Synthesis of Copolymeric Hydrogels Using Gamma Radiation and Their Utilization in the Removal of Some Dyes in Wastwater

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ABSTRACT: Copolymer hydrogels were prepared by γ-radiation copolymerization of maleic acid (MA) and 2-hydroxyethylacrylate (HEA) or acrylamide (AAm). The effect of AAm/MA and HEA/MA composition and irradiation dose on the gel fraction yield in the prepared hydrogels was determined. It was found that as the content of MA increased, the gel fraction yield decreased. The increase of irradiation dose resulted in increasing the crosslinked network structure and consequently the gel percent. The parameters of equilibrium swelling, maximum swelling, initial swelling rate, diffusion exponent, and diffusion coefficient of the hydrogels were calculated and evaluated, and it was found that water diffusion to the hydrogels generally was a non-Fickian diffusion type. Characterization of the prepared hydrogels was studied and accordingly the possibility of its practical use in the treatment of waste dyes from aqueous solution was studied. The effect of treatment time, the pH of the feed solution, initial feed concentration, and temperature on the dye uptake was also investigated. The maximum uptake of the investigated dyes was higher for HEA/MA hydrogel than that for AAm/MA hydrogel. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3720–3731, 2006

Key words: copolymer; swelling; maleic acid; dyes uptake

INTRODUCTION

Given the growing use of a large variety of dyes, pollution from dyes in wastewater is one of the major environmental problems of the world. There are about 3000 types of dyes on the world market. Dyes that have low biodegradability greatly influence natural ecosystems and thus humans. Although some treatment methods have been developed, economic removal of dyes still remains a significant problem.[1]

Dyeing and finishing wastewaters in the textile industry are generally high in both color and organic content. A combination of several processes is generally necessary to achieve adequate removal of all contaminants. Therefore, adsorption has evolved into one of the most effective physical processes for decolorization of textile wastewaters. The application of adsorbents such as peat, wood, fired clay, and other low-cost materials has been studied and recently received further attention due to their economic advantages.[2]

Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell in the aqueous environment. These materials are of great interest due to their promising applications, for example, as sensors, separation membranes, adsorbents, and materials in medicine and pharmacy as drug-delivery systems, and in solving some ecological and biological problems as well as in modern technologies. Super-swelling polymers can swell up to thousands of times their own weight in aqueous media. Many attempts have been made to develop new hydrogels through methods such as irradiation and chemical crosslinking. Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution. The latter involves two steps: in the first step, the linear polymer is synthesized in the absence of a crosslinking agent; in the second step, the synthesised polymer is crosslinked using either chemical reagents or irradiation.[3]

The objective of this work was to determine the efficiency of color removal of Astrazon Red 6B, Acid Green B, and Ismative Orange 2R dye wastewaters using (AAm/MA) and (HEA/MA) hydrogels.
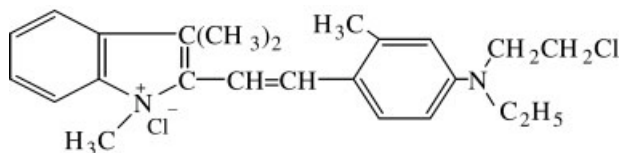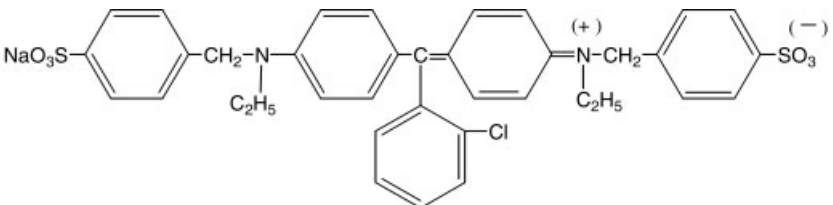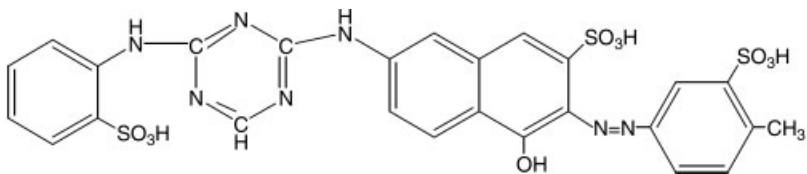
EXPERIMENTAL

Materials

Monomers

Maleic acid (MA), acrylamide, and 2-hydroxyethyl-acrylate (HEA) from Aldrich-Chemical Co., of 99% purity was used without further purification.

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Dyes

Each of the following dye solutions was prepared initially by dissolving 0.25 mg in one liter from distilled water. The concentration of the dye was measured and determined by visible spectrophotometer. The types of dyes used were Astrazon Red 6B (Ciba Co., Egypt), Acid green B and Ismative orange 2R dye (Dyestuffs and Chemicals Co., Kaffer El-Dawar, Egypt).

Type	Structure formula	C.I.
Astrazon Red 6B		BASIC/VIO/7
Acid Green B		A/GR/16
Ismative Orange 2R		R/OR/13

Preparation of hydrogel

In order to prepare hydrogel systems, 1 g of monomer (AAm; HEA) was dissolved in 1 ml distilled water and 40, 60, and 80 mg MA were added to the aqueous solutions of the monomer. The solutions were placed in PVC straws of 3 mm diameter and irradiated to 2, 3, 4, 5, and 6 kGy in air at ambient temperature in a Co^{60} Russian irradiation facility by γ rays at a fixed dose rate of 1.53 kGy hr^{-1}. The dose rate was determined using a conventional Fricke dosimeter. Freshly obtained long-cylindrical-shaped hydrogels were cut into pieces 3–4 mm in length. They were washed and thoroughly rinsed with distilled water, dried with filter paper and then dried in air, and finally the obtained hydrogels were stored in vacuum for swelling studies.

Swelling and diffusion

The clean, dried, co-polymerized hydrogels of known weight were immersed in distilled water at room temperature. The hydrogels were removed from water at various times and the excess water on the surface was removed, bottled by absorbent paper and quickly weighed, and then returned back to the distilled water until equilibrium was reached (24 h in most cases).

