

Radiation Synthesis and Application of a Hydrogel Based on Acrylic Acid and 2-Mercaptobenzimidazole

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ABSTRACT: A hydrogel based on gamma-radiation polymerization of acrylic acid (AAc) in the presence of 2-mercaptobenzimidazole (MBI) and a crosslinking agent was prepared. The properties of this AAc/MBI hydrogel were characterized in terms of gel content, swelling in different solvents, structure morphology, and IR spectroscopy. Moreover, the thermal decomposition behavior of the prepared hydrogel was investigated by thermogravimetric analysis (TGA). The TGA thermograms were also used to determine the different kinetic parameters such as order of reaction and activation energy. The sorption of some divalent metal ions such as Cu^{2+} , Pb^{2+} , Cd^{2+} , and Hg^{2+} by the AAc/MBI hydrogel also was studied. The results showed that the AAc/MBI hydrogel has a higher tendency to swell in water

and polar solvents than in nonpolar solvents. The highest metal uptake by the hydrogel was found for Hg^{2+} and Cd^{2+} , whereas the lowest was for Cu^{2+} and Pb^{2+} ions. The ratios between the distribution coefficients of the different metals [separation factors (SF)] indicate that the hydrogel has a high selectivity for Hg^{2+} over Cu^{2+} (SF = 10.923) and Pb^{2+} (SF = 19.110). However, the hydrogel prefers Hg^{2+} over Cd^{2+} (SF = 1.356) and showed a high selectivity for Cd^{2+} over Cu^{2+} (SF = 7.822) and Pb^{2+} (SF = 7.240). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1607–1614, 2002

Key words: hydrogels; crosslinking; thermal properties; structure; separation factor

INTRODUCTION

There has been increasing interest in recent years to prepare hydrogels to be used in various fields such as medicine, pharmaceuticals, contact lenses, chromatography, and artificial organs. The removal of some organic pollutants from wastewaters is another important application of hydrogels. Immobilization of enzymes in bioengineering, absorbents for pesticides, and fertilizers in the field of agriculture are examples in this regard.^{1–7}

The use of gamma radiation for the synthesis and modification of hydrogels for biomedical purposes has some general advantages.^{8–10} Practically, it solves the problem of sterilization of products and allows one to fabricate a pure product, not contaminated with residual toxic matters. Radiation polymerization studies on preparing hydrogels include the mechanism of reaction, kinetics, and structure.^{11–14} In previous work, the preparation of a hydrogel based on acrylic acid and trithioglycolic acid by radiation polymerization, and its application in the recovery of metal ions, was reported.¹⁵ It was found that the solvent mixture is a determining factor affecting the gel fraction and water

absorption. Also, it was observed that the hydrogel has a great affinity for Hg^{2+} in a separate solution but had no affinity for that metal if present with other metal ions. Therefore, the aim of this work is to synthesize another hydrogel containing a sulfur compound from 2-mercaptobenzimidazole and acrylic acid under the effect of gamma irradiation. In addition, the use of this hydrogel for absorbing some metal ions, especially heavy metals, is examined.

EXPERIMENTAL

Materials

The acrylic acid (AAc) monomer was of pure grade and supplied by Merck (Darmstadt, Germany), whereas *N,N*-methylenebisacrylamide (MBAm) was of laboratory grade and obtained from BDH (Poole, UK) and used as a crosslinking agent. A pure-grade 2-mercaptobenzimidazole (MBI) was obtained from Aldrich Chemie (Steinheim, Germany) and used without further purification. The solvents cyclohexane, toluene, benzene, chloroform, acetone, methanol, and ethanol were of pure grade and used in the swelling experiment.

Synthesis of AAc/MBI hydrogel

The preparation of the hydrogel was performed by mixing 6 mL (5.45 mol) of AAc monomer, in a solvent

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mixture of methanol and water at a ratio of 1:9 with 0.05 g (2.02×10^{-2} mol) of MBam and 0.5 g (0.21 mol) of MBI in a Pyrex glass tube with continuous stirring until complete miscibility. The polymerization of the mixture was performed by exposing the mixture to a dose of 20 kGy of gamma radiation at a dose rate of 2.057 kGy/h. Irradiation to the required dose was carried out with a Co-60 gamma source (Nuclear Research Center, Bhabha, India). On the basis of the mixed quantities of the different components used for the preparation, the yield of the hydrogel was 5.995 g.

