Recovery of Heavy Metals from Aqueous Solution by Using Radiation Crosslinked Poly(vinyl alcohol)

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ABSTRACT: Crosslinked poly(vinyl alcohol) (PVA) and PVA/acrylic acid hydrogels, prepared by γ-irradiation, were used in the removal of heavy metals from aqueous solution. Comparative studies of the properties of the two hydrogels were made. The application of the prepared hydrogels as adsorbent materials for Cu^{2+}, Co^{2+}, and Ni^{2+} from aqueous solution was studied. The chemical and physical properties of the hydrogels, before and after adsorption of the heavy metal ions, were investigated by means of thermogravimetric analysis, differential scanning calorimetry, and scanning electron microscopy. The efficiency of such hydrogels for the recovery of metal ions was determined by atomic absorption and UV spectroscopic analysis. The effect of changing pH on the metal uptake was also studied. It was found that the prepared hydrogels have a substantial ability to adsorb metal ions from their solution. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1649–1656, 2004

Key words: crosslinking; hydrogels; adsorption; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC)

INTRODUCTION

Crosslinked hydrophilic polymers that can absorb large volumes of water are termed hydrogels. Hydrogels have been widely applied in the fields of bioengineering, biomedicine, pharmaceuticals and the food industry, agriculture, and photographic technology, for example. They are also used in drug-control systems and for the production of contact lenses and artificial organs in biomedicine. The most important field for application of hydrogels is the removal of some agents in environmental and enzyme immobilization.[1–7]

Poly(vinyl alcohol) (PVA) is well known as a membrane-forming material with high hydrophilicity. Some investigations have been done on its use in the field of separation processes.[8,9] In health care technology, crosslinked PVA hydrogel is used for wound dressing.[10] However, it is difficult to use linear PVA in the treatment of wastewater. In this respect, this study covers the conversion of PVA to a completely insoluble hydrogel material through, first, crosslinking of PVA by γ-irradiation and, second, by copolymerization with acrylic acid monomer. The physical properties of the hydrogels were identified through the estimation of gel fraction and solubility. The structural and thermal properties of the prepared hydrogels were studied by using SEM, TGA, and DSC techniques. UV spectroscopic analysis and atomic absorption measurements measured the metal uptake.

EXPERIMENTAL

Materials

Laboratory-grade PVA was obtained in the form of a powder having an average molecular weight (M_w) of 125,000 from the Rasayan laboratory (S. D. Fine Chemicals Ltd., Boisar, India). Acrylic acid (AAc, purity 99%; Merck, Darmstadt, Germany) was used without further purification.

The metal salts were of pure and AR grades.

Preparation of hydrogels

Hydrogel (I) was prepared by dissolving a known weight of PVA in a known volume of distilled water at room temperature. The solution was subjected to ^{60}Co γ-rays at a dose rate of 2.13 kGy/h.

Hydrogel (II) was prepared by the addition of different amounts of AAc to PVA, depending on the required PVA/AAc composition. These mixtures were then exposed to ^{60}Co γ-irradiation at a dose rate of 2.13 kGy/h. The formed hydrogels were removed from the glass tubes, washed thoroughly several times with bidistilled water, and finally dried in a vacuum oven at 50°C.
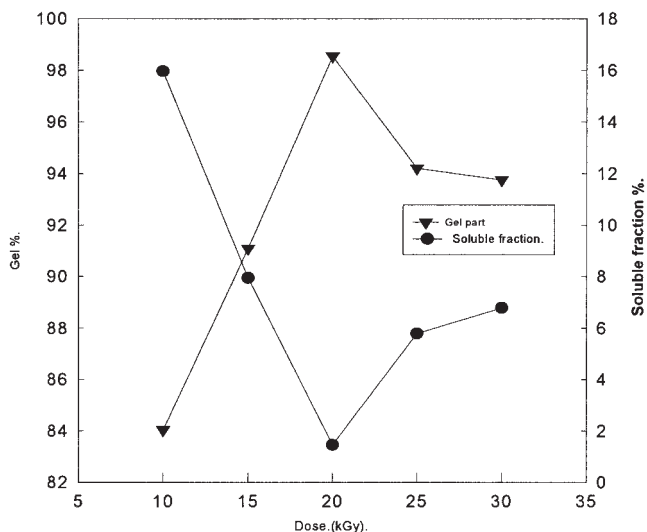
Figure 1 Effect of irradiation dose on Gel % and soluble fraction in PVA hydrogel.