Gel determination of co-polymerized hydrogels

The obtained hydrogels as well as Poly-(hydroxyethylacrylate/maleic acid) and Poly-(acrylamide/maleic acid); in dry and glassy form; were subjected to Soxhlet extraction with water for 8 h at 100°C. The uncross-linked polymer P(AAm), P(HEA) as homopolymers and unreacted maleic acid were removed from the gels as soluble fractions in boiling water by this extraction. In order to prove that the gels prepared from the above materials avoided an amount of unreacted maleic acid in the aqueous extract, a titration was conducted with NaOH (0.05 M) to a phenolphthalein end point. The gel percent in the hydrogel was determined from the following equation:

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

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

FTIR spectrometric analysis

Analysis by infrared spectroscopy was carried out using a Shimadzo IR. 408 (Japan) in the range from 500 to 4000 cm^{-1}. FTIR specra of homopolymeric hydrogels P(AAm) and P(HEA/MA); also, copoly-
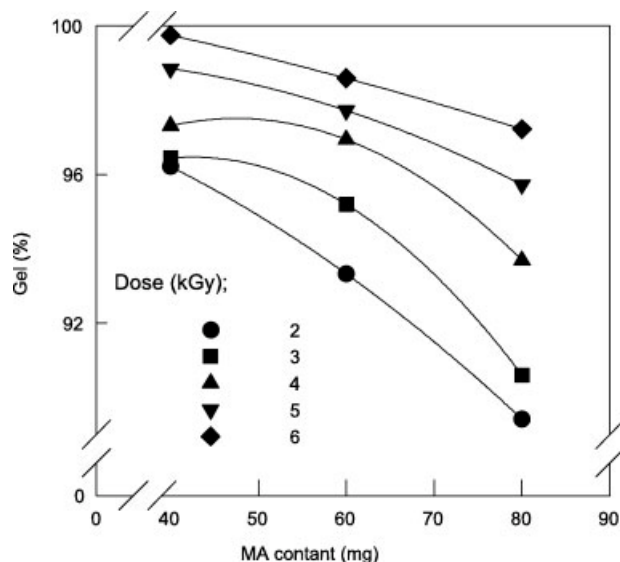
Figure 1 Effect of MA content on the Gel % for the HEA/MA hydrogel at different doses.

meric hydrogels P(AAm/MA) were investigated. Samples were throughly ground with exhaustively dried KBr and discs were prepared by compression under vacuum.

Measurement of pH

The pH of the dye solutions used in the treatment, was determined using a Jenway 3310 pH meter (Japan).

Thermal gravimetric analysis

A Shimadzu TGA-50 Thermal Gravimetric Analysis (TGA) system in 20 ml/min nitrogen atmosphere was used in this study. The temperature range was from ambient to 500°C at heating rate of 10°C/min.

Scanning electron microscopy

Scanning Electron Micrographs (SEMs) were obtained using a JEOl.JSM 5400 scanning electron microscope (Japan).

The total uncertainly for all the experiments was in the range (3%–5%).

RESULT AND DISCUSSION

Preparation of gel matrix

Hydrogels were prepared by γ-radiation-induced co-polymerization of binary monomer mixtures; AAm/MA and HEA/MA. Such radiation process is generally termed as a "clean technique", not requiring any extra chemicals and leaving some unwanted res-

idue. 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] When the irradiation dose is increased beyond a certain value from 2 to 6 kGy, the polymer chains are cross-linked and the gel is then obtained.

Effect of hydrogel composition

The influence of HEA/MA composition at different doses has an effect on the gel fraction yield, that is, the insoluble part in the AAm/MA and HEA/MA hydrogels. It was observed that as the maleic acid content increased, the gel fraction yield (the insoluble part in both AAm/MA and HEA/MA hydrogels) decreased (see Figs. 1 and 2). Moreover, the gel content was higher for HEA/MA compositions as a mole ratio percent (96.1/3.9, 94.2/5.8, and 92.5/7.5%) than that of AAm/MA compositions as a mole ratio percent (87.3/12.7, 81.6/18.2, and 77.3/22.7%). These mole ratio composition percentages indicated the higher affinity of HEA to crosslink with maleic acid more than the AAm monomer, which can be attributed to the tendency of HEA to form hydrogen bonding through carboxylic (—COOH) groups of MA monomer instead of AAm monomer. Also, the effect of radiation dose on the conversion yield of AAm/MA and HEA/MA system is shown in Figures 1 and 2. It is observed that as the irradiation dose increases, the gel fraction will also be increased up to 6 kGy at a given co-monomer composition. The results also indicate that the crosslinking process in the prepared hydrogel is enhanced at higher doses.
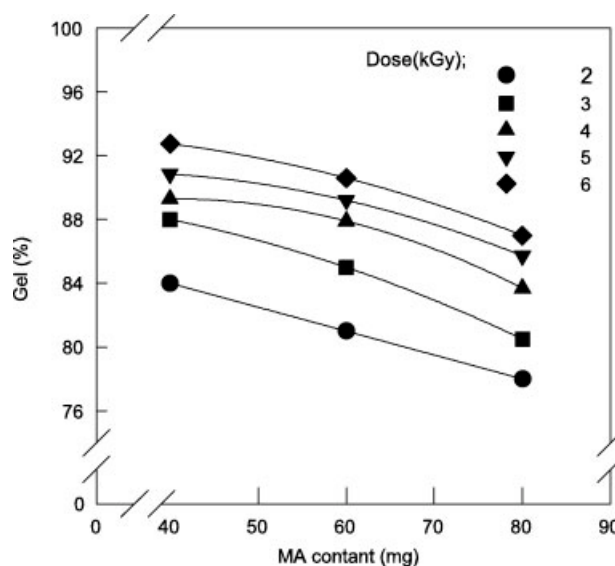
Figure 2 Effect of MA content on the Gel % for the AAm/MA hydrogel at different doses.
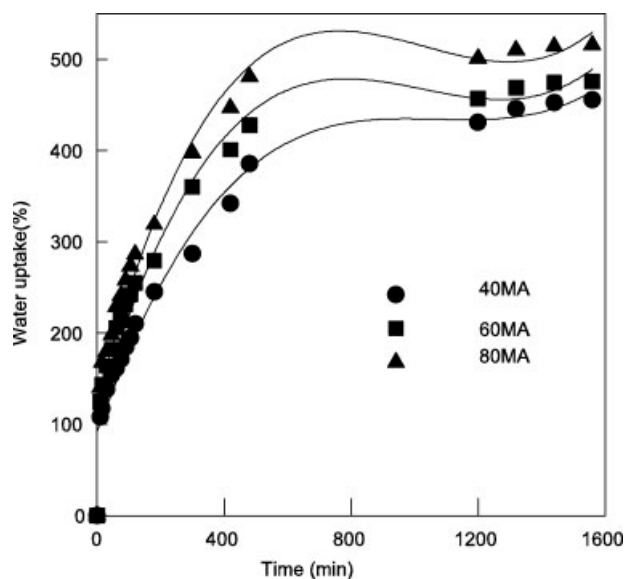
Figure 3 Effect of time (min) on the water uptake percentage for different HEA/MA compositions at constant irradiation gelation dose 2 kGy.

Figure 4 Effect of time (min) on the water uptake percentage for different AAm/MA compositions at constant irradiation gelation dose 2 kGy.