Determination of gel fraction percentage

A sample of the prepared hydrogel was accurately weighed (w_0) and subjected to extraction with bidistilled water using a Soxhlet system for 24 h. After extraction, the sample was removed and dried in a vacuum oven at 50°C to a constant weight (w_1). The soluble fraction was calculated according to the following equation:

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

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

Swelling behavior of AAc/MBI hydrogel in different solvents

A known weight of the insoluble hydrogel was soaked in bidistilled water and different solvents for 24 h at room temperature. The sample was then removed and blotted on a filter paper to remove the excess water or solvent on the surface. The swelling (%) was calculated according to the following equation:

$$\text{Swelling (\%)} = [(w_2 - w_1)/w_1] \times 100$$

where w_1 is the initial weight of the hydrogel and w_2 is the final weight of the swelled hydrogel.

IR spectroscopic analysis

The infrared spectra of the pure hydrogel before and after metal sorption were performed on a Mattson (Unicam, UK) 5000 FTIR spectrometer over the range 200–4000 cm^{-1} . The samples for IR analysis were prepared by grinding 5 mg of the hydrogel to a very fine powder and mixing with a highly dried powder (30 mg) of KBr and then pressing to a transparent disk.

Thermogravimetric analysis (TGA)

The TGA thermograms were carried out on a Shimadzu (TGA 50; Shimadzu, Kyoto, Japan) at a heating rate of 10°C/min over a temperature range from room temperature to 600°C. The primary TGA thermograms

were used to determine the different kinetic parameters such as activation energy and order of thermal decomposition reaction.

Determination of sorption of heavy metals by AAc/MBI hydrogel

The percentage metal sorption by the AAc/MBI hydrogel was determined by a complexometric method described in detail in a previous study.¹⁵

Scanning Electron Microscopy (SEM)

The morphology of the fracture surfaces of the hydrogel, before and after metal sorption, was examined by the SEM technique. SEM micrographs were taken with a JSM-5400 electron microscope (JEOL, Japan) at 50 kV. The hydrogel was fractured in liquid nitrogen and stored in sealed plastic bags. A sputter coater was used to precoat conductive gold onto the fracture surface of the dry hydrogel before observing the microstructure.

RESULTS AND DISCUSSION

Radiation synthesis of AAc/MBI hydrogel

It is known that the interaction of high ionizing radiation with unsaturated monomers such as AAc leads to polymerization through a free-radical mechanism. Thus, PAAc was first formed under the effect of gamma radiation.¹⁶ Under the effect of gamma radiation and in the presence of MBam as a crosslinking agent, PAAc gel (network structure) is formed:



× PAAc–PAAc (crosslinked polymer)

During the formation of PAAc gel, MBI, which contains an unsaturated bond, may also be affected by gamma radiation, leading to the formation of free radicals. Another possibility is that the products of the radiolysis of water and methanol (OH, H, e^- aq.) will generate free radicals, leading to the formation of AAc/MBI copolymer. When irradiation doses were increased beyond a certain value, the polymer chains crosslinked and then gel was obtained. The formed AAc/MBI hydrogel was subjected to elemental analysis. The percentages of carbon, hydrogen, nitrogen, and sulfur elements were found to be 50.3, 4.3, 7.8, and 1.4%, respectively.

TABLE I
Swelling Behavior of AAc/MBI Hydrogel in Water and Different Organic Solvents

Solvent	Swelling (%)
Water	190
Cyclohexane	20
Toluene	20
Benzene	25
Chloroform	30
Acetone	485
Methyl alcohol	670
Ethyl alcohol	775

Characterization of AAc/MBI hydrogel

A set of preliminary experiments was carried out to obtain the highest percentage of the gel part of the AAc/MBI hydrogel by changing the radiation dose and weight ratios of the different components. We were able to obtain a gel fraction of 99.0%.