Characterization

Determination of gel fraction

A known weight of the hydrogels (w_0) was extracted in a refluxing system by boiling in bidistilled water for 24 h. The samples were then removed and dried in a vacuum oven at 50°C, thus eliminating excess water, to reach a constant weight (w_1). Finally, the soluble fraction was calculated according to the following equation:

$$\text{Sol fraction (\%)} = [(w_0 - w_1)/w_0] \times 100 \quad (1)$$

where w_0 is the initial weight of the dry sample and w_1 is the weight of the dry, insoluble part after extraction.
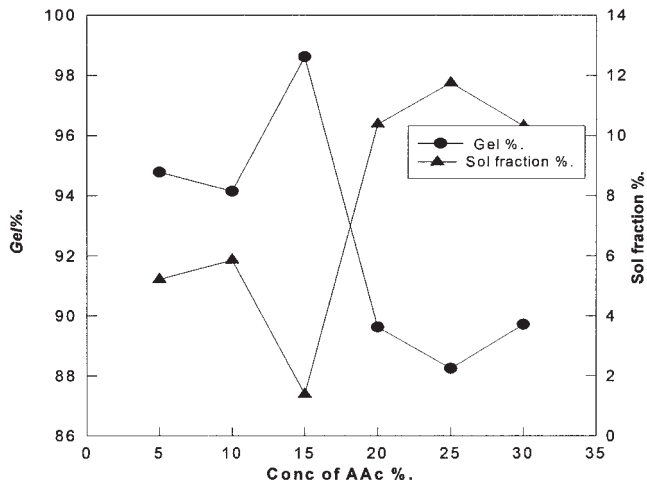

Figure 2 Effect of AAc concentration on Gel % and Sol fraction % of hydrogel at constant irradiation dose (20 kGy).
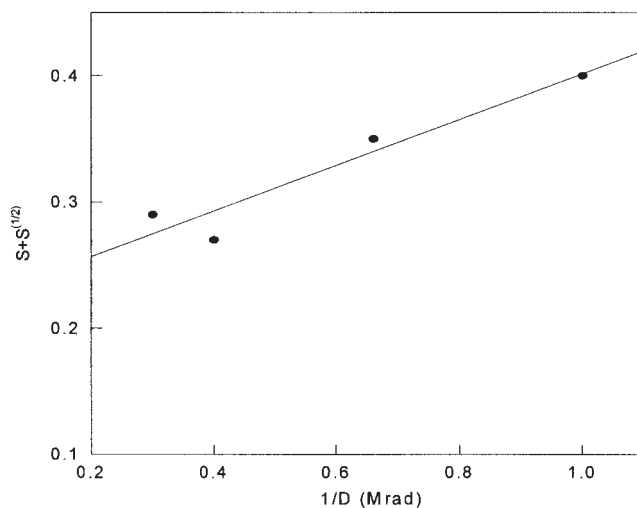

Figure 3 Charlesby–Pinner plot for irradiated PVA hydrogel.

$$\text{Gel fraction (\%)} = 100 - \text{sol fraction (\%)} \quad (2)$$

Methods used for heavy metal ion uptake

Different metal salt solutions ($CuSO_4$, $NiCl_2$, $CoSO_4$) of known concentration (2000 ppm) were first prepared. A sample of the hydrogel, of known weight (0.5 g), was then immersed in these solutions for different time intervals ranging from 1 to 24 h. UV spectroscopic analysis was used to determine C_1 and C_0. The metal uptake was determined by using the following equation:

$$\text{Metal uptake (\%)} = [(C_0 - C_1)/C_0] \times 100 \quad (3)$$

where C_1 and C_0 represent the final and initial concentrations of metal ions in solution, respectively.

Instrumentation

UV spectroscopy

A UV–vis Pye Unicam (Cambridge, UK) spectrophotometer Type Sp 8-200 was used to determine C_1 and C_0. All spectrophotometric measurements were carried out at room temperature (25°C) and at the appropriate wavelength of each metal.

Atomic absorption measurement

The hydrogels were immersed in solutions of mixtures of the metal salts of initial concentration 2000 ppm. The metal salt, remaining from its original feed concentration, was determined by atomic absorption (Unicam Model Solar 929 instrument) using lamps for Cu, Ni, and Co. Merck atomic absorption standard solutions for the above metals were used for the cali-
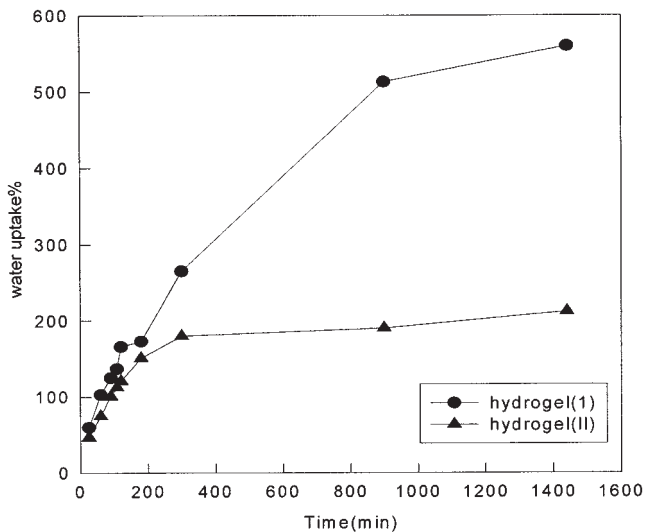
Figure 4 Effect of immersing time on water uptake % for hydrogels (I) and (II) prepared at 20 kGy.

