

New Hydrogel Containing Sulfur Compound Prepared by γ Irradiation and Its Application for Metal Recovery

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ABSTRACT: A new hydrogel that contains sulfur is prepared by radiation polymerization and its application for recovery of Hg^{2+} , Pb^{2+} , Cd^{2+} , and Cu^{2+} ions is discussed. The metal hydrogel complexes are isolated and characterized by using different spectroscopic techniques (UV-visible, IR, NMR, and mass), thermal analysis (TGA and DSC) measurements, and SEM. Also, the mode of complexation is determined using IR and NMR spectroscopy. The scanning electron micrographs show that the hydrogel has a great ability to recover the metal ions in the following order: $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$. TGA thermograms are used to investigate the mechanism of thermal decomposition. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 955–966, 2000

Key words: hydrogel; sulfur compound; γ irradiation; metal recovery

INTRODUCTION

Hydrogels may be considered as the most interesting polymeric materials that find a wide application in many fields. Some of the applications of the hydrogel are use in contact lenses, chromatography, controlled release applications, and agricultural fields. Much research has been devoted to synthesis of hydrogels using chemical techniques. A literature survey shows little information about preparation of hydrogels by radiation polymerization, especially those containing sulfur groups. However, a few studies, including recovery for metal ions by hydrogels containing sulfur groups, were reported.^{1–6} So, the present work is aimed at the γ -radiation polymerization synthesis

of a specific hydrogel containing a sulfur compound. Also, the application of this hydrogel for recovery of some metal ions, especially heavy metals that have a great tendency toward sulfur, is reported.

EXPERIMENTAL

Materials

The acrylic acid (AAc) used was pure grade (Merck, Germany). The *N,N*-methylene bisacrylamide (MEBAm) was pure grade (BDH), and it was used as a crosslinking agent. Trithioglycolic acid (TTGA) was used without further purification. The other solvents were pure grade and were used as received.

Preparation of Hydrogel

The hydrogel was prepared by mixing AAc (83 mmol) in a solvent mixture of methanol and water

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at different ratios with MEBAm (0.32 mmol) and TTGA (0.37 mmol) in a pyrex glass tube with continuous stirring until complete miscibility. The mixtures were subjected to a ^{60}Co γ source at a radiation dose of 20 kGy at a dose rate of 2.13 Gy/s. The irradiation process was carried out using the γ -cell facility at the National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt. The formed hydrogel was removed from the glass tube, washed thoroughly with bidistilled water several times, and finally dried in a vacuum oven at 50°C (mp > 300°C).

Applications

The hydrogel was used in metal ions recovery.

Characterization

Determination of Soluble Fractions Percent

Samples of the hydrogels, which were composed of poly(AAc) and sulfur (PAAc-S), were extracted in a reflux system using bidistilled water at a boil for 2 h. The samples were then removed and dried in a vacuum oven at 50°C to get rid of the water to reach a constant weight (W_1). Finally, the soluble fraction was calculated according to the following equation:

$$\text{soluble fraction (\%)} = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 is the initial weight of the dry sample and W_1 is the weight of the dry sample after extraction of the soluble fraction.

$$\text{gel fraction (\%)} = 100 - \text{soluble fraction}$$

Determination of Water Uptake Percent

A known weight of the nonsoluble hydrogel (PAAc-S, W_1) was soaked in bidistilled water for 48 h at room temperature. The sample was then removed and blotted on filter paper to remove the excess water on the surface. The water uptake was calculated using the following equation:

$$\text{water uptake (\%)} = \frac{W_2 - W_1}{W_2} \times 100$$

where W_1 is the initial weight of the hydrogel and W_2 is the final weight of the swollen hydrogel.

Preparation of PAAc-S Hydrogel Complexes

A known concentration (0.5 g/50 mL distilled water) of the metal salts [HgCl_2 , $\text{Pb}(\text{NO}_3)_2$, CdCl_2 , and CuSO_4] was prepared. The solution was divided into two equal portions. In the first portion (0.25 g/25 mL) a piece of the hydrogel (PAAc-S) was immersed and left for 48 h. The concentration of the metal ion in the flask was determined by complexometry with backtitration in all cases, except the cadmium complex that was determined by the direct method. In all cases, xylenol orange was used as the indicator and hexamine as a buffering agent.⁷ The swelled piece of PAAc-S hydrogel was removed after 48 h and then dried in a vacuum oven at 50°C to dryness. The assay of the total metal ion was determined from the second portion. Also, the concentration of the mixture of metal ions was determined by masking the mercuric ion using thiosemicarbazide.⁸

Instrumentation

IR Spectroscopy

The IR spectra of the PAAc-S and its complexes were found with a Mattson 5000 FTIR spectrometer over a 200–4000 cm^{-1} range at Mansoura University, Egypt.

UV Spectroscopy

The UV-visible spectrum of the solid CuSO_4 complex was carried out using a Unicam UV/Vis Spectrometer UV2 at Mansoura University, Egypt.

NMR

The ^1H -NMR spectrum for the PAAc-S in d_6 -DMSO was recorded on a Varian Gemini (200 MHz) instrument at Cairo University, Egypt.

Mass Spectroscopy

The mass spectrum of the hydrogel was recorded on a Shimadzu GCS-QP 1000 Ex spectrometer using a direct inlet system at Cairo University, Egypt.

Thermal Analysis

The TGA thermograms were carried out on a Shimadzu TGA-50H at Mansoura University while the DSC analysis was performed using Perkin-Elmer DSC 7 at the National Center for Radiation Research and Technology, Nasr City, Egypt. A

Table I Effect of MeOH/H₂O Solvent Composition on Preparation of PAAc-S Hydrogel; Gel Fraction, and Water Uptake, and Soluble Fraction

MeOH/H ₂ O Composition (mL/mL)	Gel Fraction (%)	Water Uptake (%)	Soluble Fraction (%)
1 : 9	99.9	134	0.09
2 : 8	97.6	100	2.39
4 : 6	96.4	99	3.58
5 : 5	39.4	90	6.59

[AAc] = 83 mmol, [TTGA] = 0.37 mmol, [MEBAm] = 0.32 mmol, irradiation dose = 20 kGy/s, dose rate = 2.13 Gy/s.

heating rate of 10°C/min was utilized under a nitrogen atmosphere in the TGA thermograms and 20°C/min was used in the DSC scans.