The results suggest that the concentration of free radicals formed in the AAm/MA and HEA/MA hydrogels increases with irradiation dose.
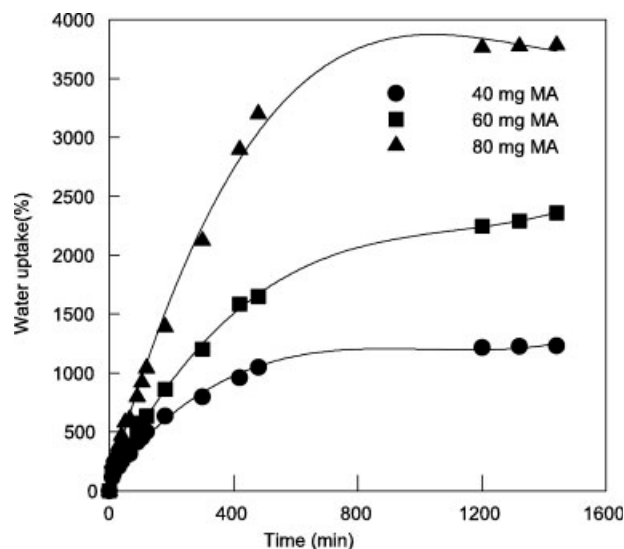
Characterization of the prepared hydrogel

Swelling behavior

Fundamental relationship exists between the swelling of a polymer in solvent and the nature of the polymer and the solvent. The percentage of water uptake (swelling) is an important parameter. The water uptake (swelling %) was calculated by the following equation:

$$\text{Water uptake \%} = \frac{w_s - w_d}{w_d} \times 100$$

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

The influence of soaking time on the water uptake percent for hydrogel at various comonomer compositions is shown in Figures 3 and 4. It can be seen that the water uptake percent increases as the soaking time increases to reach a certain limiting value when it becomes constant. This value may be called the equilibrium swelling (S_{eq}). It is well known that the swelling of hydrogel is induced by electrostatic repulsion of the ionic charges of its network.[1,2] The ionic charge content is important. Maleic acid contains many ionic units (—COOH). As can be seen from Table I, the water uptake increase is due to an increase in the anionic units. The hydrophilic group numbers of AAm/MA copolymers are more than these of HEA/MA, so the water uptake of AAm/MA copolymers is more

than that of HEA/MA copolymers. If the content of maleic acid in all investigated copolymers is increased, then the equilibrium swelling of the copolymers is increased.

Diffusion

Swelling of the hydrogel involves large scale segmental motion resulting, ultimately, in an increased distance of separation between hydrogel chains. Analysis of the mechanisms of water diffusion in swell able polymeric systems has received considerable attention in recent years, because of important applications of swell able polymers in fields of biomedical, environment agriculture engineering and pharmaceuticals.[4]

To determine the nature of water diffusion into the hydrogel, Fick's law[5] was applied as follows:

$$F = W_t/W_\infty = kt^n \tag{1}$$

where W_t and W_∞ represent the amount of water uptake by the hydrogel at time t and at equilibrium,

TABLE I
Swelling Exponents and Swelling Constant of HEA/MA and AAm/MA Hydrogels

| | Maleic acid (MA) [mg] | | | | | |
| | HEA/MA hydrogels | | | AAm/MA hydrogels | | |
Parameters	40	60	80	40	60	80
Swelling exponents (n)	0.75	0.74	0.73	0.54	0.61	0.65
Swelling constants (k)	0.507	0.75	0.905	0.045	0.026	0.02
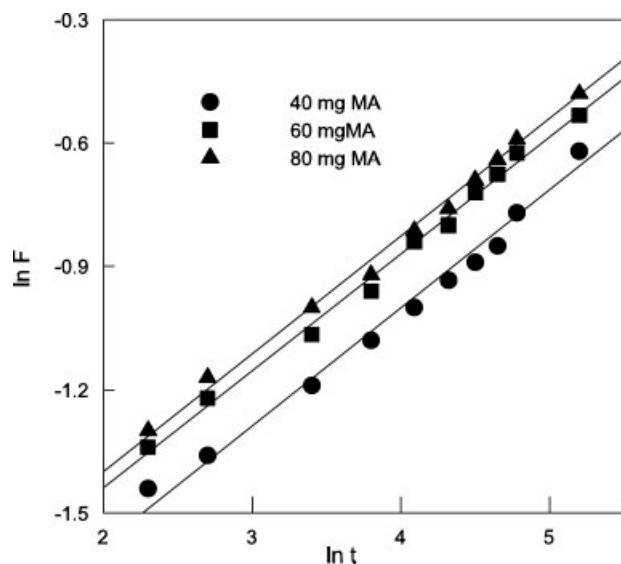
Figure 5 $\ln F - \ln t$ curves of HEA/MA compositions at a constant irradiation gelation dose of 2 kGy.
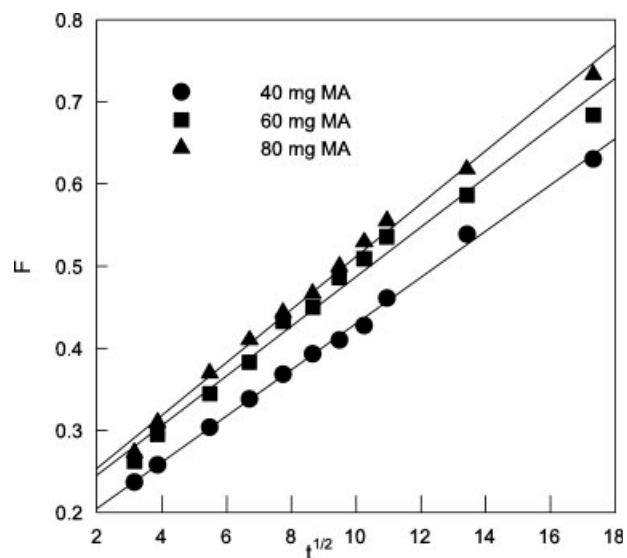
Figure 7 $F - t^{1/2}$ curves of HEA/MA compositions at a constant irradiation gelation dose of 2 kGy.

F is the fractional uptake at time t, k is a constant incorporating the characteristics of the macromolecular network system and the penetrate, and n is the diffusional exponent, which is indicative of the transport mechanism. Equation (1) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n and are equal to 1/2 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected by n between 1/2 and 1.[5]

For radiation induced hydrogels, the $\ln F$ versus $\ln t$ graphs were plotted, as shown in Figures 5 and 6, and n exponents and k parameters were calculated

from the slopes and intercepts of the lines, respectively, as listed in Table I.