bration process. The metal uptake, adsorbed by the prepared hydrogel, was calculated as follows:

$$\text{Metal uptake (ppm)} = C_o - C_f \qquad (4)$$

where C_o is the original feed solution concentration and C_f is the remaining concentration detected by atomic absorption.

Thermogravimetric analysis

TGA studies were carried out using a TGA-30 apparatus (Shimadzu, Kyoto, Japan), at a heating rate of
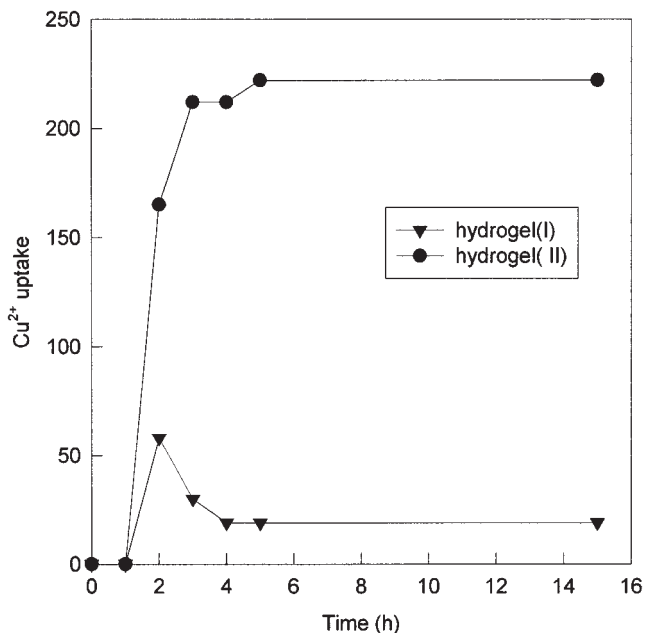

Figure 5 Cu^{2+} uptake versus treatment time using hydrogels (I) and (II) prepared at 20 kGy, 30°C, and initial concentration 2000 ppm.

Figure 6 Ni^{2+} uptake versus treatment time using hydrogels (I) and (II) prepared at 20 kGy, 30°C, and initial concentration 2000 ppm.

10°C/min in air, over a temperature range from room temperature to 500°C.

Differential scanning calorimetry

DSC measurements were carried out using a Shimadzu DSC-50 instrument. The rate of heating for all samples was set at 10°C/min.

Scanning electron microscopy

The surface morphologies of hydrogels (I) and (II), and those loaded with different metal ions, were in-