RESULTS AND DISCUSSION

Characterization of PAAc-S Hydrogel

The effect of solvent mixtures containing various ratios of water and methanol on the yield product, water uptake, soluble fraction, and gel fraction was investigated and is shown in Table I. It can be seen that the solvent mixture plays an important role in the different physical properties of the

prepared hydrogel. However, it is obvious that the highest gel fraction and water uptake percent was obtained by using a solvent mixture composed of the least amount of methanol as the medium for the preparation of the hydrogel (Figs. 1, 2). Even though the solvent mixture is the dominant factor affecting the gel fraction and water uptake, it was found that the yield of the product was a constant 6.31 g in all cases.

Behavior of PAAc-S Hydrogel Toward Organic Solvents

The swellability of the prepared hydrogel in different organic solvents was investigated and is shown in Table II. It can be observed that the hydrogel has a great affinity toward polar solvents rather than nonpolar solvents. The uptake percent of the polar solvents by the PAAc-S can be arranged according to the following order:

ethanol \gg DMF > acetone > methanol.

Chemical Stability of PAAc-S Hydrogel Against Acids and Alkalis

It is known that hydrogels containing acidic moiety can be neutralized with NaOH to obtain the corresponding sodium salt. In this case, the swellability of the sodium salt and consequently, its ion exchange capacity should increase. Thus,

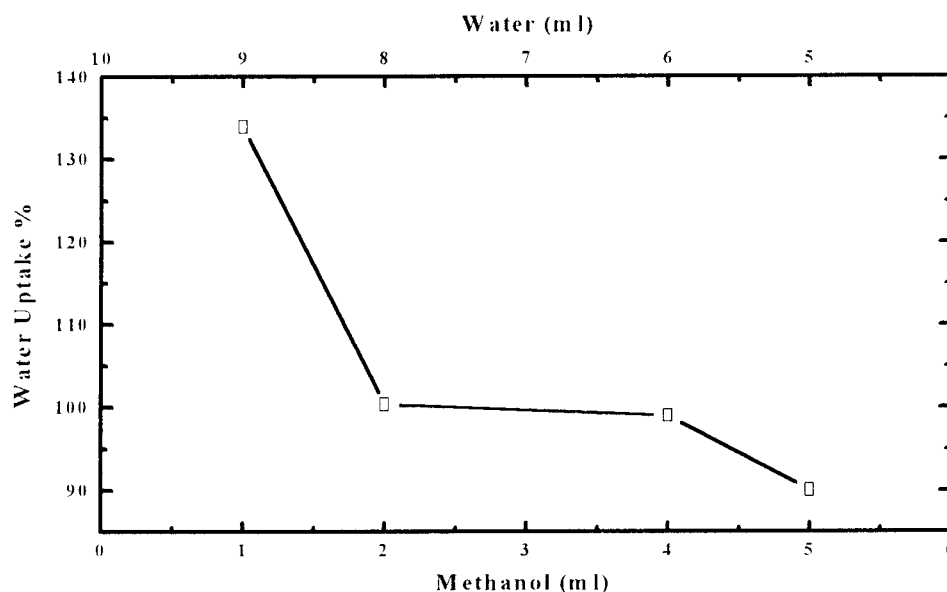


Figure 1 The effect of the mixture of solvents on the water uptake (%).

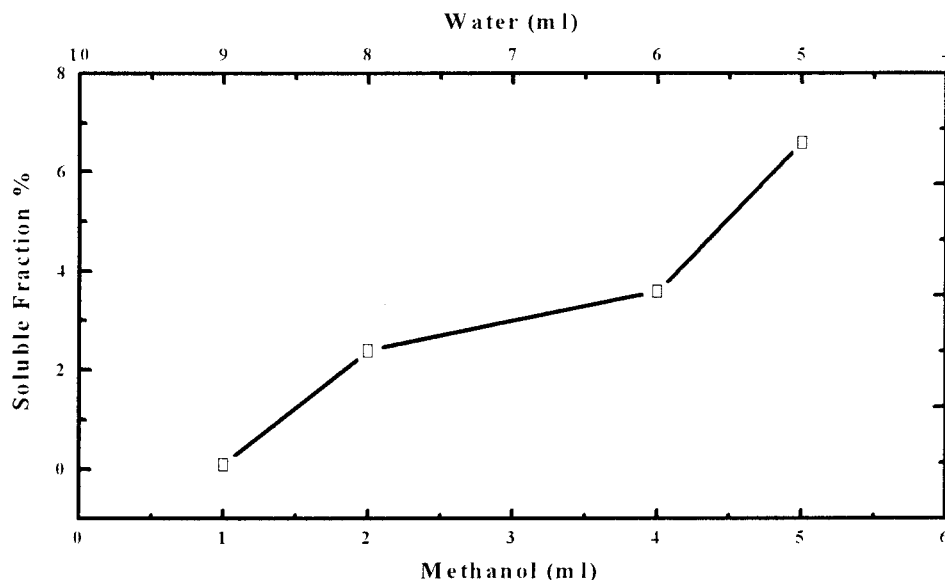


Figure 2 The effect of the mixture of solvents on the soluble fraction (%).

trials were made to obtain the sodium salt of the prepared PAAc-S hydrogel containing PAAc in its chemical structure. So, the obtained hydrogel was treated with dilute NaOH. However, such treatment did not result in obtaining the sodium salt of the crosslinked PAAc-S. On the contrary, a gelatinous product was formed. This behavior may be attributed to the destruction of the crosslinks; the decrease in crosslink density leads to a gelatinous product.

