clearly shown in Table I, which shows the effect of the irradiation dose on S_{max} for hydrogels prepared from different comonomer compositions.

The influence of the swelling time on the water uptake percentage for different hydrogels prepared at various comonomer compositions was also investigated and is shown in Figures 6 and 7 for the NVP/AAc and NVP/AAm copolymers, respectively. The rich NVP content in the initial comonomer feed solution results in a hydrogel with a higher swelling behavior. It also shows an S_{max} value at a certain swelling time, which varies with the comonomer composition and swelling time.

The alkaline treatment of the NVP/AAc copolymer resulted in a very pronounced increase in its swelling, which was almost 20 times higher than that of the untreated copolymer (Fig. 8). This was probably due to the conversion of free —COOH groups of AAc into the sodium salt, which more easily possessed ionizable and electrolytic groups, having much higher hydrophilic properties in comparison with those of free carboxylic groups.
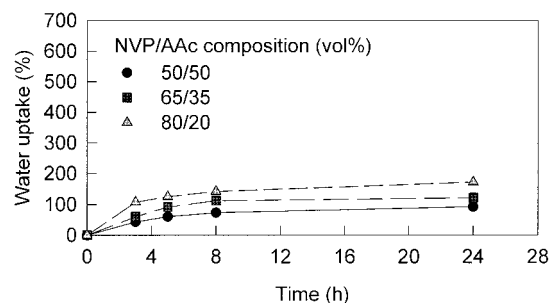

Figure 5 Effect of the swelling time on the water uptake percentage for 80/20 (v/v) NVP/AAm copolymer hydrogels at different doses.

Figure 6 Effect of the swelling time on the water uptake percentage for different NVP/AAc compositions at a gelation dose of 15 kGy.
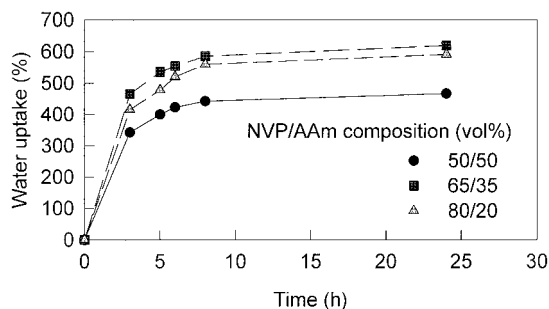
Figure 7 Effect of the swelling time on the water uptake percentage for different NVP/AAm compositions at a gelation dose of 15 kGy.

The results suggest that the hydrogen bonding in the hydrogel containing free —COOH groups results in a crosslinked network structure. As a result, the water uptake is reduced. However, the chemically treated hydrogel possesses higher water uptake because of the formation of easily ionizable —COO⁻Na⁺ groups, which have good hydrophilic properties.[13]

The prepared polymeric hydrogel is highly hydrophilic in nature; that is, it has high diffusivity and porosity, which have not been measured yet. The NVP/AAc and NVP/AAm samples that we used had surface areas of 0.785 and 0.5024 cm^{-2} and sizes of 0.157 and 0.07536, respectively.

FTIR spectroscopy

FTIR spectroscopy can be used to characterize the structures of organic compounds. Figure 9 shows the FTIR spectra of NVP/AAm and NVP/AAc hydrogels. The characteristic absorption bands for the AAm monomer include vibration stretching bands at 3400–3200 cm^{-1} characteristic of N—H and a stretching vibration band at 1750 cm^{-1} for C=O. NVP/AAm hydrogels have a broad band at 3600–3500 cm^{-1} characteristic of OH of NVP, which results from keto–enol form overlap with the N—H stretching of an amide
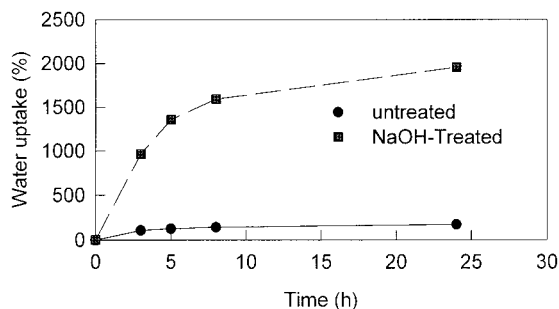