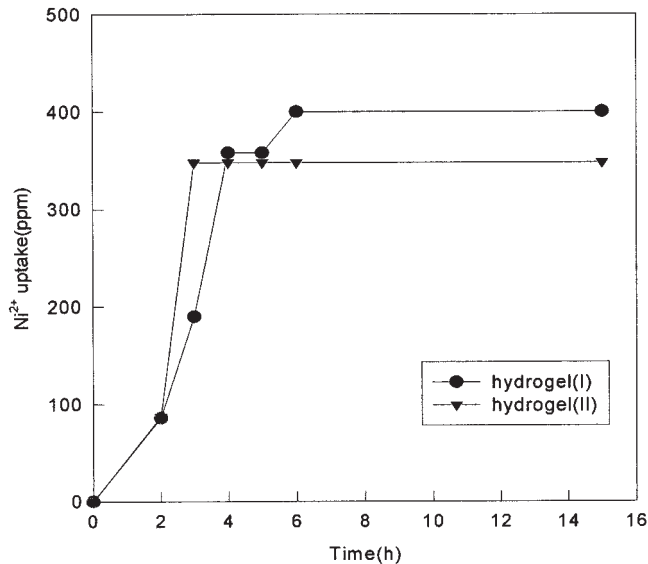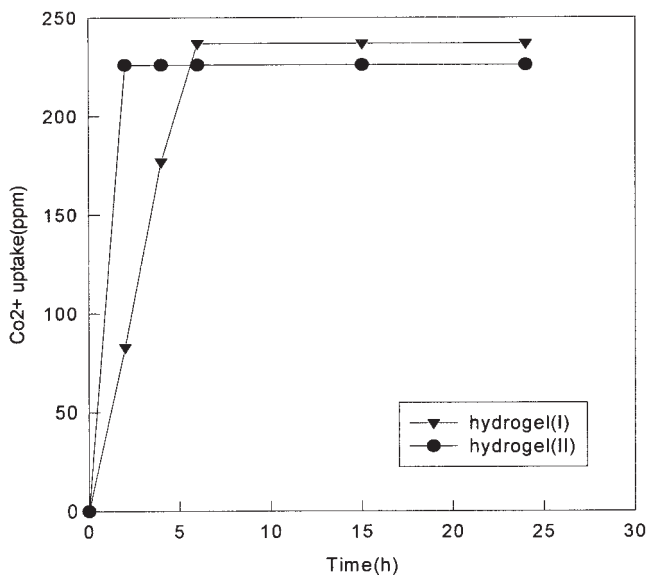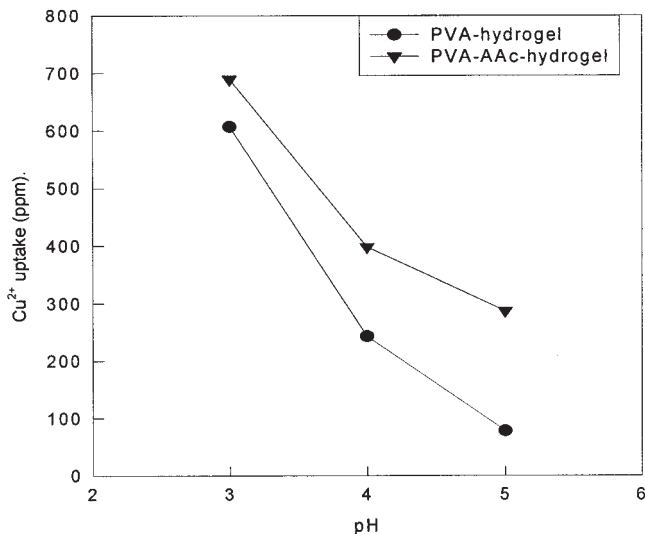**Figure 7** Co^{2+} uptake versus treatment time using hydrogels (I) and (II) prepared at 20 kGy, 30°C, and initial concentration 2000 ppm.
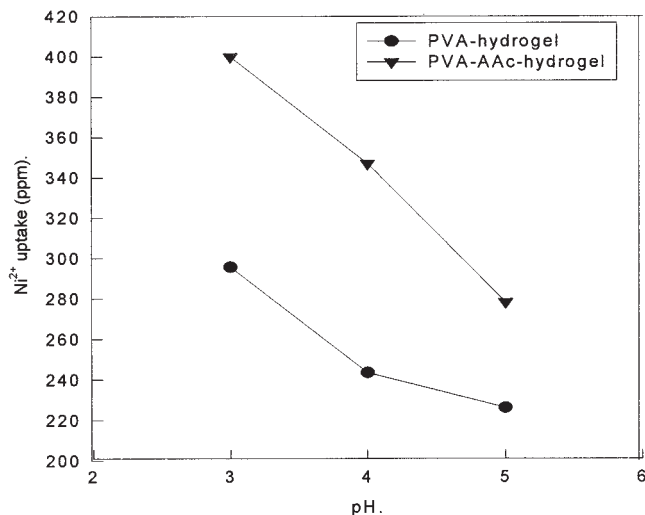
Figure 8 Cu^{2+} uptake versus different pH values. Initial Cu^{2+} concentration: 2000 ppm; soaking time: 24 h.

vestigated by the SEM technique using a JSM-5400 instrument (JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Preparation of crosslinked PVA hydrogel by radiation

Two hydrophilic hydrogels were prepared: hydrogel (I) was prepared by changing the irradiation dose and changing the concentration of PVA solution; hydrogel (II) was prepared by radiation-induced copolymerization of PVA–AAc aqueous solutions by changing the concentration of acrylic acid and irradiation dose. A series of preliminary experiments were carried out with the objective of obtaining the highest percentage