Table I shows the number that determines that the type of diffusion (n) is more than 1/2. The diffusion of water into the super water-retainer hydrogel is taken to be non-Fickian in character. In anomalous diffusion, solvent diffusion rate and polymer relaxation rate are about the same order of the magnitude.[6]

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. For hydrogel characterization, diffusion coefficient can be calculated by various methods. The short time approximation method is used for calculation of diffusion coefficients of AAm/MA
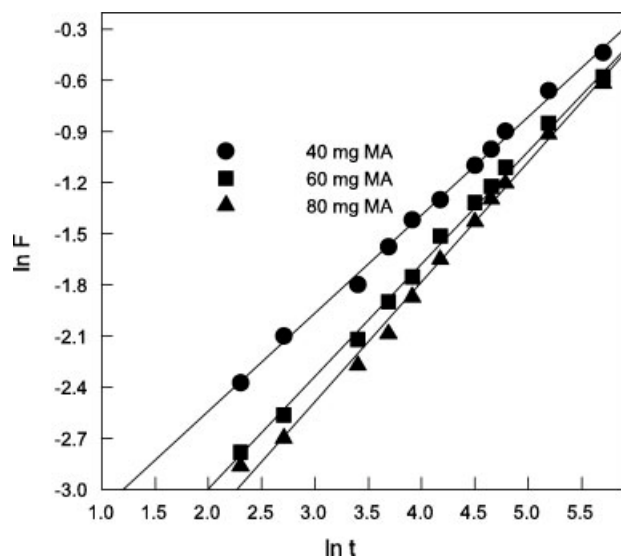
Figure 6 $\ln F - \ln t$ curves of AAm/MA compositions at a constant irradiation gelation dose of 2 kGy.
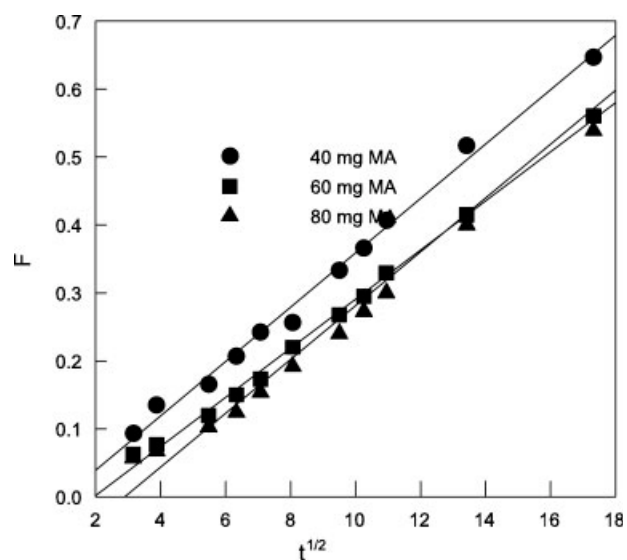
Figure 8 $F - t^{1/2}$ curves of AAm/MA compositions at a constant irradiation gelation dose of 2 kGy.

HEA/MA hydrogels. The short time approximation is valid for the first 60% of initial swelling.[7,8]

The diffusion coefficients D (with D in cm^2 s^{-1}) of the HEA/MA hydrogels are calculated from the following equation:[7]

$$\frac{W_t}{W_\infty} = \left(\frac{4Dt}{\pi l^2}\right)^{1/2}$$

where l is the thickness of the hydrogel disc.

The F versus $t^{1/2}$ values for the hydrogels were plotted, as shown in Figures 7 and 8. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient calculated for the hydrogels are listed in Table II. It is clear from the data that the D values vary with the mechanism of water transport.

FTIR spectroscopic analysis of the prepared hydrogels

FTIR spectra of MA, AAm, P (AAm/MA), and P (HEA/MA) were evaluated, as presented in Figure 9. In these spectra, the stretching vibration bands appearing in the wave-number range 2400–3500 cm^{-1} are due to NH$_2$ and COOH groups in P(AAm/MA) hydrogel. This wide wave-number range made it a broad band due to some intramolecular and intermolecular hydrogen bonding in the copolymer. When MA is introduced into this copolymer, these peaks have increased in its intensity gradually with the increasing of COOH groups of maleic acid. It has been also observed similar situations in P(HEA/MA) hydrogel due to stretching vibration bands as a wide broad band ranged 2400–3600 cm^{-1} due to OH and COOH groups. The peak at 1750 cm^{-1} appears and characteristic for carbonyl group (C=O) stretch for both amide (CO—NH$_2$) and carboxylic (COOH) groups absorption and its intensity increased with incorporation of maleic acid to both hydrogels. This band shifted to left frequencies as appeared at 1750 to 2210 due to the steric strain effect on anhydride structure which may be formed by water dehydration.
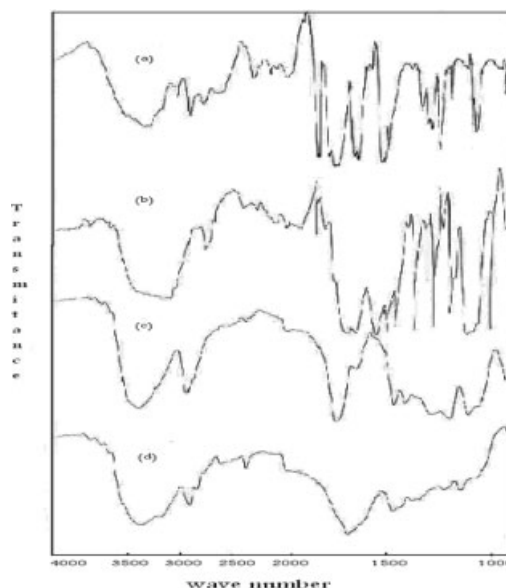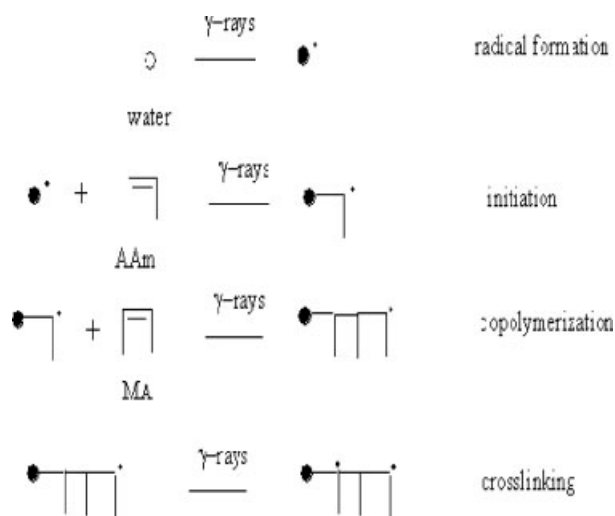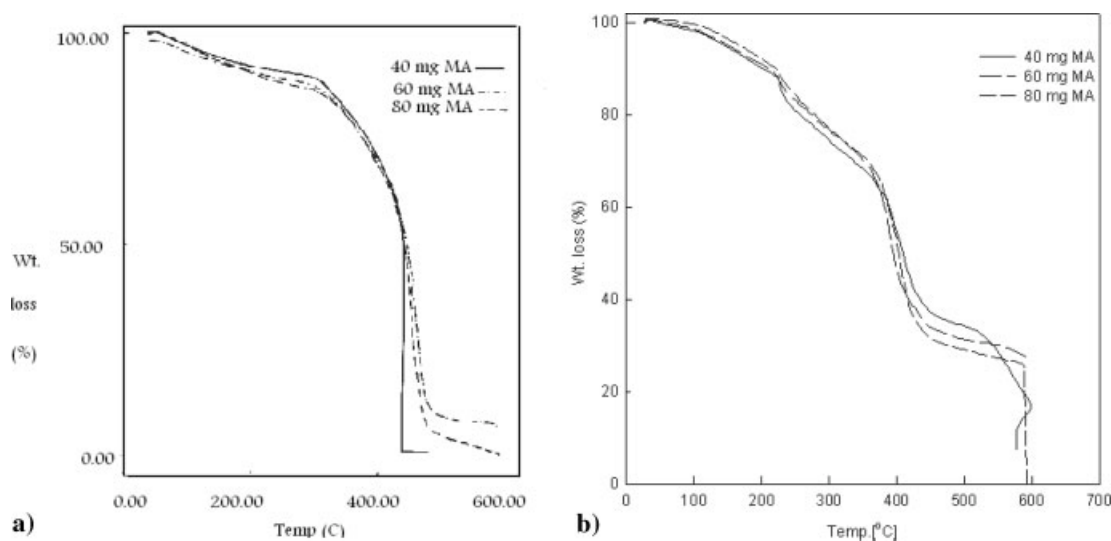