Figure 8 Effect of the swelling time on the water uptake percentage for NaOH-treated and untreated 80/20 (v/v) NVP/AAc copolymer hydrogels prepared at 15 kGy.
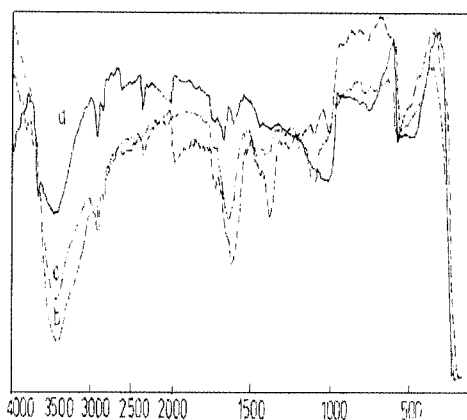

Figure 9 FTIR spectra of different hydrogels: (a) untreated NVP/AAc, (b) treated NVP/AAc, and NVP/AAm hydrogels.

group at 3200 cm^{-1}. Other evidence of NVP/AAm hydrogels includes the appearance of C=O at 1670 cm^{-1} as a stretching vibration characteristic of the crosslinking of an amide group into NVP.

For the NVP/AAc copolymer, carboxyl bands characteristic of carboxylic acid appear at 3600, 1730, 1260, and 930 cm^{-1} for very broad O—H stretching, C=O, O—C=O, and a broad band attributed to a hydrogen-bonded O—H out-of-plane bending vibration.

The IR spectra of the NaOH-treated hydrogels of NVP/AAc show characteristic peaks of the carboxylate salt at about 1545 and 1412 cm^{-1} and of OH at 3600 cm^{-1}, which do not completely disappear by hydrolysis and result from the keto–enol form.

TGA

From a practical point of view, a prepared hydrogel should possess good thermal stability in the range of applicable temperatures. Figures 10 and 11 show the TGA curves and weight losses of the prepared hydrogels as functions of the temperature. The TGA curves of the different hydrogels reveal that there are three distinct steps of weight loss. It is suggested that during the initial stage of the thermal diagram, from the ambient temperature to 250°C, the weight loss is due to a dehydration process of the water contained in such hydrophilic hydrogels. During the second stage, from 250 to 450°C, there is decomposition in the side groups and branches of the hydrogels. During the third stage, beyond 450°C, the weight loss is due to main-chain scission in the polymer chain and matrices. Heating a hydrogel at a temperature higher than 450°C results in rapid decomposition into carbon dioxide and volatile hydrocarbons.

It has been reported that the TGA of poly(acrylic acid) shows four degradation steps. The evolution of water is associated with the polymer at temperatures
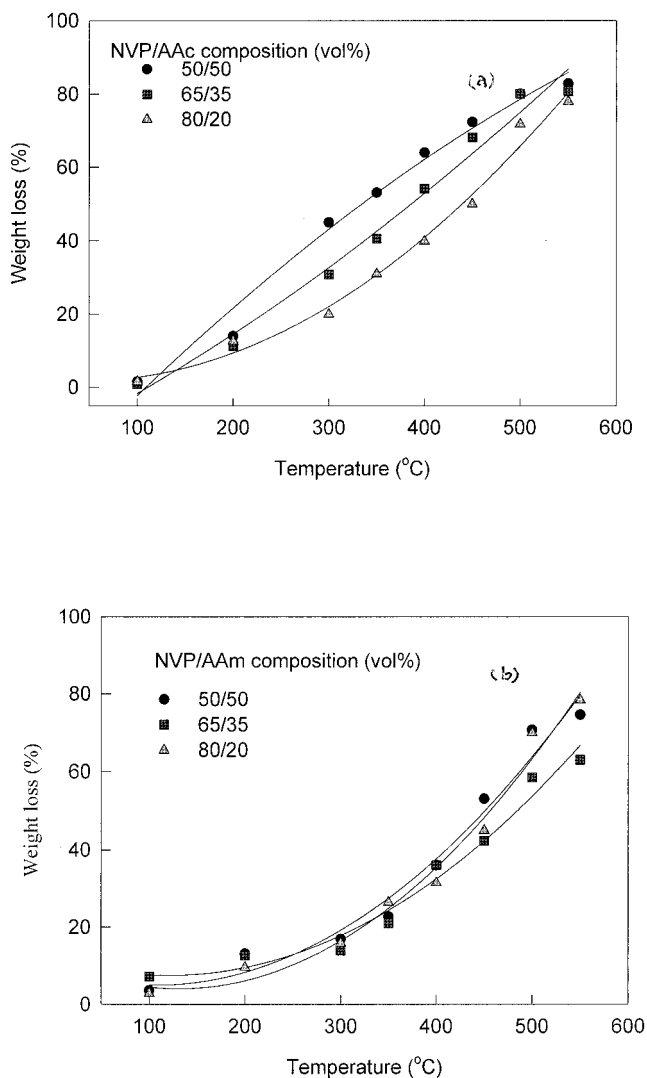
Figure 10 Effect of the comonomer composition on the weight loss (%) at various elevated temperatures for (a) NVP/AAc and (b) NVP/AAm hydrogels prepared at 20 kGy.