Figure 9 Ni^{2+} uptake versus different pH values. Initial Ni^{2+} concentration: 2000 ppm; soaking time: 24 h.
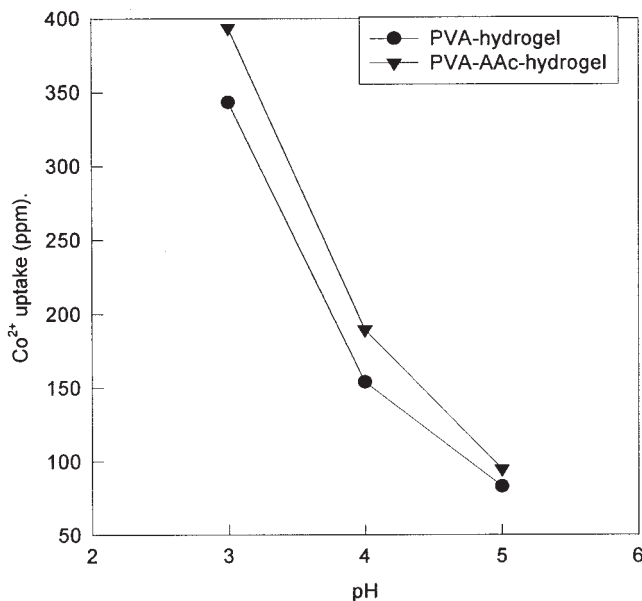
Figure 10 Co^{2+} uptake versus different pH values. Initial Co^{2+} concentration: 2000 ppm; soaking time: 24 h.

of gel (gel %) from PVA by changing the irradiation dose. Figure 1 shows the relation between gel %, soluble fraction, and irradiation dose. From this relation we determined the maximum gel % was at 20 kGy (designated the gelation dose). This selected dose was used in the preparation of hydrogel (II) with changing acrylic acid concentrations. Figure 2 shows the relation between gel % and soluble fraction and concentration of AAc (volumes). The decrease in gel % at high doses, shown in Figure 1, is attributed to the degradation processes of PVA at such doses (R). Figure 2 shows that the decrease in gel %, with the concentration of acrylic acid, is attributed to the formation of some polyacrylic acid homopolymer, which is soluble in hot water. By applying the Charlesby–Pinner equation for random molecular weight,[11] as shown in Figure 3, it is possible to calculate the crosslinking as well as degradation probabilities caused by irradiation. This equation is expressed as follows:

$$S + \sqrt{S} = p_0/q_0 + (1/q_0)MR \qquad (5)$$

where p_0 and q_0 are the probabilities of main chain scission or crosslinking, respectively; R is the radiation dose; M is the number-average degree of polymerization; and S is the soluble fraction after extraction.

From the plot of $(S + \sqrt{S})$ versus $(1/R)$ (Fig. 3) we can calculate the intercept that represents the ratio of probabilities of chain scission to crosslinking (p_0/q_0), which was determined to be 0.25. The probability of crosslinking q_0, calculated from the slope of this curve,

TABLE I
Atomic Adsorption (Selectivity)

Polymer–M$^+$	Metal uptake (ppm)
PVA–Cu	50
PVA–AAc–Cu	84.5
PVA–Ni	7.86
PVA–AAc–Ni	66.8
PVA–Co	26.08
PVA–AAc–Co	65.16

was determined to be 6.67. The probability of chain scission p_0 was 1.5.

From these calculations, it can be concluded that PVA has an outstanding ability to crosslink by irradiation, so it can be used successfully as a hydrogel. The introduction of acrylic monomer in PVA also has an important effect in the metal uptake recovery, as shown in the following results.

Characterization and some selected properties of the two prepared hydrogels

Water uptake

From a practical perspective, hydrogels should exhibit suitable hydrophilic properties if they are used in removing metal cations from aqueous solution. The hydrophilic property of a hydrogel is investigated by measuring the water uptake. Figure 4 shows the change of water uptake % with time, of hydrogels (I) and (II). The water uptake % obtained for hydrogel (I) is greater than that obtained for hydrogel (II). This is explained by the increase of crosslinking density in hydrogel (II) attributed to the presence of polyacrylic acid crosslinked chains in PVA matrices.

Metals are among the most important trace-level constituents of natural water.[13] Many heavy metals are quite toxic and drinking such water containing these metals at low levels is thought to have detrimental effects on human health. Among the factors that affect the adsorption process of metal ions from their solution are soaking time in metals and the pH of the metal ion solution. The metal uptake % was deter-

TABLE II
Weight Loss (%) at Different Decomposition Temperatures for Pure PVA and PVA Loaded with Different Metals

Hydrogel	Weight loss (%)					
	Temperature (°C)					
	300	350	400	450	500	550
PVA pure	27.0	28.1	50.0	69.4	87.5	94.1
PVA + Cu	37.3	38.4	50.0	65.4	76.9	85.0
PVA + Ni	11.7	41.4	54.5	76.5	89.4	89.4
PVA + Co	26.6	42.8	50.0	74.3	85.7	85.7

TABLE III
Effect of Different Metal Ions on the Thermal Stability of PVA/AAc Hydrogel at Various Elevated Temperatures[a]

Hydrogel	Weight loss (%)						
	Temperature (°C)						
	200	300	350	400	450	500	550
PVA + Aac	7.00	22.3	38.7	52.1	65.8	77.9	85.0
PVA + AAc + Cu	0	2.8	23.8	38.17	49.4	66.76	79.7
PVA + AAc + Ni	5.16	28.9	43.3	54.2	68.7	81.9	98.9
PVA + AAc + Co	8.68	16.6	39.9	54.0	66.6	74.0	89.1

[a] Preparation conditions; irradiation dose, 20 kGy; acrylic acid concentration, 15%.

mined by UV–vis spectrophotometric analysis based on measuring the absorption of solutions of the different metal ions before and after the metal uptake process. Metal content also was determined by atomic absorption measurements.