Swelling behavior of AAc/MBI hydrogel in water and different organic solvents

The swelling behavior of AAc/MBI in water and different organic solvents is shown in Table I. It can be seen that the AAc/MBI hydrogel has a high tendency to swell in water. Also, it can be observed that the hydrogel has a greater affinity for polar solvents than for nonpolar solvents.

The percentage uptake of AAc/MBI hydrogel can be arranged according to the following order: ethanol > methanol > acetone \gg water > chloroform > benzene > toluene > cyclohexane.

IR spectroscopic analysis of AAc/MBI hydrogel

IR spectroscopic analysis was used to determine the chemical structure of the AAc/MBI hydrogel and possibly the nature of the bond formation between PAAC and MBI components in the presence of the MBam as a crosslinking agent: Figure 1(A) shows the IR spectra of pure MBI. The presence of a benzene ring in an aromatic compound can often be determined by inspection of two regions in the IR spectra. The aromatic absorption for C—H stretching, which is generally weak, usually falls near 3030 cm^{-1} and cannot be identified. However, the absorption for the aryl C—C vibration gives a series of four peaks at 1463 , 1511 , 1570 , and 1620 cm^{-1} . It can be seen that the first, second, and fourth peaks are visible, whereas the third peak is barely visible as a shoulder. Amines or imides exhibit two IR stretching bands, one arising from N—H stretching and the other from C—N stretching.

Also in Figure 1(A), a very distinctive absorption band can be seen at 1176 cm^{-1} , which is assigned to the C—N stretching, and multiple absorption bands

around $3000\text{--}3200\text{ cm}^{-1}$, which are assigned to hydrogen bonding formed between the N-H of imides.

As shown in Figure 1(B), for the AAc/MBI hydrogel synthesized by gamma-radiation polymerization, the presence of the carboxyl group of polyacrylic acid can be clearly identified from the absorption band at 1713 cm^{-1} , which arises from the carbonyl stretching. Also, the IR spectra shows a broad absorption band attributed to O-H stretching, which begins at about 3100 and slopes to 3600 cm^{-1} .

Thermal decomposition behavior of AAc/MBI hydrogel

Figure 2 shows the initial TGA thermogram for AAc/MBI hydrogel, from which the weight loss (%) at different decomposition temperatures was calculated as shown in Table II. It can be seen that the AAc/MBI hydrogel is stable up to about 100°C and loses about 6.5 and 20 wt % at 200 and 280°C , respectively. By increasing the heating temperature from 280 to 420°C , a further loss in weight occurred. To determine the thermal stability of this hydrogel, the percentage loss in weight was compared with the corresponding PAAC without MBI at the same decomposition temperatures. It was found that the percentage loss in weight for the thermal decomposition behavior for PAAC at 100 , 200 , 250 , 300 , 350 , and 400°C was 0, 3.59, 5.00, 7.75, 20.52, and 51.70%, respectively. Thus, it may be concluded that the AAc/MBI hydrogel is relatively less stable than PAAC within the range from 100 to 400°C .

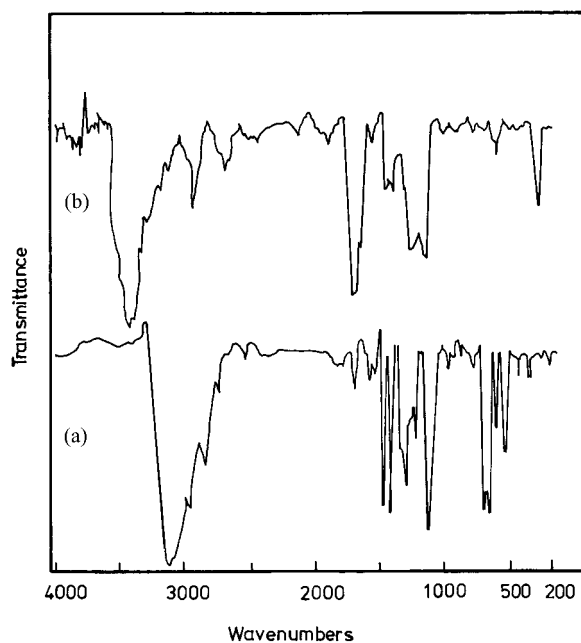


Figure 1 IR spectra of 2-mercaptobenzimidazole compound (A) and AAc/MBI hydrogel (B).