below 180°C. The degradation step at 250°C is interpreted as the result of intermolecular or intramolecular dehydration followed by decarboxylation.[14,15] The last degradation step starts beyond 350°C, at which temperature the bulk decomposition of the polymer takes place, giving rise to a highly unsaturated structure.[14] Also, the TGA of polyacrylamide shows three degradation steps: the first region (the ambient temperature to 220°C) corresponds to loss bound water, the second region (220–340°C) corresponds to the loss of NH_3 by imidization (intramolecular and intermolecular) and H_2O by dehydration, and the third region (>340°C) represents substantial mass loss and is normally attributed to main-chain breakdown.[10] Pure poly(N-vinyl-2-pyrrolidone) shows characteristic single-step degradation with a maximum at 458°C and a 98% weight loss.[16]

Metal-ion removal from wastewater

This study was designed to investigate the efficiency of prepared hydrogels, including treated NVP/AAc, untreated NVP/AAc, and NVP/AAm, in the removal of cupper, nickel, cobalt, and chrome from their wastes. Among the factors affecting the treatment processes of such metal ions from their wastes with the prepared hydrogels are the following:

1. The treatment time.
2. The pH of the metal-ion feed solution.
3. The initial metal concentration in the feed solution.
4. The temperature of the feed solution.

Effect of the treatment time

From an economical point of view, the time of treatment is an important factor. Also, the efficiency of hydrogels in waste treatment can be determined from the time required to adsorb the maximum capacity of metal ions by chelation or complexation with the functional groups.

Table II shows the metal uptake as a function of time for different metals with the prepared hydrogels. The metal uptake increases with time to reach its maximum value (which is called the maximum hydrogel capacity) at almost 7 h for the different metal ions investigated. Increasing the treatment time to more than 7 h causes no significant increase in metal uptake even after 24 h. The maximum metal uptake is ordered in the sequence of Co^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}. The initial rate of chelated metal ions and the maximum uptake value are very dependent on the type of metal ion, its coordination and stability constant, and the steric effect of these copolymer complexes. However, the ionic size of the investigated metal ions has a great influence not only on the maximum uptake but also on the initial rate. This can be reasonably explained by a consideration of the diffusion of these metals through the porous ionic hydrogels, which is mainly dependent on their polarity, electronic configuration, ionic radii, and so forth and also is dependent on the nature of the interaction with the functional groups of the hydrogels. The highest metal uptake was observed for Co^{2+}, and the lowest was observed for Cr^{3+}. Therefore, the ionic size is a very important factor because of permeability and diffusivity problems through porous hydrogels of certain diameters and pore sizes.