Metal uptake % by hydrogel (I) and hydrogel (II)

In the present work, a constant concentration of different metal ions (2000 ppm) under investigation was prepared. The uptake of different metal ions by hydrogels (I) and (II) was measured as a function of immersion time and pH of the metal ion feed solution at room temperature, and is shown in Figures 5, 6, and 7. It was found that, generally, the metal uptake by hydrogel (II) is higher than that obtained by hydrogel (I). This is explained by the higher affinity of hydrogel (II), which has poly(acrylic acid) chains with reactive –COOH groups. Such –COOH groups have high affinity for adsorption and complexation with metal ions.

Effect of immersion time. From the perspective of economics, the time of treatment is an important factor in metal uptake, and thus the effect of immersion time on metal uptake of different metal ions was investigated. The efficiency of the hydrogel in metal uptake can be determined from the time required to reach maximum adsorption of metal ions by chelation through functional groups of the hydrogel. Figures 5, 6, and 7 show the relation between metal uptake and time of immersion: the metal ion uptake % increases with time to reach its maximum value after 5 h of soaking, after which it tends to level off.

Effect of pH of feed solution. The adsorption behavior of metal ions on the hydrogel, at different pH levels at a fixed treatment time (24 h), was examined and the results are shown in Figures 8, 9, and 10 It is clear that increasing the pH value [i.e., decreasing the hydrogen ion concentration in the solution according to the following relation (pH $= -\log$ H)] is accompanied by a detectable reduction in the uptake % values for the

TABLE IV
Effect of Different Metal Ions on the Glass Transition and Melting Temperature of PVA and PVA–AAc Hydrogels

Polymer	T_g (°C)	T_m (°C)
PVA	90	195
PVA–AAc	140	240
PVA–Cu	165	220
PVA–AAc–Cu	160	220
PVA–Ni	120	175
PVA–AAc–Ni	160	240
PVA–Co	100	180
PVA–AAc–Co	142	190

three metals under investigation. This reduction may be attributable to the hydrolysis of the metal ions at higher pH values.[13]

The metal uptake of hydrogels (I) and (II) may be explained on the basis of the following points:

- The affinity of hydrogels for the different metals is essentially dependent on the hydrophilic groups present in the hydrogel. The metal uptake will

also eventually undergo bond complex formation between metals and hydroxyl or carboxyl groups present in the hydrogels.

- The greater concentration, in the case of hydrogel (II) than that of hydrogel (I), is ascribed to the presence of carboxylic groups in its structure.
- Moreover, the opening up of the hydrogel structure, during the crosslinking and copolymerization process, may facilitate the adsorption of different metal ions into the hydrogel.

