Radiation Synthesis and Characterization of 2-Hydroxyethyl-methacrylate-Based Hydrogels Containing Di- and Tri-Protic Acid and Its Application on Wastewater Treatment

Samia E. Abdel-Aal, El-Sayed A. Hegazy, M. F. Abou Taleb, Ahmed M. Dessouki

Department of Polymer Chemistry, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

ABSTRACT: Radiation-crosslinked 2-hydroxyethylmethacrylate/citric acid (HEMA/CAc), 2-hydroxyethylmethacrylate/tartaric acid (HEMA/TA), and 2-hydroxyethylmethacrylate/succinic acid (HEMA/Sc) copolymers were prepared by using ^{60}Co γ-rays. The gel fraction yield and the swelling behavior of the prepared hydrogels were studied. It was shown that increasing irradiation doses was accompanied by an increase in yield of gel fraction and a decrease in swelling degree. The parameters of equilibrium swelling, maximum swelling, initial swelling rate, swelling exponent, and diffusion coefficient of the hydrogels were determined by studying the swelling behavior of the hydrogels prepared. It was seen that the equilibrium swelling degree increases as the content of acid increases, as a result of introducing more hydrophilic groups. When the hydrophilic polymer (acids) varies in the content range of 40–80 mg, swelling exponents (n) decreases, thereby indicating a shift in the water-transport mechanism from the anomalous (non-Fickian)-type to the Fickian-type. Characterization and some selected properties of the prepared hydrogels were studied, and accordingly the possibility of its practical use in the treatment of industrial wastes such as dyes and heavy metals (Fe, Ni, Co, and Cu) were also studied. The effect of treatment time, pH of feed solution, initial feed concentration, and temperature on the dye and heavy metals uptake was determined. The uptake order for a given metal was HEMA/TA hydrogel > HEMA/CAc > HEMA/Sc hydrogel. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1759–1776, 2008

Key words: hydrogel; radiation copolymerization; protic acid; wastewater

INTRODUCTION

Hydrogels are networked structures of polymer chains crosslinked to each other and surrounded by an aqueous solution. The polymer chains contain acidic or basic groups bound to them. The acidic groups on the chains deprotonate at high pH, whereas the basic groups protonate at low pH. In the presence of an aqueous solution, the polymer chains absorb water, and the association, dissociation, and binding of various ions to polymer chains causes the hydrogel to swell.

Polymeric hydrogels have series of particular characteristics; they are hydrophilic, insoluble in water, soft, elastic, and swell with water, keeping up their shapes but increasing in volume until reaching a physical–chemical equilibrium. Hydrogel properties depend strongly on (1) the degree of crosslinking, (2) the chemical composition of the polymer chains, and (3) the interactions of network and surrounding liquid. The properties of hydrogels as adsorbent materials can be changed with pH and temperature.[1,2]

The equilibrium degree of swelling of electrolyte-type hydrogel is mainly influenced by the charge of the ionic monomer, dissociation constant, pKa of the ionizable group, degree of ionization, concentration of ionizable monomer in the network, crosslinking density, structure of the polymer backbone, pH, ionic strength, and composition of the swelling solution. The concentration of ionizable monomer in the hydrogel is important for the swelling and pH-sensitivity of the gel. This effect is a result of relative hydrophilicity of the ionizable monomer to the neutral monomer. In recent years, new hydrogels from the copolymers of N-vinyl-2-pyrrolidone and mono-, di-, tri-protic acids such as acrylic, itaconic, tartaric, and citric acid were synthesized.[3–5]

In this study, 2-hydroxyethyl-methacrylate (HEMA)-based hydrogels containing mono-, di-, and tri-protic acid moieties were prepared by using γ-

radiation at various doses. Swelling properties and diffusion parameters of these hydrogels were studied and their application to the adsorption of metals ions (Fe, Ni, Co, and Cu) and dyes (Maxilon C.I. Basic dye and Acid fast yellow G) was investigated.
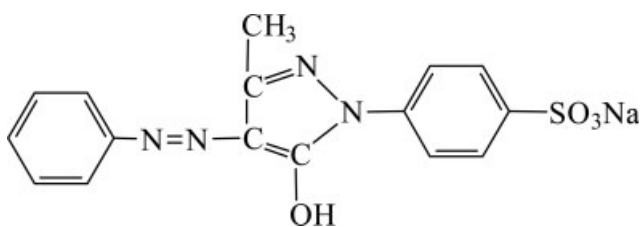
EXPERIMENTAL

Dyestuffs

Two types of dyes, acidic and basic dyes, were used as reagent grades (Dyestuffs and Chemicals, Kaffer El-Dawar, Egypt).