Under the same reaction conditions, when the —COOH groups are converted into the acrylate by a reaction with NaOH, there is a higher tendency to metal chelation or complexation than for the NVP/AAc hydrogel. The stability of the complex depends mainly on two factors:
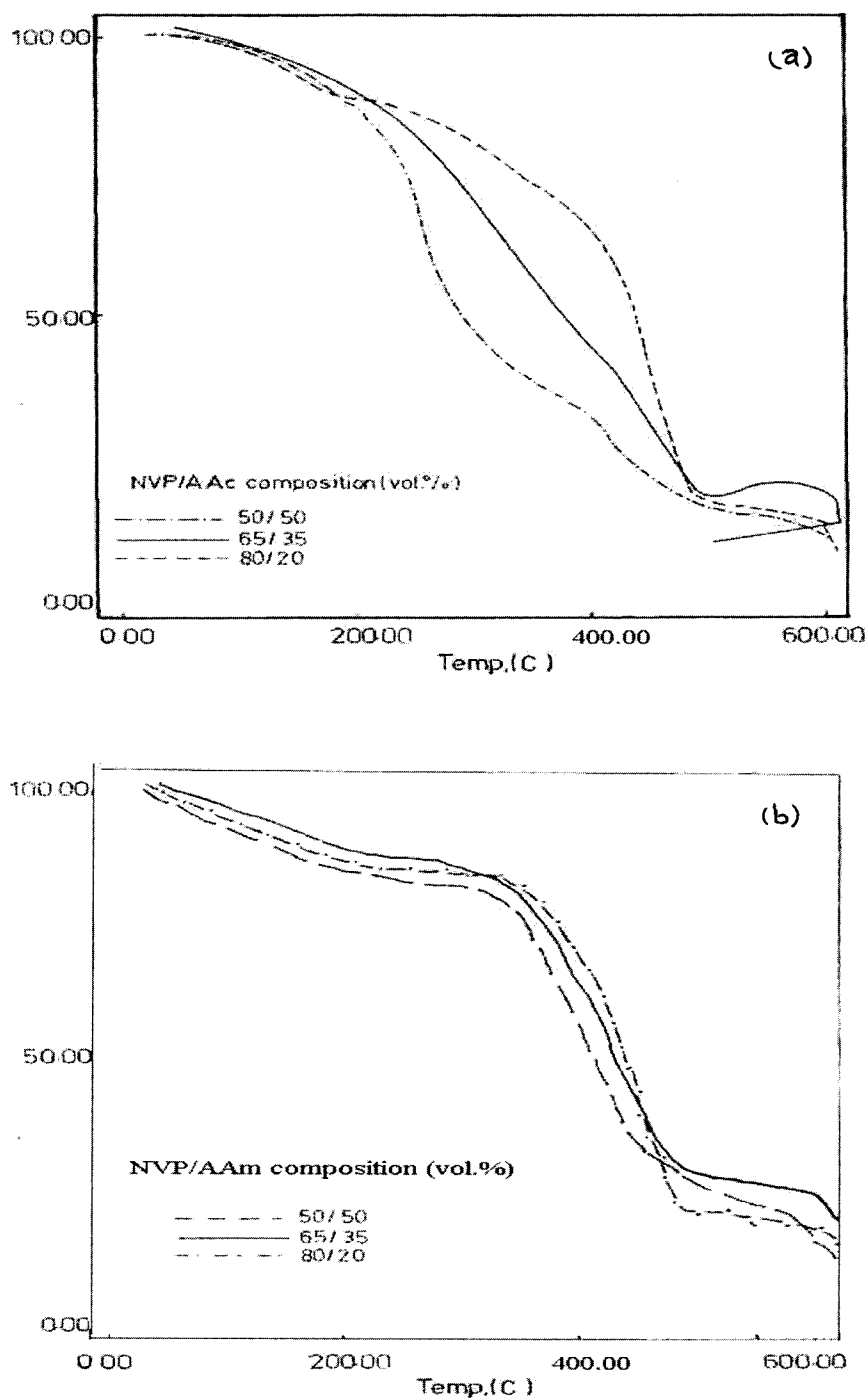
Figure 11 TGA thermograms for different (a) NVP/AAc and (b) NVP/AAm hydrogel compositions.

The complexing ability of the metal ion involved. The characteristics of the ligand.

The complexing ability of the metal ion is highly dependent on its ionic radius, valence, and hydration energy. The sequence order of the metal uptake remains the same after treatment with NaOH: Co^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}. The efficiency of such hydrogels is high, and the maximum metal uptake is reached after 7 h of treatment.