Figure 9 FTIR spectra of different hydrogels: (a) maleic acid (MA); (b) acrylamide(AAm); (c) MA/Aam; (d) MA/HEA.

Cyano group (C—N) on the chains of AAm/MA give absorption band at 1450 cm^{-1} while the peak at 1200 cm^{-1} can be attributed to (C—C) stretching vibration along the co-polymeric chain structure.

The very important view, in the infrared investigation for the two prepared hydrogels was focused on the vinyl group (C=C) which appeared at 1620 cm^{-1} streatching vibration for both AAm and HEA monomers while it disappeared in both P(AAm/MA) and P(HEA/MA) spectrum. These results explained the breaking of bi-bond (π) and formation free radicals of each monomer through γ irradiation to form the hydrogel as show in Scheme 1. This data confirmed the

TABLE II
Diffusion Coefficient of HEA/MA and AAm/MA Hydrogels

	Maleic acid (MA) [mg]					
	HEA/MA hydrogels			AAm/MA hydrogels		
Parameters	40	60	80	40	60	80
Diffusion coefficient[a] ($D \times 10^{-5}$)	58.50	69.3	75.4	15.6	29.04	31.7

[a] D is in cm^2 s^{-1}.

Scheme 1 The possible copolymerization mechanism of MA with AAm.

Figure 10 TGA thermograms for different hydrogel compositions: (a) HEA/MA; (b) AAm/MA.

radiation copolymerization of both P(AAm/MA) and P(HEA/MA) hydrogel.

Thermal gravimetric analysis

Investigating the change in thermal properties of AAm/MA and HEA/MA hydrogels is important for its application as well as characterization and determination of the chemical and physical changes occurring by copolymerization.

From the practical point of view, the prepared hydrogel should possess good thermal stability in the range of applicable temperature less than 60°C which is the maximum temperature in the environment to remove the pollutants such as textile dyes. Figure 10 Shows the thermal properties of the different hydrogels at elevated temperatures. TGA curves of different hydrogels reveal that there are three distinct steps of weight loss. It is suggested that the initial stage of thermal diagram in the range from ambient temperature to 250°C, the weight loss is due to dehydration process of the water contained in such hydrophilic hydrogel. At the second stage from 250°C to 450°C, there is decomposition in the side groups and branches of the hydrogel. However, at the third stage above 450°C, the weight loss is due to the main chain scission in the polymer. It was reported that the TGA of polyacrylamide (PAAm) shows three degradation steps; the first region (ambient-220°C) corresponds to loss of bound water, in the second region (220°C–340°C) due to loss of NH_3 by imidization (intra and intermolecular), and H_2O by dehydration. The third region (> 340°C) represents substantial mass loss, and is normally attributed to main chain breakdown.[9] Also, it shows the

mass loss of poly (2-Hydroxy ethylacrylate) begins at $\sim$ 322°C and reaches maximum at 361°C.[10]

Adsorption of dye pollutants

To study the adsorption of the dyes, (AAm/MA and HEA/MA) hydrogels were placed in aqueous solutions of cationic dye (characteristic by presence of NH_2 groups and NO_2 groups to mono-azo dye); Astrazon Red 6B, and the aqueous solutions of anionic dyes (characteristic by presence of sulphonic SO_3H and carboxylic group to mono-azo dye) Acid green B and Ismative orange 2R and allowed to equilibrate for 5 days. At the end of this time, AAm/MA and HEA/MA hydrogels of the aqueous solutions Astrazon Red 6B showed a dark coloration. The amounts adsorbed per unit mass of the hydrogels were calculated by using the following equation:

$$q_e = [(C_0 - C_e)V]/W, \qquad (2)$$

where q_e is the amount of dye adsorbed onto unit dry mass of the hydrogel (mg g^{-1}), C_0 and C_e are the concentrations of the dye in the initial solution and the