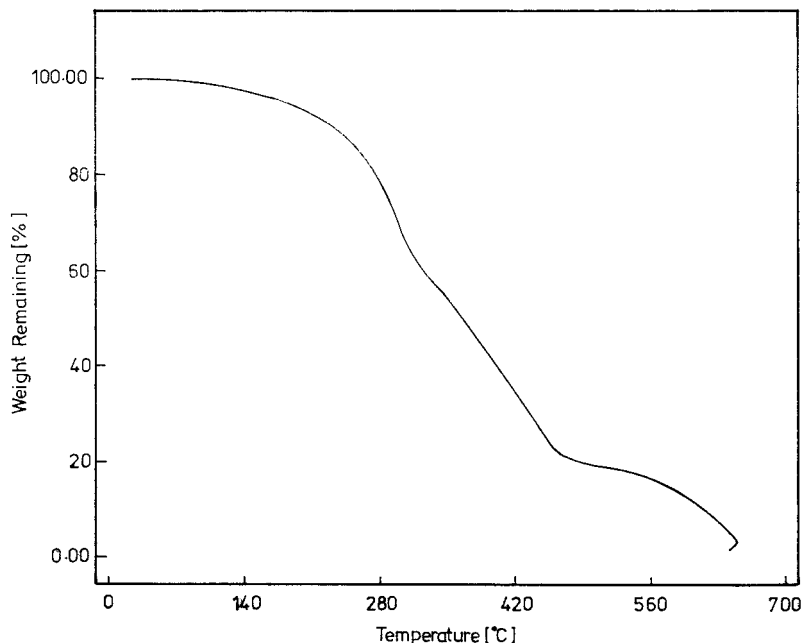


Figure 2 Initial TGA thermogram of pure AAc/MBI hydrogel.

The thermal stability of any polymeric material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The calculated dissociation energies for the different covalent bonds C—H, C—O, O—H, C=O, C=C, C—N, C=N, N—H, C—S, and S—H were found to be 414, 347, 351, 464, 741, 611, 293, 615, 389, 259, and 339 kJ/mol, respectively.¹⁷ Based on these values, it can be calculated that the average dissociation energy of PAAc is 437 kJ/mol and 420 kJ/mol for MBI. Thus, on the basis of these theoretical calculations, the presence of MBI with PAAc gel will not greatly change the thermal stability of the AAc/MBI hydrogel. The thermal stability of the prepared hydrogel was further confirmed by plotting the rate of reaction, or the derivative of the TGA thermogram curve DTGA (taken from the initial TGA) against $1/T$ for pure AAc and AAc/MBI hydrogel, as shown in Figure 3. The temperatures of the maximum values of the rate of reaction (T_{\max}) for the hydrogel were found to be 294 and 477°C; that is, the thermal decomposition reaction of AAc/MBI goes through two maxima. On the other hand, pure PAAc displayed one maximum at 504°C. The T_{\max} at 294°C is probably attributable to the decomposition of the MBI component present in

AAc/MBI hydrogel because it was not observed in the case of pure AAc. However, the second T_{\max} at 477°C is still lower than that for pure PAAc gel. Accordingly, it may be concluded that AAc/MBI possesses a reasonable thermal stability compared to that of the corresponding PAAc.