Effect of the pH of the feed solution

The availability of the hydrogels under investigation for metal-ion complexation is pH-dependent. The sorption characteristics of the hydrogels toward Cu^{2+}, Ni^{2+}, Co^{2+}, and Cr^{3+} metal ions were investigated from pH 1 to pH 7. The sorption affinity of the sorbent is plotted as a function of pH in Figure 12(a–c). The amount of metal-ion uptake by the chelating polymer increases significantly as the pH increases for Ni^{2+},

TABLE II
Metal-Ion Uptake by Different hydrogels
after 7 h treatment

	Metal-ion uptake (mmol/g)		
Metal cation	NVP/AAc hydrogel	Treated NVP/AAc hydrogel	NVP/AAm hydrogel
$CoCl_2 \cdot 6H_2O$	9.1	10	7
$Cu\,SO_4 \cdot 5H_2O$	7.5	8.3	5.9
$NiCl_2 \cdot 6H_2O$	5.3	7.2	5.1
$Cr(NO_3)_3 \cdot 9H_2O$	3.6	5.1	3.4

Co^{2+}, and Cr^{3+} up to pH 7. However, the maximum Cu^{2+} uptake is reached at pH 5; thereafter, it decreases because of the formation of their hydroxides. However, the metal-ion uptake under highly acidic conditions is sharply reduced because of the competition of hydrogen ions. These results indicate that the metal uptake is pH-dependent.
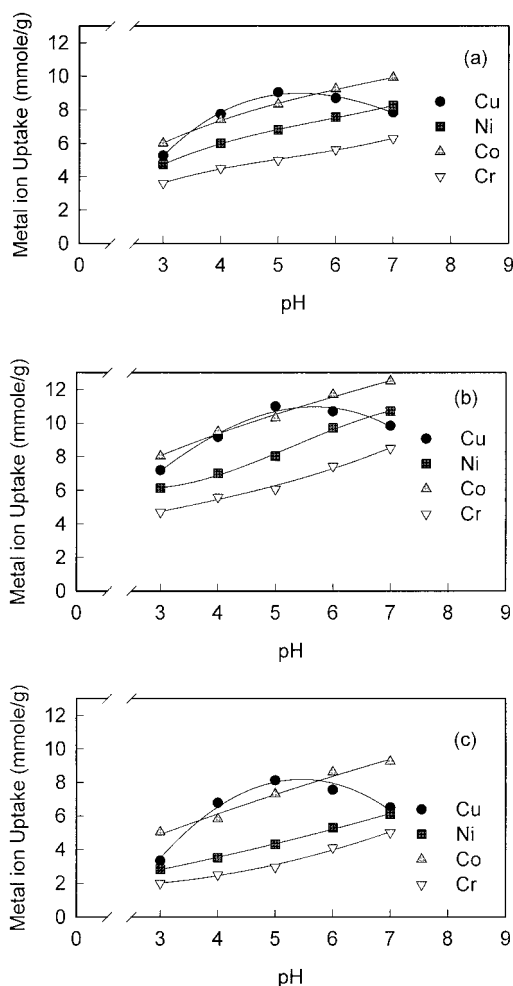
Effect of the initial concentration of the metal feed solution

In exploring the applicability of the sorbent hydrogels, we found it informative to obtain knowledge of their sorption capacity toward different metal ions. This was done by the equilibration of a fixed amount of the sorbent hydrogel with a series of initial metal-ion concentrations, which could be removed from the solution when the chelating sites of the sorbent were saturated.

Figure 13(a–c) shows that the metal uptake increases with the concentration of the metal ions to reach a certain limiting value. Thereafter, it levels off at higher feed concentrations (>1000 ppm).

These results reveal that the chelating sites of the sorbent become saturated when the concentration of the feed solution is reached, 1000 ppm, above which no more metal-ion uptake occurs.