On the other hand, we found that HCl has no adverse effect on the hydrolysis of the crosslinks and practically no change in the chemical structure was observed. However, we found that the addition of dilute HCl leads to a slight increase in the swelling equilibrium of the PAAc-S hydrogel. Also, if the hydrogel was treated with boiling con-

centrated HCl a detectable shrinkage in the hydrogel volume occurred. This can be explained on the basis of the osmotic pressure that causes the water to diffuse from the hydrogel to the concentrated solution of HCl, leading to shrinkage in the volume of the hydrogel sample. Meanwhile, the percentages of HCl and NaOH uptake at equilibrium were found to be 92.3 and 182.7%, respectively.

Spectroscopic Analysis

IR, $^1\text{H-NMR}$, and Mass Spectra

The IR spectrum of the PAAc-S hydrogel shows two distinctly strong absorption bands with a shoulder at 1730, 1704, and 1680 cm^{-1} , which are assigned to the carbonyl groups (C=O) as shown in Figure 3. The two bands may be assigned to the carbonyl groups of the carboxylic residue of AAC and TTGA, respectively. The shoulder at 1680 cm^{-1} is attributed to the carbonyl group of the crosslinking agent. Also, the strong and broad band centered at 3400 cm^{-1} is assigned to the OH group of the acid moiety. Moreover, the IR spectrum of the PAAc-S shows three bands at 1452, 1240, and 811 cm^{-1} that are attributed to the C=S group.

The $^1\text{H-NMR}$ spectrum of the PAAc-S hydrogel (Fig. 4) shows five signals at 1.8, 2.15, 2.6, 4.15, and 12.3 ppm, which are downfield of tetramethyl silane. These signals are attributed to the CH_2

Table II Behavior of PAAc-S Hydrogel Toward Organic Solvents

Solvent	Uptake (%)
Benzene	0.0
Chloroform	0.1
Cyclohexane	0.5
Toluene	2.9
Methanol	121
Acetone	124
DMF	189
Ethanol	517

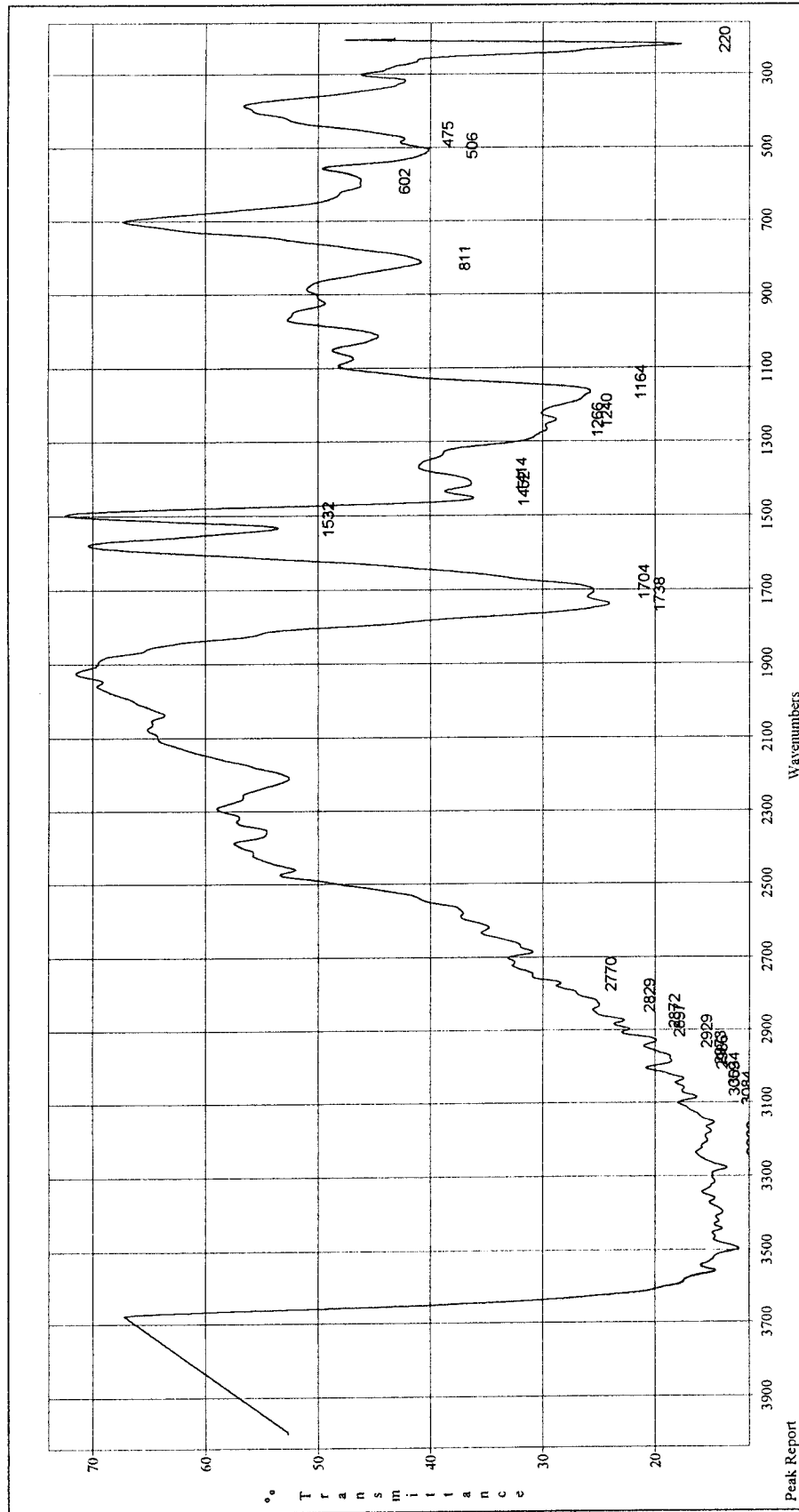


Figure 3 The IR spectrum of the PAAc-S hydrogel.