The activation energy and order of reaction of the hydrogel were determined on the basis of the Anderson and Freeman relationship given below¹⁸:

$$\Delta \log(dw/dt) = n\Delta \log w - (E^*/2.303R) \Delta(1/T)$$

where dw/dt is the rate of thermal decomposition reaction, w is the reactant weight, R is the gas constant, E^* is the activation energy, and n is the order of reaction. In this method, the quantities $\Delta \log(-dw/dt)$ and $\Delta \log w$, corresponding to a constant small interval of $\Delta(1/T)$ over the course of the initial TGA thermogram, were first determined. When $\Delta \log w$ was plotted against $\Delta \log(dw/dt)$ for the hydrogel AAc/MBI, to determine the activation energy and order of reaction on the basis of the Anderson and Freeman procedure, the data points do not fall on a straight line. It follows that the thermal decomposition reac-

TABLE II
Weight Loss (%) at Different Decomposition Temperatures for Pure PAAc and AAc/MBI Hydrogel

Polymer type	Weight loss (%)						
	100°C	200°C	250°C	300°C	350°C	400°C	450°C
Pure PAAc	0.00	3.59	5.00	7.75	20.52	51.70	70.22
AAc/MBI hydrogel	0.90	6.43	13.20	26.80	44.30	60.00	72.30

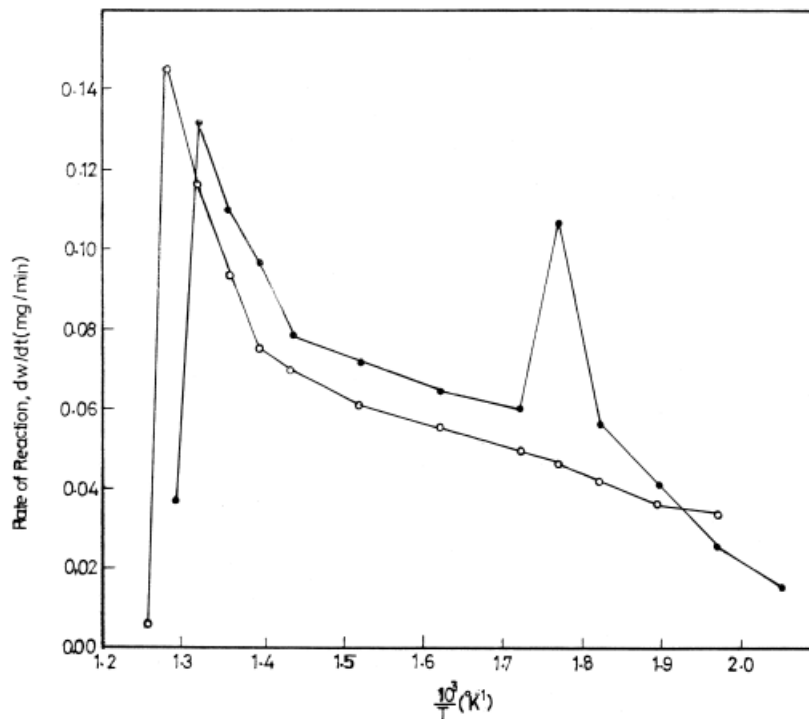


Figure 3 Derivative of the TGA thermogram (DTGA) of pure PAAc (●) and AAc/MBIL hydrogel (○).

tion does not depend on the weight of reactant but, rather, depends on the thermal decomposition temperature, and the reaction follows a zero-order mechanism. This means that the first term on the right-hand side of the Anderson and Freeman equation equals zero because n , the order of reaction, equals zero. In this case, $\log(dw/dt)$ is plotted versus $1/T$ and the slope will be $E^*/2.303R$, from which the activation energy can be calculated, as shown in Figure 4. It is clear that the temperature dependency of the thermal

decomposition of the hydrogel goes through two stages corresponding to the two maxima on Figure 3. The calculated average activation energies over the entire range of temperature, corresponding to each of the two stages (I, II), were found to be 31.52 and 51.41 kJ/mol, respectively. However, a break in the line, representing the temperature dependency at the higher stage from 352–496°C, can be observed. This elbow may be attributed to the occurrence of phase separation between PAAc and MBI inside the hydro-