The weakness of the adsorbent–adsorbate forces will cause the uptake at low concentrations to be small, but once a molecule has become adsorbed, the
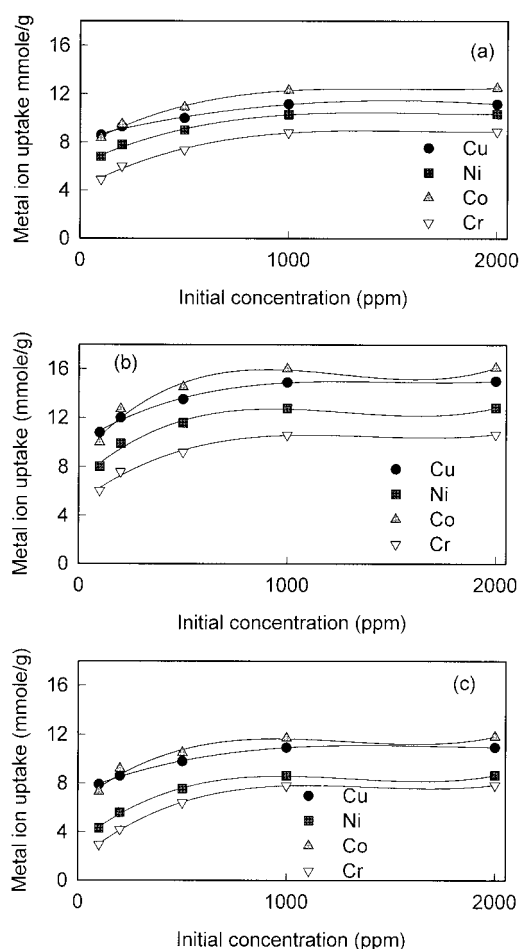

Figure 12 Effect of the pH on the metal-ion uptake for different hydrogels: (a) NVP/AAc, (b) treated NVP/AAc, and (c) NVP/AAm. The initial metal concentration was 100 ppm, and the soaking time was 7 h.

Figure 13 Effect of the initial concentration on the metal uptake for different hydrogels: (a) NVP/AAc, (b) treated NVP/AAc, and (c) NVP/AAm. The soaking time was 7 h, the pH was 5, and the temperature was 70°C.
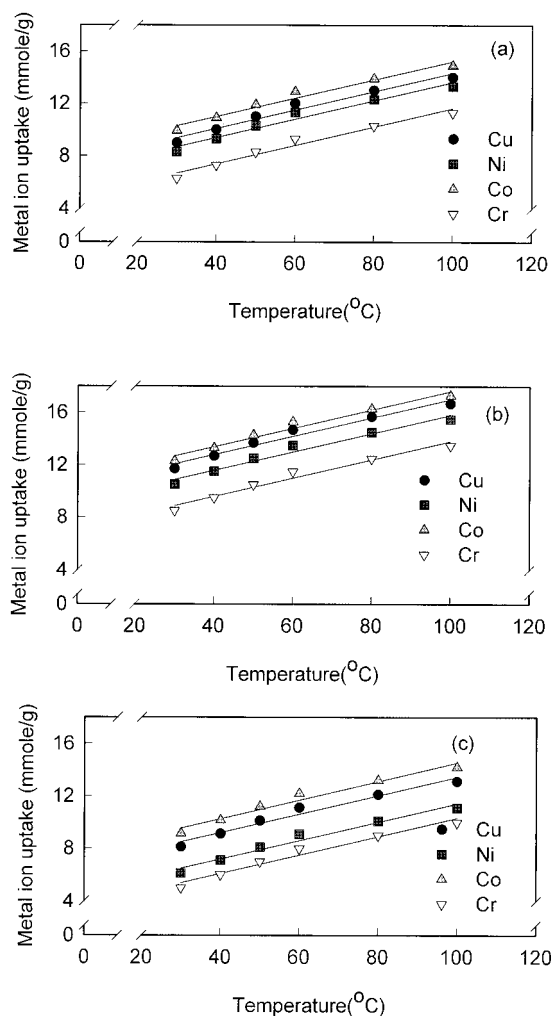
Figure 14 Effect of the temperature on the metal uptake for different hydrogels: (a) NVP/AAc, (b) treated NVP/AAc, and (c) NVP/AAm. The initial metal concentration was 100 ppm, and the pH was 7.

adsorbate–adsorbate forces will promote the adsorption of further molecules; this is a cooperative process, and so the isotherm will become convex to the concentration axis. The adsorption of either nonpolar molecules or polar molecules occurs if the adsorbent–adsorbate force is relatively weak. A polar adsorbate of particular interest in this context is water because

the dispersion contribution to its overall interaction energy is unusually small in comparison with the polar contribution. The hydrogel is covered with a layer of adsorbed water; however, the adsorbent–adsorbate interaction would be virtually reduced to the weak dispersion energy of water with metals. Multiple layers are built up on some parts of the surface, whereas a monolayer is still incomplete on other parts.