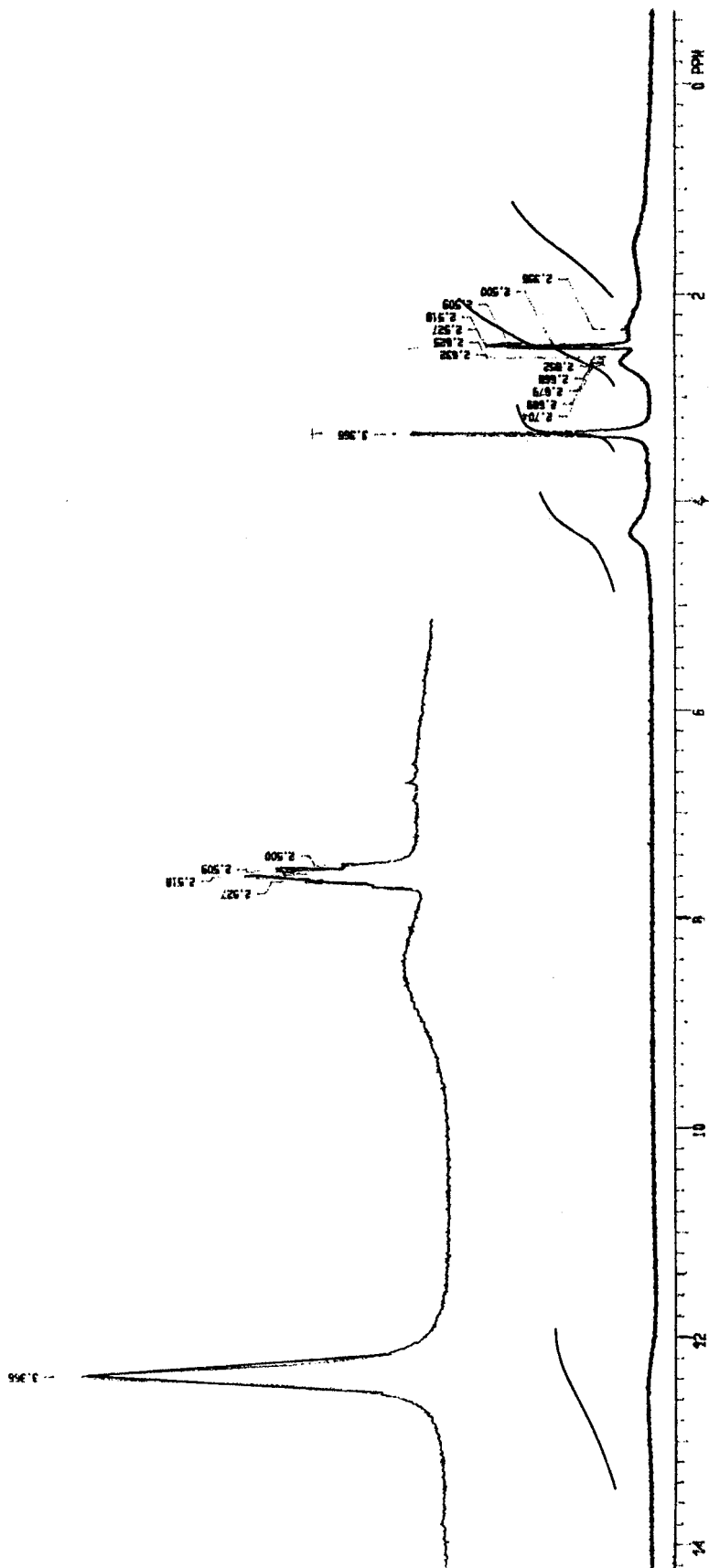


Figure 4 ¹H-NMR spectrum of the PAAc-S hydrogel in d₆-DMSO.