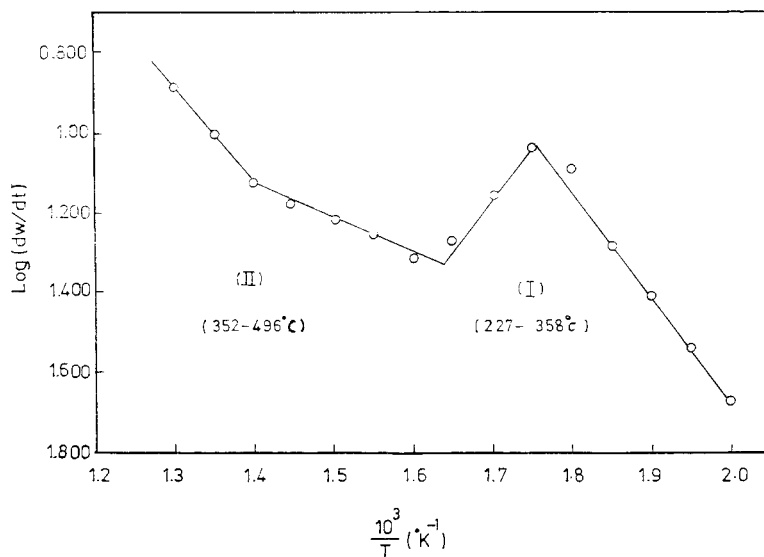


Figure 4 The plotting of $\log(dw/dt)$ against $1/T$ for the thermal decomposition reaction of pure AAc/MBI hydrogel.

TABLE III
Affinity of AAc/MBI Hydrogel Toward Metal Ions^a

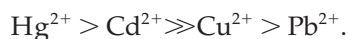
Metal salt	Weight of hydrogel (g)	SS (g/25 mL)	SR (g/25 mL)	SI (g/25 mL)	Metal uptake (%)
CuSO ₄	0.6830	0.062	0.050	0.012	19.35
Pb(NO ₃) ₂	0.6078	0.160	0.130	0.030	18.75
CdCl ₂	0.5457	0.050	0.020	0.030	60.00
HgCl ₂	0.5645	0.190	0.060	0.130	68.42

^aSS, strength of metal ions in the standard solution; SR, strength of the metal ions in the solution after removal of the hydrogel; SI, strength of the metal ions inside the hydrogel.

gel. On the other hand, the average activation energy for the thermal decomposition of pure PAAc polymer was calculated to be 59.89 kJ/mol.

Sorption of metal ions by AAc/MBI hydrogel

The affinity of AAc/MBI hydrogel for different metal ions is shown in Table III. The data showed that the hydrogel has a great affinity for Hg²⁺ and Cd²⁺ ions with respect to the other metals, according to the following order:



These trends can be explained on the basis that Hg²⁺ has a great tendency to combine with the sulfur groups inside the matrix of the hydrogel, according to Pearson's rule.¹⁹ Also, the bond between sulfur atoms and Hg²⁺ ion is much stronger than that with the other ions, Pb²⁺ and Cu²⁺. Consequently, no dissociation occurs in the case of Hg²⁺, whereas in the case of other ions some dissociation resulting from the weakness of the bond may occur.

Moreover, the distribution coefficient of the different metal ions was determined according to the following equation:²⁰

$$D = (C_1/C_2) \times (V/M)$$

where C_1 is the concentration of metal ions in hydrogel (mol), C_2 is the concentration of metal ions in filtrate, V is the volume of filtrate (mL), and M is the mass of hydrogel. According to this equation, and on the basis of the data on Table III, the calculated D of the Hg²⁺, Cd²⁺, Pb²⁺, and Cu²⁺ was found to be 8.785, 7.713, 13.302, and 13.987, respectively. It should be noted that the initial concentrations of the metal ions in solution were equal in all cases.

The ratio between the distribution coefficient of the different metals [separation factor (SF) = D_1/D_2] is an important factor in separation science. The greater the deviation of this factor from unity, the easier the separation. In this contest, the separation factors for different pairs of metals with the hydrogel have been determined. It is clear that the hydrogel tends to prefer Cu²⁺ over Pb²⁺ ions (SF = 1.08), Cd²⁺ over Cu²⁺ ions

(SF = 7.822), and Cd²⁺ over Pb²⁺ ions (SF = 7.240). Moreover, the hydrogel shows a relatively higher preference for Hg²⁺ over Cu²⁺ (SF = 10.923) and Pb²⁺ ions (SF = 10.110). However, the hydrogel showed a relatively low selectivity for Hg²⁺ over Cd²⁺ (SF = 1.396). Accordingly, it may be concluded that the highest selectivity of the AAc/MBE hydrogel is for Hg²⁺ and Cd²⁺ over Cu²⁺ and Pb²⁺ ions.