TABLE III
Dyes Uptake by (AAm/MA) and (HEA/MA)
Hydrogels After Five Days

| Dyes | Dyes uptake (mg/g) | |
	AAm/MA hydrogel	HEA/MA hydrogel
Astrazon Red 6B	5.5	10.7
Acid Green B	3.1	7.4
Ismative Orange 2R	4.0	5.3
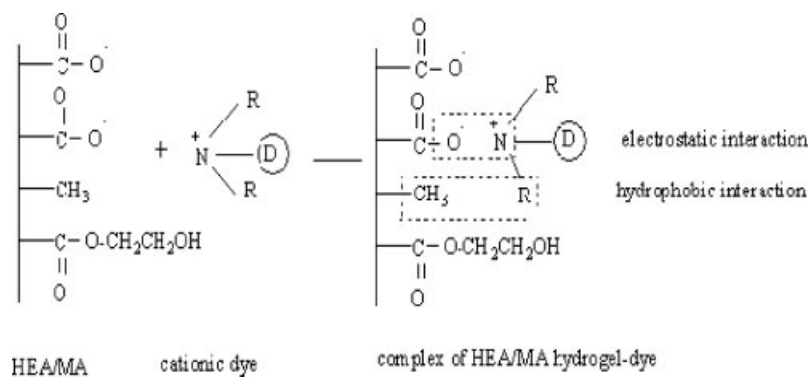
Scheme 2 Possible complexation process between HEA/MA hydrogel and the dye molecule.
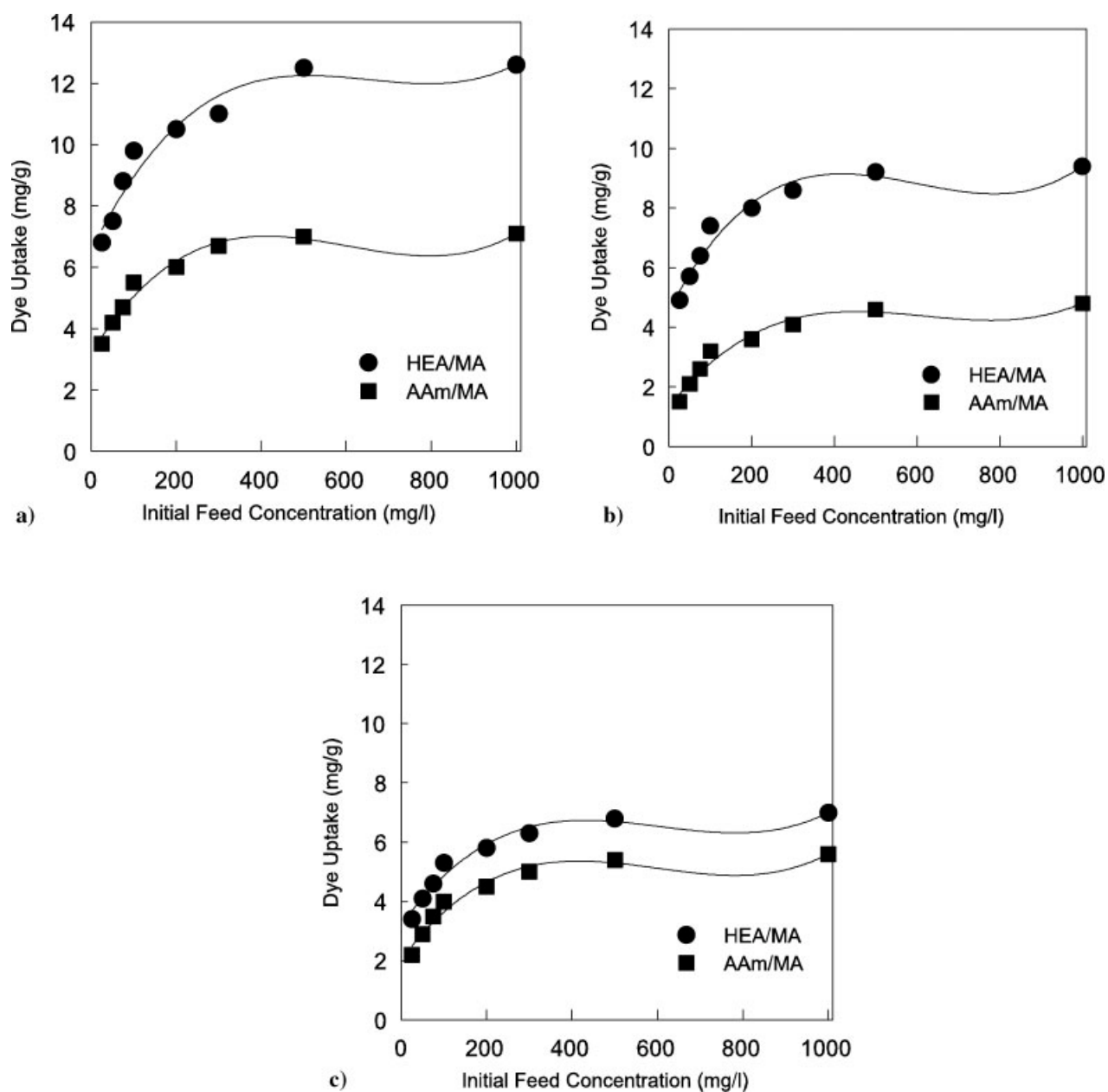
Figure 11 Effect of initial concentration on the different dye for different hydrogel over five days: (a) Astrazon Red 6B; (b) Acid Green B; (c) Ismative Orange 2R.

aqueous phase after treatment for a certain period of time, respectively, $(mg\,l^{-1})$ V is the volume of the aqueous phase (l) and W is the amount of dry hydrogel (g). The concentration of surrounding solution was monitored using UV-VIS spectroscopy.

Table III shows the dye uptake as a function of time for the different dyes using the prepared hydrogels. It can be seen that the adsorption increases with time to reach its maximum value (which is termed here as the maximum hydrogel capacity) after almost five days. This behavior is observed for all dyes investigated here (Astrazon Red 6B, Acid Green B, and Ismative Orange 2R). These hydrogels have many carboxyl groups that can increase interaction between the cationic groups of the dye and carboxyl groups of the hydrogels. On the other hand, there will be anionic repulsion between the anionic groups of the dyes and the carboxyl group of MA in the hydrogels.