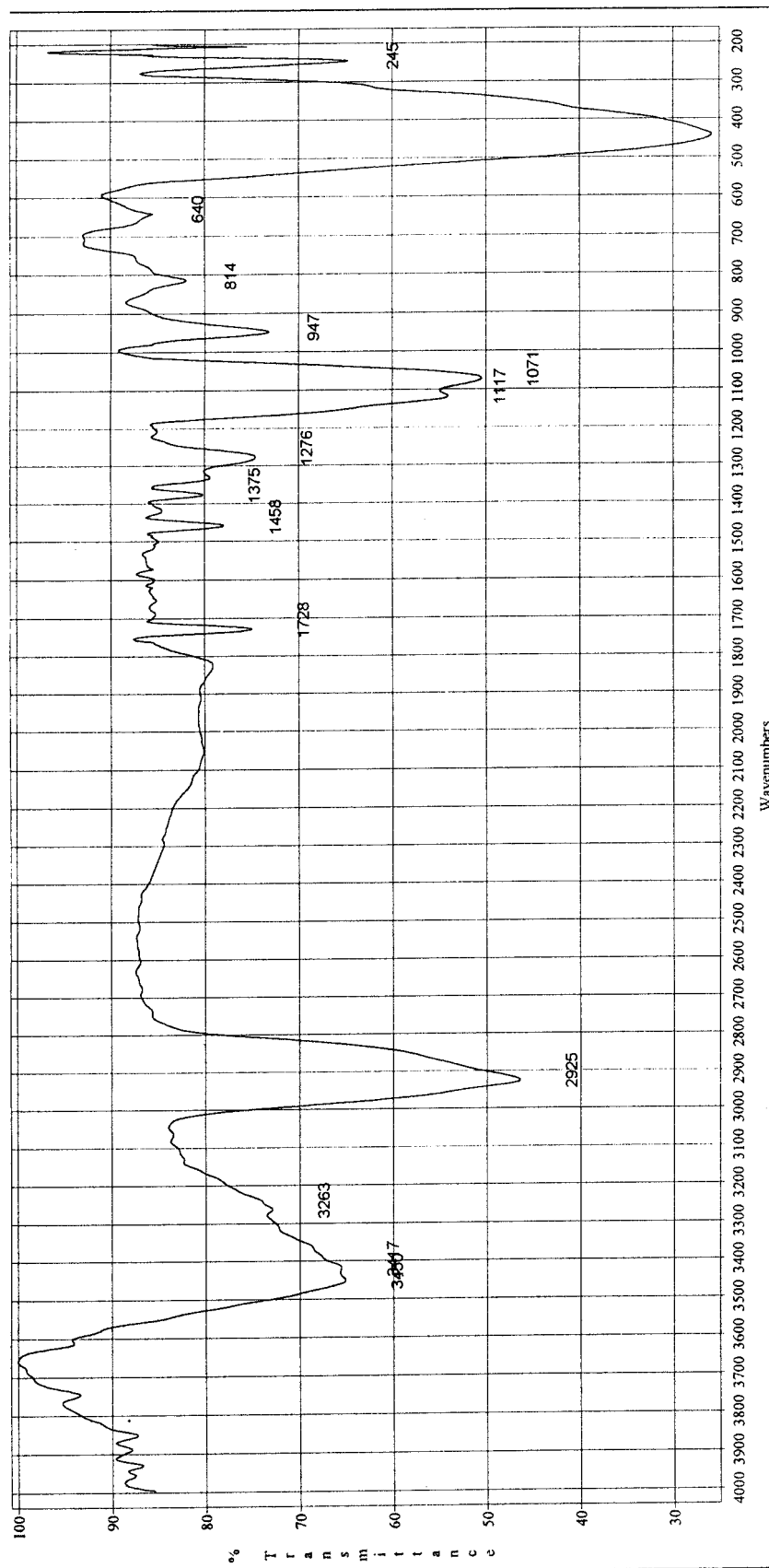


Figure 5 IR spectrum of the PAAc-S hydrogel complex with CuSO₄.

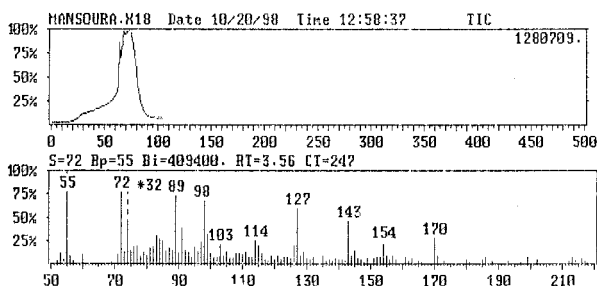


Figure 6 mass spectrum of the PAAC-S hydrogel.

(crosslinking), CH_2 (TTGA), $\text{H}(\text{NH})$, and OH groups (of both AAc and TTGA), respectively.

The IR and NMR spectra suggest that the main constituents of the hydrogel are AAc, TTGA, and the crosslinking agent.

In comparing the IR spectra of the PAAC-S hydrogel with its metal complexes with CuSO_4 , CdCl_2 , $\text{Pb}(\text{NO}_3)_2$, and HgCl_2 , it can be observed that the carbonyl groups corresponding to TTGA and AAc are shifted to lower wave numbers (Fig. 5). This is due to the participation of the carbonyl groups in metal complexation. Also, the band appearing at 3400 cm^{-1} suggests that the OH group of the carboxylic acid still exists. Moreover, it also suggests that the PAAC-S contains water molecules inside its cavity. The broad and weak bands observed in the $2000\text{--}2200\text{ cm}^{-1}$ range suggest the existence of hydrogen bonding. This hydrogen bonding may occur between the OH (carboxylic) or OH (H_2O) and the carbonyl groups of the constituents of the hydrogel.

The obscuring of the band at 990 cm^{-1} assigned to the $\text{CH}_2=\text{CH}$ group indicates that the polymerization is occurring through this group.

The molecular ion in the mass spectrum (Fig. 6) of the PAAC-S hydrogel was found to be 369. This means that the hydrogel contains three main components (AAc, MEBAm, and TTGA). Also, the fragmentation in the spectrum of the PAAC-S shows that the hydrogel contains AAc ($M = 72$), MEBAm ($M = 154$), and TTGA ($M = 170$).

In comparing the mass spectrum of the PAAC-S hydrogel complex (Fig. 7) with that for the PAAC-S hydrogel alone, a new peak is observed. The m/z for the copper(II) hydrogel complex is 544 while that for the hydrogel alone is 369. This suggests that the hydrogel combines with CuSO_4 and one molecule of water. Also, the fragmentation pattern for the spectrum of the hydrogel complex with $\text{Cu}(\text{II})$ metal (Fig. 7) shows a completely different one than the spectrum for the pure hy-

drogel. For the pure hydrogel the spectrum consists of three main peaks at $m/e = 72$, 154, and 170 corresponding to AAc, MEBAm, and TTGA, respectively. The fragmentation pattern of the hydrogel complex with the $\text{Cu}(\text{II})$ metal shows new peaks at $m/e = 91$, 161, 195, and 221 and does not show the peaks of the main components of the hydrogel. The peak at $m/e = 91$ may have come from the breakdown of the TTGA to mercaptoacetic acid, that at $m/e = 161$ may be due to the CuSO_4 salt, and that at $m/e = 195$ may be from the copper salt combined with two molecules of water.

TGA

The TGA thermogram of the PAAC-S hydrogel (Fig. 8) shows that the thermal decomposition of the hydrogel occurs in three steps. It is clear that the PAAC-S is stable up to 180°C and starts to decompose above this temperature. In the first step the hydrogel loses about 39% of its weight, in the second step 67%, and in the third step 77% in the vicinity of 600°C . Moreover, it can be observed that the maximum rate of thermal decomposition reaction occurs at 255°C as shown from the derivative of the TGA thermogram.