The IR spectra of the AAc/MBI hydrogel complexed with Hg²⁺ ions is shown in Figure 5. The broad absorption band attributed to O—H stretching is seen around 3100–3700 cm⁻¹, similar to that displayed by the pure AAc/MBI hydrogel (Fig. 2). Also, the absorption band attributed to C=O stretching can be seen at 1721 cm⁻¹. Thus, it can be concluded that the complexation with Hg²⁺ ions does not go through the carboxyl groups of AAc polymer. The complexation with Cu²⁺ ions goes through carboxyl groups according to the electrochemical series principle. The characteristic bands of MBI are seen, in which absorption for the aryl—C—C vibration series can be seen as three peaks at 1406, 1450, and 1503 cm⁻¹ and the fourth one as a

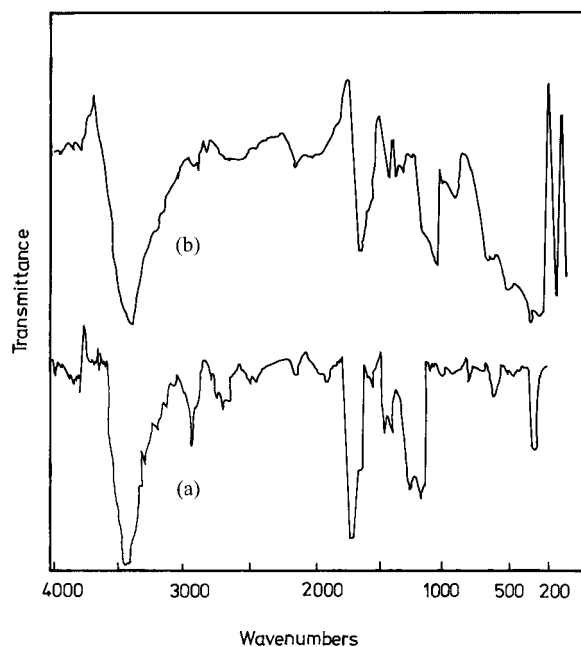


Figure 5 IR spectra of AAc/MBIL hydrogel complex with Hg²⁺ (A) and AAc/MBI hydrogel (B).

shoulder to the C=O absorption band. Also, the absorption bands assigned to the ortho-disubstitution on the benzene ring of MBI can be seen as a broad band around 759–795 cm^{-1} . This absorption band is seen in the IR spectra of pure MBI as sharp adjacent peaks at 710 and 741 cm^{-1} . Therefore, it may indicate that the complexation of Hg^{2+} ions goes through the S-H group of MBI. It is noted that the absorption band attributed to C–N stretching is still present and seen at 1169 cm^{-1} , as shown in the IR spectra of pure MBI at 1176 cm^{-1} (Fig. 1).

Scanning electron microscopy (SEM)

Figure 6 shows SEM micrographs of the fracture surfaces of the AAc/MBI hydrogel before and after absorbing different metal ions. The SEM micrograph of pure hydrogel, shown in Figure 6(A), showed a somewhat smooth surface with continuous and uniform morphology. There are a limited number of white particles dispersed in the matrix, which may be the result of the residual MBam used as a crosslinking agent, not participating in the formation of the PAAc/MBI hydrogel. The SEM micrographs of the AAc/MBI hydrogel, after absorbing different metals, showed a different morphology in which the smooth surface no longer occurs. It seems that the introduction of metal ions inside the matrix causes a large disruption to the surface. The metallic crystals formed are clearly shown along the fracture surfaces, however, the size and geometry of these crystals depend on the type of absorbed metal ion, as shown in Figure 6(B) and (C). The ionic radii of Hg^{2+} and Cd^{2+} are reported to be 1.1×10^{-4} and 0.97×10^{-4} μm .¹⁷ The size of the complexes on these surfaces is in accordance with the ionic radii of the different metals occupying the lattice sites. However, the type and shape of these crystal lattice sites need more investigation by X-ray diffraction from the point of view of inorganic chemistry.