The other type of interaction between the hydrogels and the cationic dyes may be hydrophobic and hydrogen bonding. Hydrophobic effects are specifically aqueous solution interactions, which in the present case involve the aromatic rings and the methyl and methine groups on the dyes' molecule and methine groups on the gel. Hydrogen bonding is expected to occur between amine groups and the
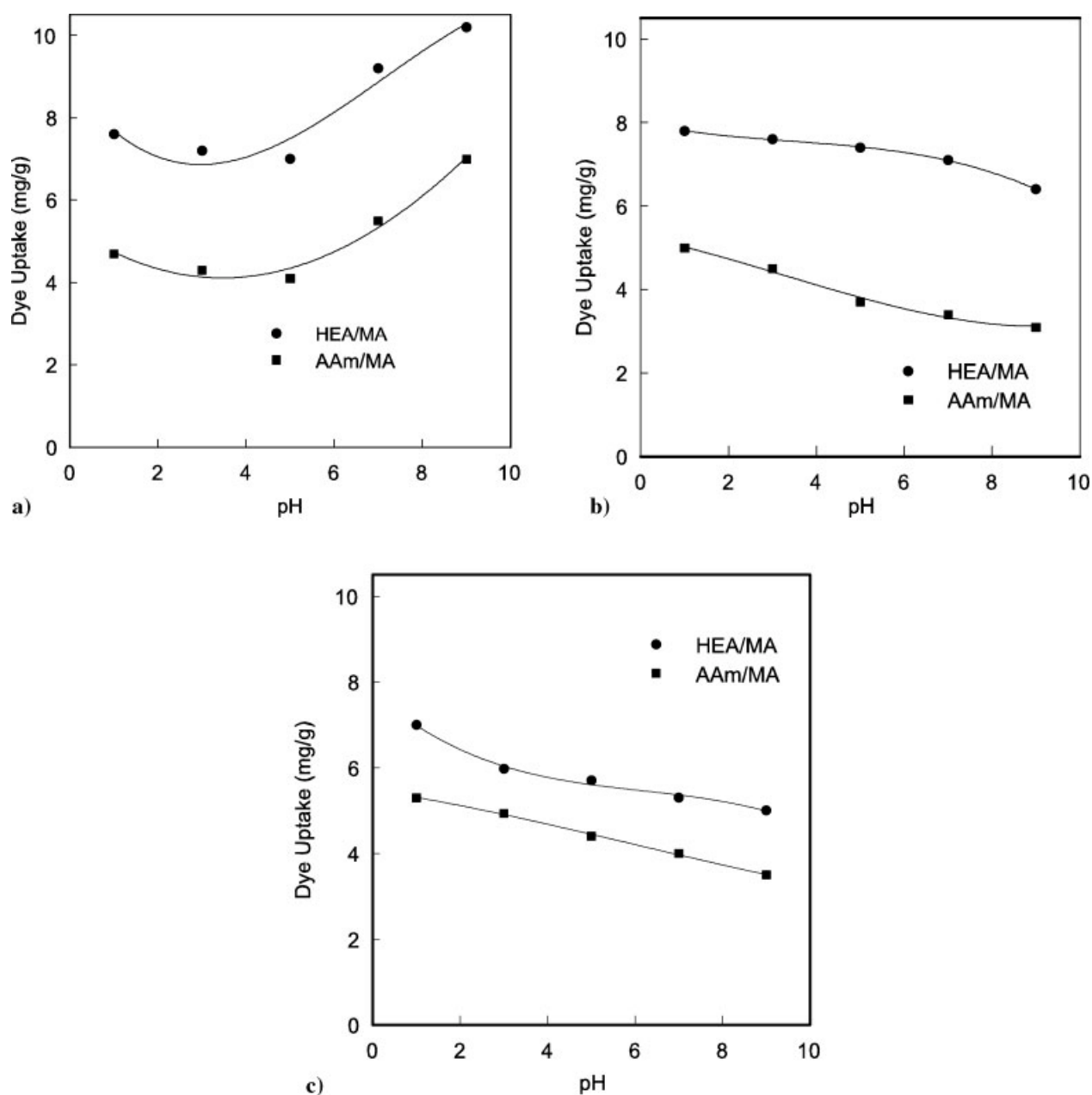
Figure 12 Effect of pH on the different dye (initial concentration is 100 ppm): (a) Astrazon Red 6B; (b) Acid Green B; (c) Ismative Orange 2R for different hydrogels.

nitrogen or sulfur atoms on the dye molecules and the carbonyl groups on the monomer units of the crosslinked copolymer. But electrostatic interactions between the dye molecules and the hydrogel are very dominant due to the hydrophobic and hydrogen bonds (see Scheme 2).[11]
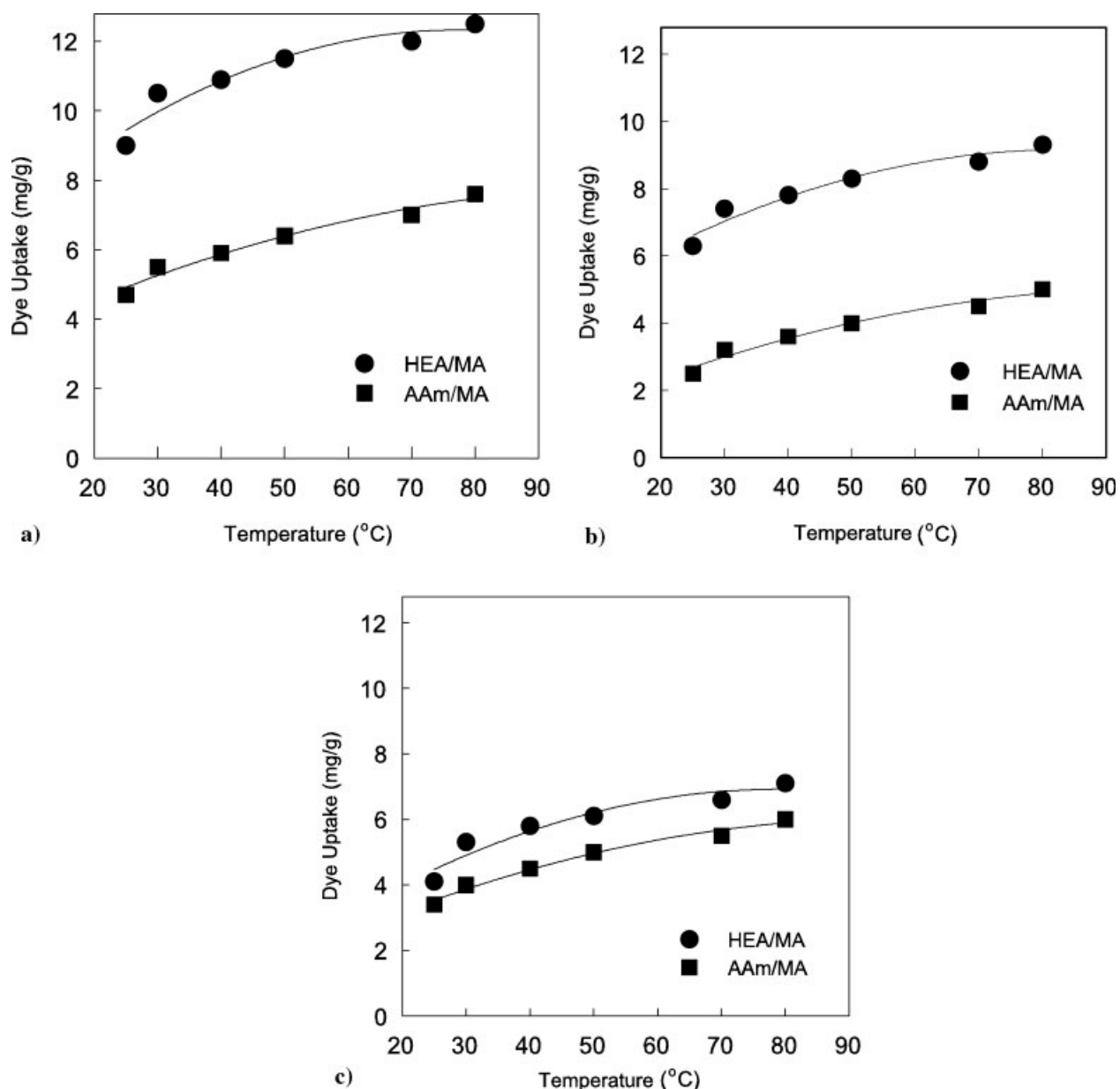
Effect of initial feed concentration

The effect of the initial feed concentration of different dyes was investigated and the results are shown in Figure 11(a–c). It can be seen that the dye uptake initially increases with the feed concentration up to 200 mg/l and tends to level off thereafter. This behavior is observed for all types of dyes investigated and as well as the different hydrogels. The (HEA/MA) hydrogel possesses higher affinity towards dye uptake than (AAm/MA) hydrogel.