Atomic absorption measurements

The selectivity of hydrogels (I) and (II) toward different metal ions was measured by atomic absorption and the results are shown in Table I. The selectivity of these metals was determined at room temperature (30°C) using mixtures of different metal ions. From Table I, it is obvious that the affinity of hydrogels (I) and (II) toward Cu^{2+} is substantially higher when it exists in a mixture containing the other two metal ions. This phenomenon is attributed to the smaller atomic radius of Cu^{2+}, its low valency, and its small molecular size, and because it is easy to form a chelate, compared to formation with the
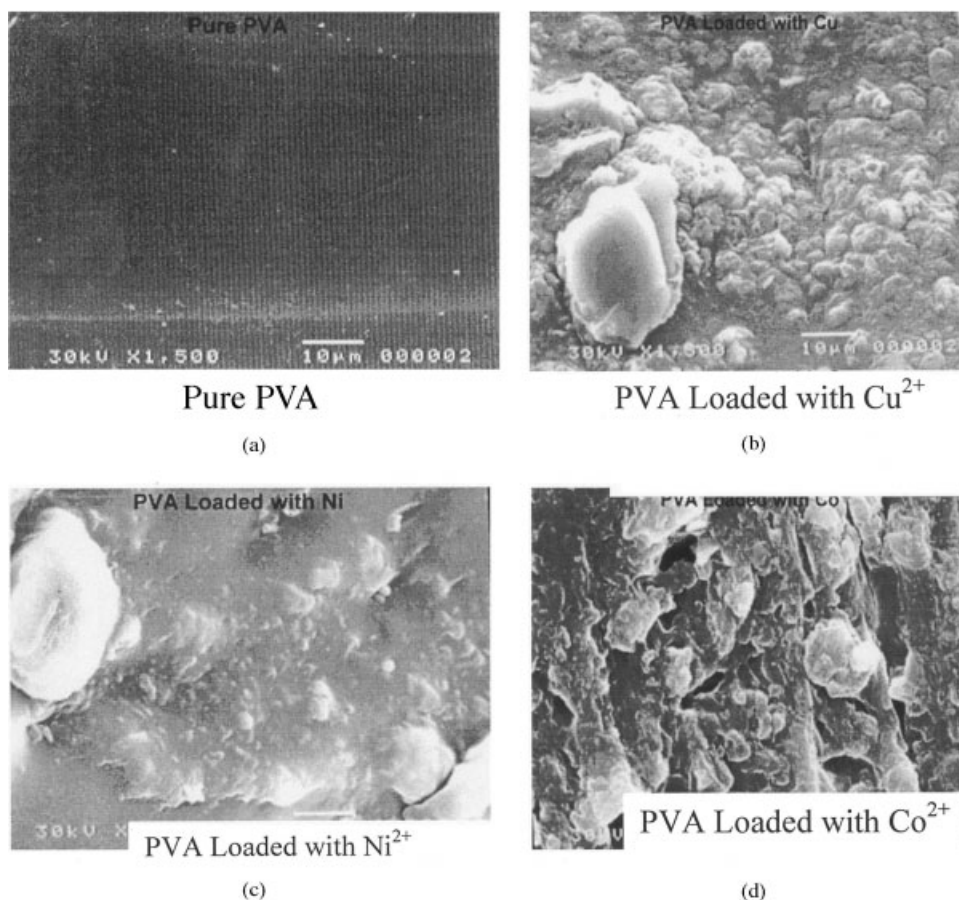
Figure 11 Scanning electron micrographs of pure PVA and loaded PVA with different metal ions: (a) pure PVA; (b) PVA loaded with Cu^{2+}; (c) PVA loaded with Ni^{2+}; (d) PVA loaded with CO^{2+}.
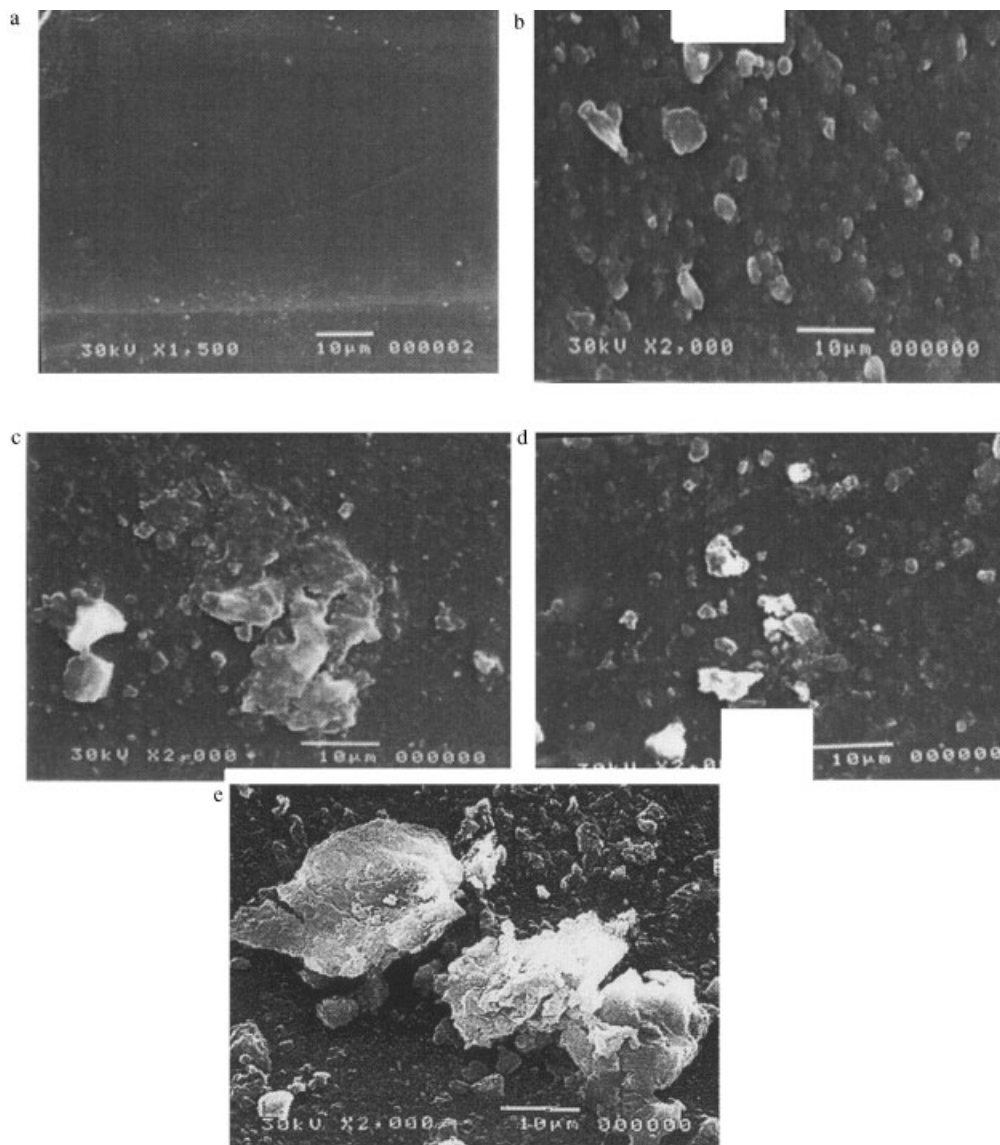
Figure 12 Scanning electron micrographs of pure PVA, PVA–AAc, and PVA–AAc loaded with different metal ions: (a) pure PVA; (b) PVA–AAc; (c) PVA–AAc–Cu^{2+}; (d) PVA–AAc–Ni^{2+}; (e) PVA–AAc–Co^{2+}.