CONCLUSIONS

Removal or separation of heavy metals from wastewater is an objective of increasing importance in a variety of environmental fields. The results presented in this work demonstrate the synthesis of a hydrogel containing a sulfur compound under the effect of gamma radiation. It is expected that this hydrogel will be of use for absorbing some heavy metals from wastewater as the experimental data showed. The thermogravimetric analysis showed that the presence of 2-mercaptobenzimidazole as a component of the hydrogel does not change its thermal decomposition behavior. Also, it was found that the prepared hydrogel has a great tendency to swell in water, suggesting ease in its applicability to wastewater treatment. The results showed that the AAc/MBI hydrogel has a

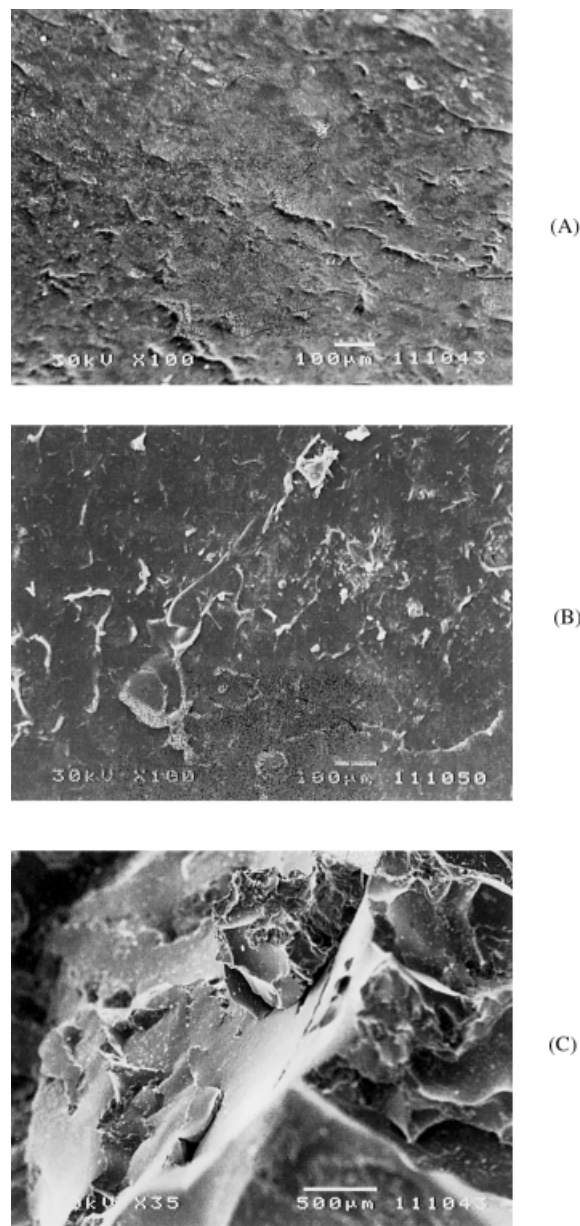


Figure 6 SEM micrographs of the fracture surfaces of AAc/MBI hydrogel before and after absorption of different metal ions: (A) pure hydrogel, (B) Cd^{2+} , (C) Hg^{2+} .

great affinity to take up the most toxic metal ions, Hg^{2+} and Cd^{2+} , in wastewater. Moreover, the calculated separation factor indicates that AAc/MBI hydrogel can be used to separate Hg^{2+} from Cu^{2+} as well as Pb^{2+} from wastewater. Even though PAAc constitutes the major component of the hydrogel, the sulfur groups of MBI still seem responsible for the affinity for heavy metals, except for Cu^{2+} ions. These findings were confirmed by IR analysis of the complexed hydrogel with Hg^{2+} , in which the band attributed to O-H stretching still exists.

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