DSC Analysis

The DSC scan of the hydrogel complex with $\text{Cu}(\text{II})$ exhibits two endothermic peaks at 215 and 253°C (Fig. 9). The first endothermic peak is due to the removal of water molecules whereas the second endothermic peak corresponds to the melting transition temperature of the hydrogel complex with $\text{Cu}(\text{II})$. Meanwhile, the measured melting point of the pure hydrogel before complexation was found to be $> 300^\circ\text{C}$. Thus, the depression in the melting point from >300 to 253°C may suggest

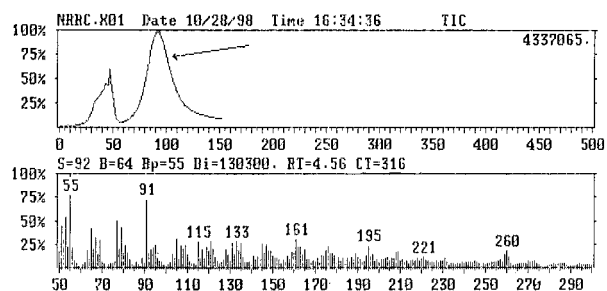


Figure 7 mass spectrum of the PAAC-S hydrogel complex with CuSO_4 .

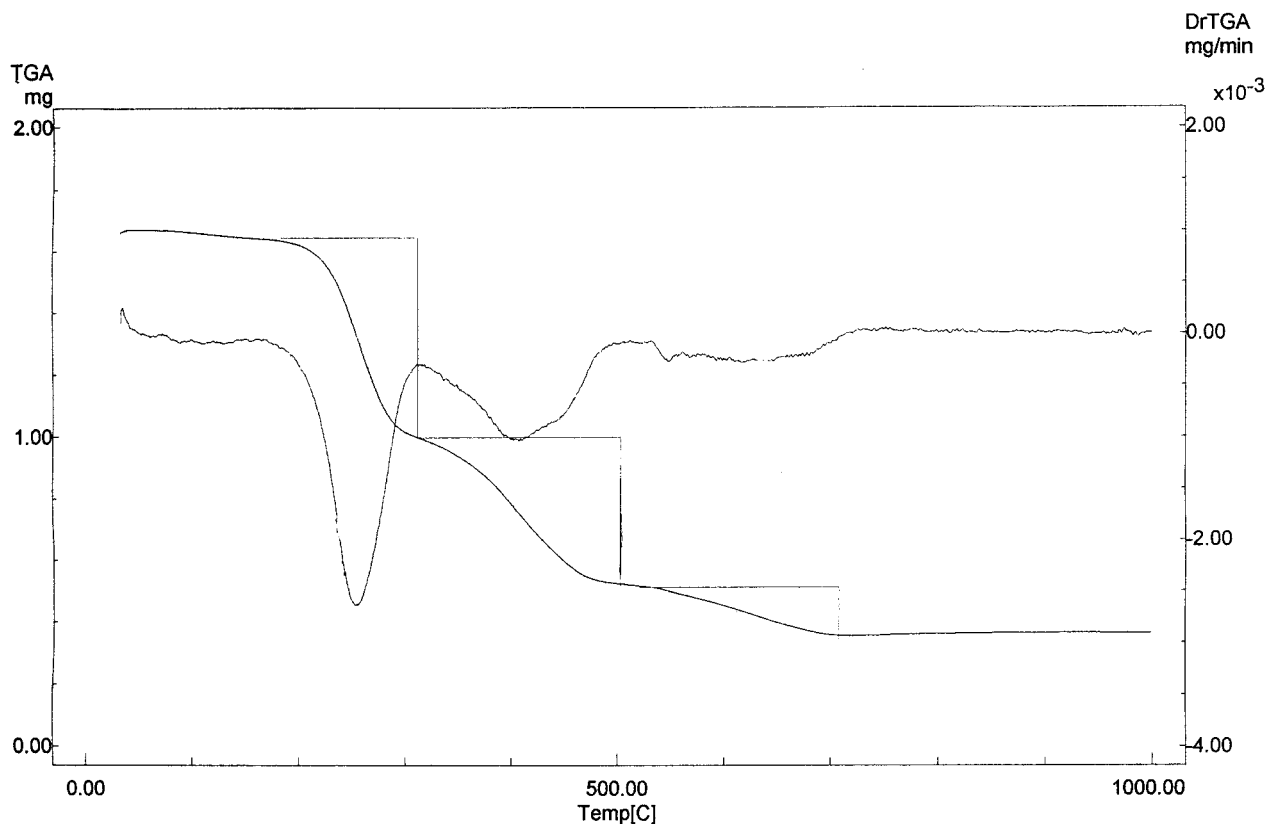


Figure 8 TGA curve of the PAAC-S hydrogel.

the presence of Cu(II) metal in the hydrogel that is due to the reduction in the crystalline part induced by complexation.

Efficiency of PAAC-S Hydrogel Toward Metal Ions Recovery

The recovery efficiency of the hydrogel for different metal ions is shown in Table III. The data indicate that the PAAC-S has a great tendency to adsorb Hg^{2+} ions in particular and other metals according to the following order:



This phenomenon is explained on the basis that the Hg^{2+} combines with sulfur groups along the hydrogel structure according to Pearson's rule.⁹ Also, the bond between sulfur atoms and Hg^{2+} ions is much stronger than the other Cd^{2+} , Pb^{2+} , and Cu^{2+} ions. Consequently, no dissociation occurs in the Hg^{2+} while in the other ions some dissociation due to the weakness of the bond

may occur. All these findings suggest the high uptake percentage of Hg^{2+} in comparison to the Cu^{2+} ion.

On the contrary, it was observed that the PAAC-S hydrogel has no tendency to adsorb Hg^{2+} ions when it is present with other metal salts (Table IV). Also, the results indicate that the hydrogel has a greater tendency toward Cd^{2+} ions than the other metal ions and follows the order $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$.