other two metal ions in the case of hydrogel (I), and its position in the electrochemical series with respect to the hydrogen ion. The affinity of hydrogel (II), by chelation, toward Co and Ni is nearly identical (66.8 and 65, respectively), but the affinity of hydrogel (I) toward Co and Ni is 26.08 and 7.87, respectively. The propensity for complex formation for Co ions is higher than that for Ni ions in hydrogel (I) because of its electronic configuration.

Thermal properties of pure hydrogels (I) and (II) and those loaded with different metal ions

Investigation of the change in thermal properties of pure hydrogels (I) and (II) and those loaded with different metal ions is important for its application as

well as characterization and determination of the chemical and physical changes occurring in the hydrogels. The thermal stability of metal-loaded hydrogel was also studied because it may have other applications, as a metal–polymer complex material, for example. Specific techniques to provide useful information for such applications include thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM), for the measurement of structural morphology.

TGA

The TGA curve reveals the formation of intermediate compounds, and also indicates the effect of tempera-

ture on the compounds formed. Tables II and III show the thermal weight loss for pure and loaded hydrogels at various elevated temperatures. Decomposition, attributed to the side groups and branches in the hydrogel, can be seen at the stage from 0 to 350°C. Above 350°C the weight loss is attributed to main chain scission in the polymer chain and matrices. Results show that the hydrogel, loaded with different metal ions, is thermally stable at temperatures up to about 350°C, which is suitable for most practical uses.

Change in thermal parameters of hydrogels (I) and (II), and those loaded with different ions, by DSC

The glass-transition temperature (T_g) and the melting temperature (T_m) were calculated from the DSC scan and the results obtained are shown in Table IV. The increase in the value of T_g for hydrogel (II) over that of hydrogel (I) is attributed to the incorporation of amorphous acrylic acid polymer, and the increase of T_m is also attributed to the increase in the crosslinking density and increase of network structure in hydrogel (II). The increase in T_g and T_m of hydrogels (I) and (II), loaded with different metal ions, is attributed to complex formation between polymer and metal; the bond strength between these metal ions and polymer results in increasing T_g and T_m.

SEM

SEM was used to detect the topography of the hydrogel surface before and after loading with metal ions: Figure 11 relates to pure PVA and Figure 12 to PVA–AAc hydrogels. These micrographs show that the surface of the pure hydrogel is smooth; however, samples loaded with metal ions show a disruption of the polymer structure.[14]

From these results, it can be assumed that the metal ions undergo adsorption with the hydroxyl groups because of their high hydrophilicity. However, in the presence of carboxylic acid groups, the metal ions may undergo chelation or complexation.

CONCLUSION

In this work, the synthesis and characterization of two different hydrogels were performed: PVA hydrogel was prepared by radiation crosslinking and PVA–AAc by radiation induced copolymerization. Also, the gelation dose was identified and was equal to 20 kGy.

It can be concluded that the prepared hydrogels have an outstanding affinity to recover metal ions from their solutions. In addition the hydrogels loaded with metal possess good thermal stability.

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