Effect of the temperature

The temperature is an important factor that affect the chelation or complexation of metal ions with the functional groups in the hydrogels. Figure 14(a–c) shows the relationship between the amount of metal-ion uptake (mmol/g) and the temperature for the prepared hydrogels: treated NVP/AAc, untreated NVP/AAc, and NVP/AAm. The amount of metal-ion uptake increases as the temperature increases for the hydrogels investigated here. This is attributed to the increase in the kinetic energy of the metal ions with the temperature, and the flexibility of the hydrogel increases as well. Consequently, the diffusion of the metal-ion solution in the hydrogel increases with temperature, and the amount of metal-ion uptake increases. The maximum metal-ion uptake was obtained at the boiling point, at which the highest diffusion occurred.

XRD

XRD of the NVP/AAc hydrogel before and after metal adsorption is shown in Table III. We used this technique to determine the changes in the morphological structure and the changes in its crystal form due to the effects of swelling and the interaction of pollutant compounds on the hydrogel polymer matrix. The diffraction curves of the metal uptake in the hydrogel record the same region, and there is no significant change in 2θ for NVP/AAc before and after metal uptake. However, a difference in the particle size (d; Å) was found, and it was determined with the Schrer equation:[17]

$$d \ (\text{Å}) = \frac{K\lambda}{\beta_{1/2}\cos\theta}$$

TABLE III
XRD Patterns for NVP/AAc Hydrogels Before and After the Adsorption of Some Heavy Metals

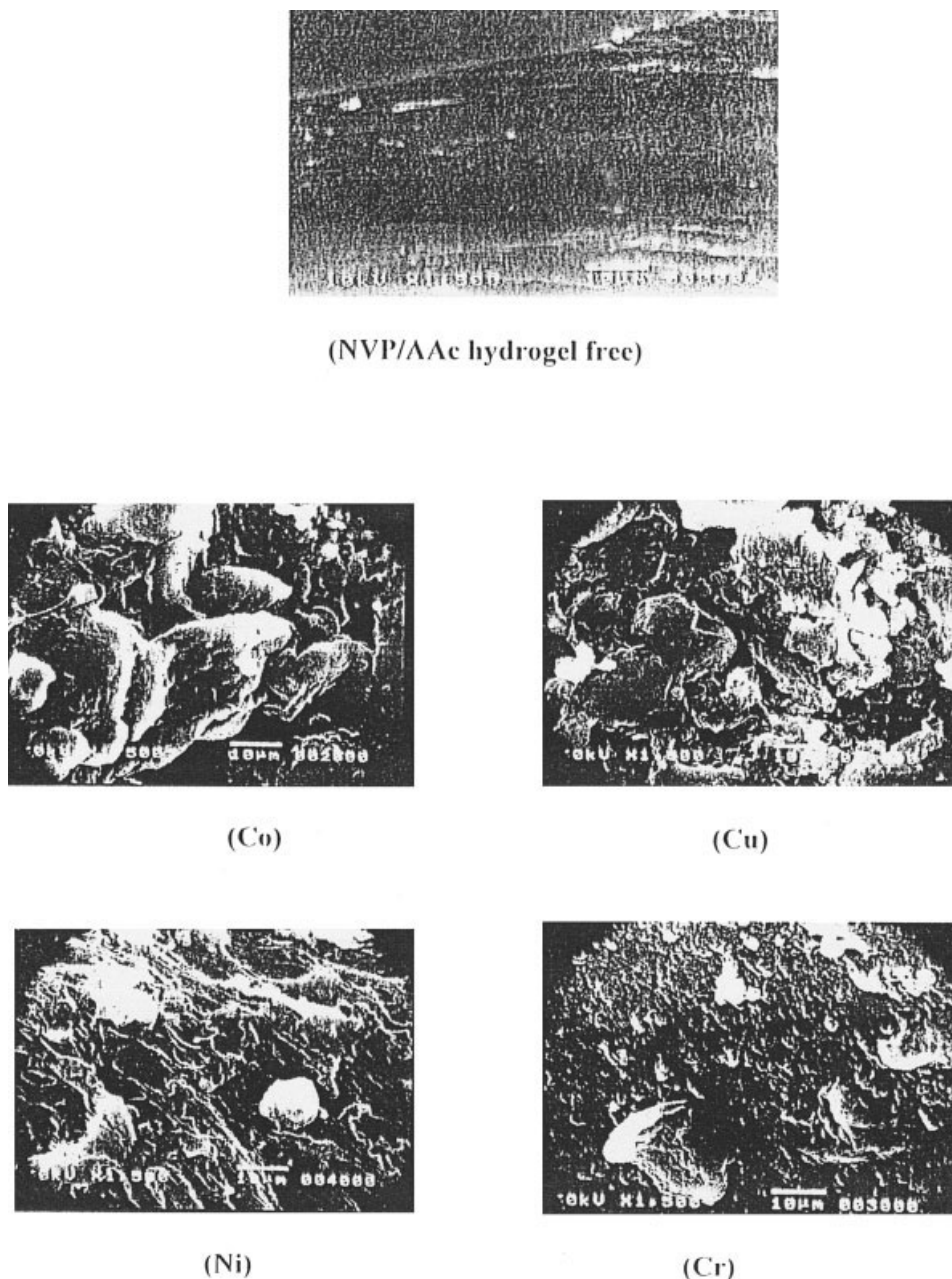| Lattice parameter	NVP/AAm hydrogel	NVP/AAc hydrogel				
		Blank	Co	Cu	Ni	Cr
2θ	23.29	14.618	14.108	36.582	16.828	13.768
Fwhm	1.695	1.983	0.935	1.642	4.462	2.019
$\beta_{1/2}$ (rad)	0.0296	0.0346	0.0163	0.0286	0.0778	0.0352
d (Å)	47.34	40.13	84.75	50.7	17.87	39.21
Integrated intensity (counts)	1160	213	199	111	1270	149