In order to explain this phenomenon it is better to discuss each case alone. First, in the mixture of CdCl_2 and HgCl_2 , both the salts have the same anion (Cl^-). So, the main factor here is the ionic radius of the metal ion. The ionic radius of the Cd^{2+} ion (0.97 Å) is less than that for the Hg^{2+} ion (1.1 Å), and both of them are in competition to enter the hydrogel. Thus, the small size of the Cd^{2+} ion facilitates its diffusion and combination with the sulfur groups inside the PAAC-S. Second, in the mixture of $\text{Pb}(\text{NO}_3)_2$ and HgCl_2 , the two salts differ in their anions. The existence of the NO_3^- ion assists the precipitation of the Hg^{2+} ion

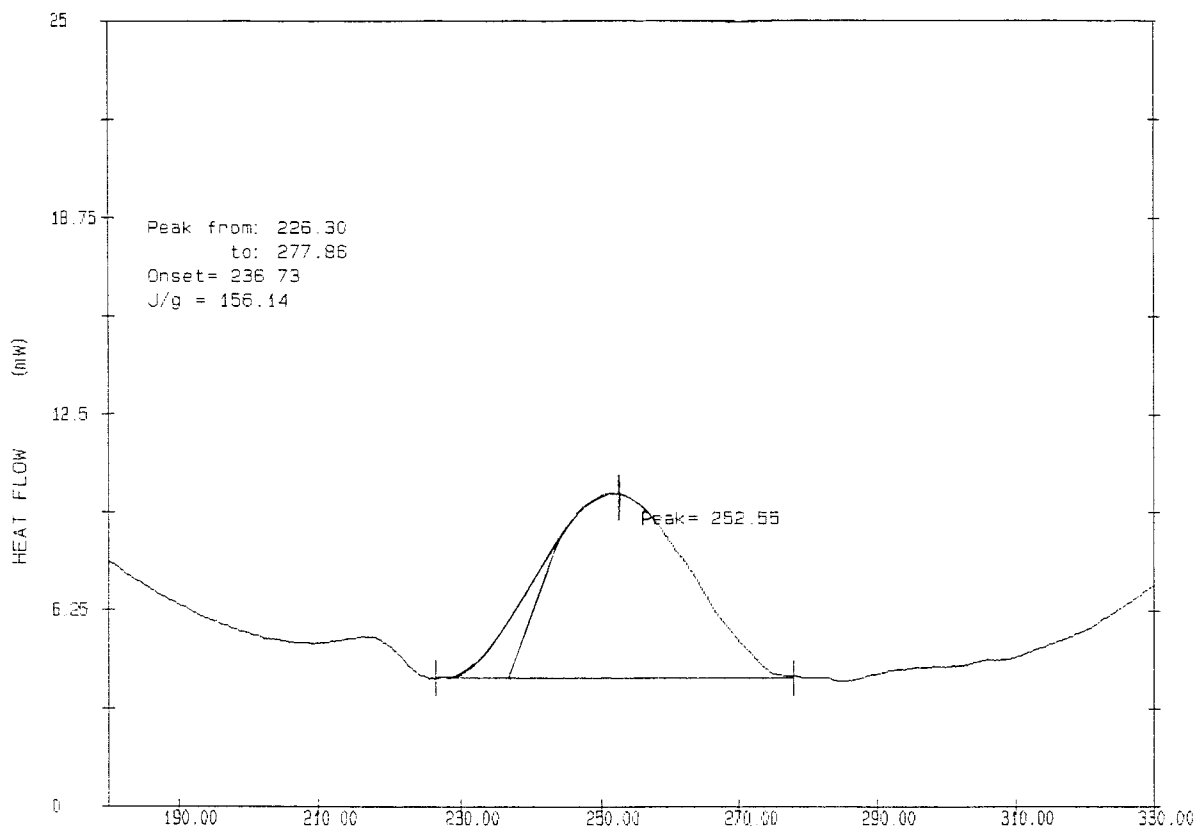


Figure 9 DSC curve of the PAAC-S hydrogel complex with copper.

as $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO} \cdot \text{H}_2\text{O}$ before entering the hydrogel cavity.¹⁰ Consequently, the Pb^{2+} ion, which has a larger ionic radius (1.21 Å), diffuses into the cavity of the hydrogel without any competition from Hg^{2+} ion. Third, the mixture of HgCl_2 and CuSO_4 also contains different anions. The existence of sulfate ions in solution helps the precipitation of $\text{HgSO}_4 \cdot 2\text{HgO}$ before entering the hydrogel cavity.¹⁰ Consequently, the Cu^{2+} ion will easily diffuse into the cavity of the hydrogel.

SEM

Figure 10 shows SEM micrographs of the fracture surfaces of the PAAC-S hydrogel before and after it had been complexed with $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Hg}(\text{II})$. As can be seen in Figure 10(A) for the pure hydrogel, the surface is not smooth: it is full of irregularity, holes, and cavities. However, it can be observed that the surface is full of spherical particles that may due to the polyacrylic polymer.

Table III Efficiency of PAAC-S Hydrogel Toward Metal Ions Recovery

Metal Salts	Weight of Hydrogel	SS (g/25 mL)	SR (g/25 mL)	SI (g/25 mL)	<i>E</i> /g Hydrogel	Metal Ion Uptake (%)
CuSO_4	0.8412	0.0650	0.0630	0.0020	0.03	0.30
$\text{Pb}(\text{NO}_3)_2$	0.9823	0.1590	0.1510	0.0080	0.05	0.80
CdCl_2	0.5798	0.0750	0.0660	0.0090	0.20	1.60
HgCl_2	0.5055	0.1879	0.1655	0.0224	0.24	4.43

SS, The strength of the standard solution; SR, the strength of the solution after the removal of the PAAC-S hydrogel; SI, the strength inside the PAAC-S hydrogel; and the efficiency per gram of PAAC-S hydrogel (*E*).