Effect of the pH of the dye solution on adsorption

The influence of the pH on the adsorption of the dyes into the prepared hydrogels was investigated, as shown in Figure 12(a–c). From the results it can be seen that the dye uptake of basic dye decreases with an increasing pH if up to pH = 7; beyond that, it starts to increase at a faster rate beyond. This

Figure 13 Effect of temperature on the different dye (initial concentration is 100 ppm): (a) Astrazon Red 6B; (b) Acid Green B; (c) Ismative Orange 2R for different hydrogels.

behavior may be due to the protonation of the carboxylic acid groups of the hydrogels and amine groups of the dye. At a pH of 5, adsorption decreases since there is less protonation of the amine groups of the dye and the diffusion of the dye solution decreases. For acid dye, the dye uptake decrease with increase pH.

Effect of temperature

The temperature of the medium is an important factor in determining the dye uptake by hydrogels. Figure 13(a–c) shows the relation between the amount of dye uptake and temperature. It can be seen that the dye uptake increases with temperature. This means that as the temperature increases, the diffusion of the dye takes place directly into the hydrogels, which are in the mobile phase due to thermal effect that enhancing the diffusion of the dyes. The kinetic energy of the dye molecule increases as well as the temperature, thus leading to higher diffu-

sion of the dye molecules in the polymeric matrix. Diffusion is a function of the ease of penetration of the dye molecules through the polymer matrix.

Scanning electron microscopy

Scanning Electron Micrographs of (HEA/MA) hydrogel before and after dyes uptake are shown in Figure 14. It is shown that the surface of (HEA/MA) hydrogel before uptake of dyes was smooth, but the surface after uptake of dyes was rough. The dyes appear as small white spots adsorbed on the hydrogel, indicate the existence of dye uptake by the hydrogel via the adsorption process.

CONCLUSION

Hydrogels prepared by the radiation-induced copolymerization of HEA/MA and AAm/MA solutions are interesting for some practical uses, such as industrial wastewater treatment. The gel percentage increased
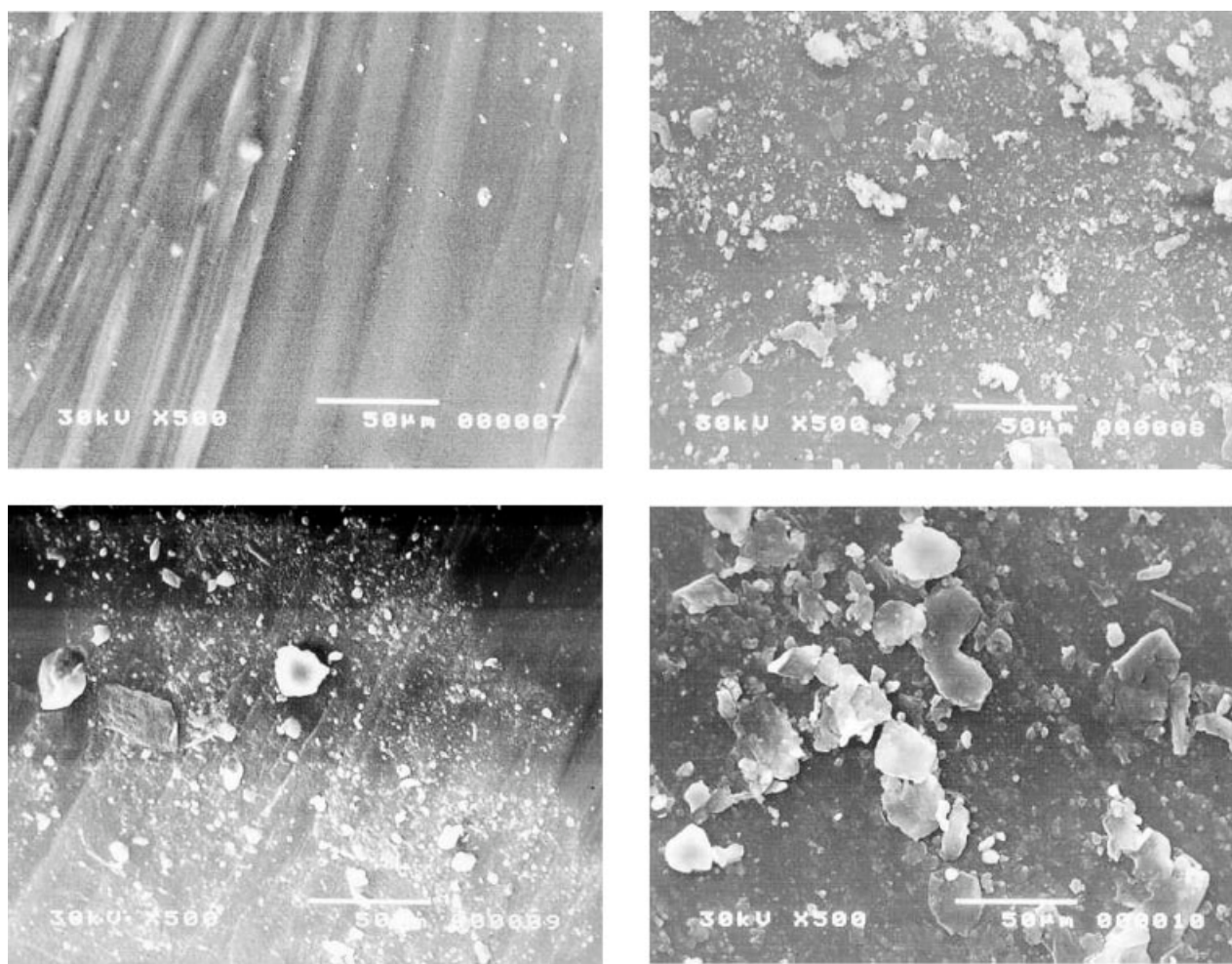
Figure 14 Scanning electron microscopy for HEA/MA hydrogel (free and containing different dyes): (a) HEA/MA hydrogel; (b) Acid Green B; (c) Ismative Orange 2R; (d) Astrazon Red 6B.

with the irradiation dose and as the content of maleic acid (MA) increased; the equilibrium swelling of such copolymers was increased as well. Diffusion of water within hydrogels was found to be of a non-Fickian character. The prepared hydrogels showed good hydrophilic properties and thermal stability, which may make them acceptable for practical uses.

The uptake of hydrogel capacity increased with time to reach its maximum value (equilibrium state) after almost five days for all the dyes investigated. The maximum uptake for a given dye was higher for the HEA/MA hydrogel than for the AAm/MA hydrogel. The adsorption capacity of the investigated hydrogels was dependent on the pH of the aqueous dye solutions.

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