(NVP/AAc hydrogel free)

(Co)

(Cu)

(Ni)

(Cr)

Figure 15 SEM images of NVP/AAc hydrogels before and after the adsorption of different metals.

where K is the Schrer constant (0.89), λ is the wavelength of the X-ray beam (1.5405), $\beta_{1/2}$ is the full width at half-maximum (fwhm; rad), and θ is the diffraction angle of the main diffraction line.

The integrated intensity (counts) is taken as an indication of the amorphousness and crystallinity percentage of the polymer according to the area under the peak obtained from the charts of XRD patterns. When the integrated intensity increases, the crystallinity also increases. Table III shows that the metal-free hydrogels and hydrogel–metal complexes were in the amorphous state, and no significant change was observed.

SEM

Scanning electron micrographs of the NVP/AAc hydrogel before and after the adsorption of metal ions are shown in Figure 15. The surface of the NVP/AAc hydrogel before metal uptake was smooth. However, the surface of the hydrogel after metal uptake was tough. The metal salts appeared as small, white spots adsorbed on the hydrogel. These spots indicated metal uptake by the hydrogel via complexation with its —COOH functional groups.

CONCLUSIONS

The hydrogels prepared by the radiation-induced co-polymerization of NVP/AAc and NVP/AAm solutions are interesting for some practical uses, such as industrial wastewater treatment. The gel percentage increased with the irradiation dose and improved in the presence of AAc. S_{max} increased with the irradiation dose up to 15 kGy and thereafter decreased because of the enhancement of the crosslinking process at higher doses. The alkaline treatment of the NVP/AAc hydrogel significantly improved its swelling behavior. The hydrogels possessed good hydrophilic properties and thermal stability, which may make them acceptable for practical use. The maximum metal uptake was in the following order: $Co^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$. The maximum uptake for a given metal was higher for the treated NVP/AAc hydrogel than for the untreated NVP/AAc hydrogel and was higher for the untreated NVP/AAc hydrogel than that for the NVP/AAm hydrogel. The adsorption capacity of the investigated hydrogels was dependent on the pH of the aqueous metal solutions.

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