Table IV Selectivity of PAAc-S Hydrogel Toward Mixture of Metal Salts

Inorganic Mixture	Weight of Hydrogel	SS (g/25 mL)	SR (g/25 mL)	SI (g/25 mL)	<i>E</i> /g Hydrogel	Metal Ion Uptake (%)
CuSO ₄ + HgCl ₂	0.5023	0.25	0.231	0.019	0.15	3.78
		0.25	0.250	0.000	0.00	0.00
		0.25	0.223	0.027	0.23	5.72
Pb(NO ₃) ₂ + HgCl ₂	0.4721	0.25	0.250	0.000	0.00	0.00
		0.25	0.207	0.043	0.34	8.61
CdCl ₂ + HgCl ₂	0.4994	0.25	0.250	0.000	0.00	0.00

SS, the strength of the standard solution; SR, the strength of the solution after the removal of the PAAc-S hydrogel; SI, the strength inside the PAAc-S hydrogel; and efficiency per gram of PAAc-S hydrogel (*E*).

On the other hand, the SEM micrographs of the PAAc-S hydrogel complex with Cu(II) ions in Figure 10(B) clearly shows in the crystal structure a

limited quantity of copper ions dispersed on the surface. Also, the Hg(II) ions can be clearly seen on the surface of the hydrogel in Figure 10(C),

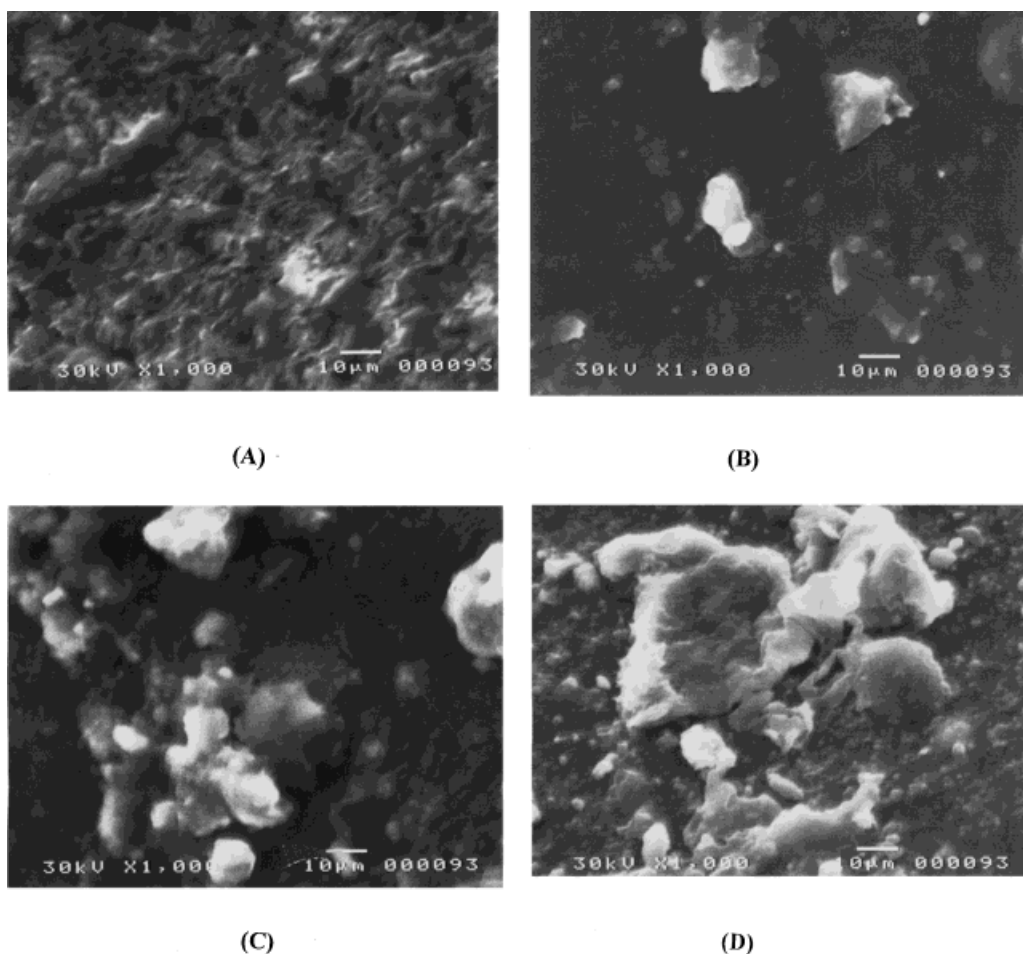


Figure 10 SEM micrographs of the PAAc-S hydrogel (A) before and (B–D) after complexation with (B) Cu(II), (C) Hg(II), and (D) Cd(II).

which is covered with larger particles. The SEM micrograph of the hydrogel complex with Cd(II) in Figure 10(D) shows the same texture as that with Hg(II). The SEM micrograms give further support to the results of metal uptake and to the respective affinity of the hydrogel for the different metals under investigation.

CONCLUSIONS

The results presented in this work were mainly concerned with the radiation polymerization synthesis and application in metal recovery of a hydrogel containing a sulfur compound. The characterization of the prepared hydrogel showed that the solvent mixture is a determining factor affecting the gel fraction and water absorption. Even though the hydrogel contained an acidic group, it did not form a sodium salt when treated with sodium hydroxide. However, dilute acids had no effect on the chemical structure of the hydrogel. Concentrated acid caused a shrinking in the volume. The FTIR and mass spectroscopic analysis of the hydrogel showed that it contained three components: AAc, TTGA, and MEBAm. Meanwhile, the DSC of the hydrogel indicated that the melting temperature was greatly decreased after

complexation with Cu(II) metal. On the other hand, we found that the hydrogel had a great tendency for Hg(II) in separate solution and it had no tendency for that metal if present with other metal salts. The capacity of the prepared hydrogel was confirmed by SEM micrographs.

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