Acid dyes (Acid fast yellow G)

Molecular formula: $C_{16}H_{13}O_4N_4SNa$
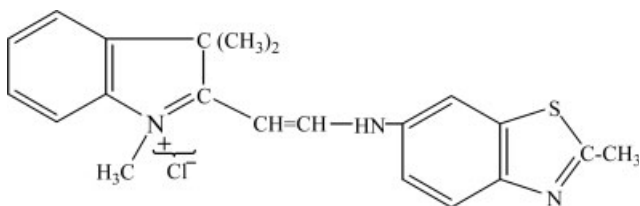Molecular weight = 381
λ_{max} = 406 nm

Maxilon C.I. basic (Yellow 45)

Molecular formula: $C_{21}H_{22}N_3SCl$
Molecular weight = 383.5
λ_{max} = 435 nm

γ-Radiation source

The samples were irradiated with the Co^{60} Russian irradiation facility γ-rays at a dose rate of 1.43 Gy/s. The irradiation facility was constructed by the National Center for Radiation Research and Technology, Atomic Energy Authority of Egypt.

Preparation of hydrogel

Aqueous solutions of monomer of 1 mL HEMA and 40, 60, and 80 mg of acid (citric, tartaric and succinic acid) were prepared in 1 mL of distilled water in dif-

ferent compositions. Solutions were prepared and subjected to Co^{60} Russian irradiation facility γ-rays to various doses (2, 3, 4, 5, and 6 kGy) at a fixed dose rate of 1.43 Gy/s. The hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm and dried at room temperature and weighed (w_d).

Gel determination in the copolymerized hydrogels

The dried hydrogels were extracted with water for 48 h at 100°C to extract the insoluble parts of the hydrogel. The insoluble parts, i.e., the gelled parts, were taken out and washed with hot water to remove the soluble part, then dried and weighed. This extraction cycle was repeated until the weight became constant. The gel fraction yield in the hydrogel was determined from the following equation:

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

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

Swelling measurements

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

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

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

Kinetics of swelling

The progress of the water-intake process was monitored by determining the swelling ratio of the hydrogel at desired time intervals as previously described. For the kinetic analysis of the results, Fick's law[6] was applied:

$$F = \frac{W_t}{W_\infty} = kt^n$$

where F denotes the amount of solvent fraction at time t; k is the swelling rate front factor; n is the

swelling exponent; and W_t and W_∞ are the water-intakes at time t and the equilibrium time, respectively. The equation is a phenomenological rate law in which n provides insight into the type of water-sorption mechanism that is operative. For instance, $n = 0.5$ shows Fickian kinetics in which the sorption is diffusion-controlled, whereas a value of n between 0.5 and 1.0 indicates a non-Fickian process in which chain relaxation also contributes to the water-sorption process.

The diffusion constant of water (D) through the hydrogel was calculated according to the following equation:[7]

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

where l is the thickness of the hydrogel.

Ultraviolet measurements

Analysis by an UV spectrophotometer was carried out using a Milton Roy spectronic 1201 in the range from 190 to 900 Å.

X-ray diffraction

X-ray diffraction patterns were obtained with a XD-DI Series, Shimadzu apparatus using nickel-filtered and Cu-Kα target. This technique was performed to clarify the changes in morphological structure caused by the copolymerization of the different comonomer compositions.

Thermal gravimetric analysis

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

Metal uptake measurements

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

The metal uptake (E) was calculated as follows:

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

where W is the weight of the dry hydrogel (g); A is the atomic weight of metal ion; C_i and C_f are the initial and remaining concentrations of metal ions in mg/L, respectively (ppm); we divide by 10, as 100 mL of the metal ions solution were used instead of 1 L.

The total uncertainly for all experiments ranged from 3 to 5%.

Measurements of adsorption capacity

Adsorption isotherms were determined by the batch method for all adsorbents. Accurately weighed dry samples were placed in a solution of a definite volume and allowed to stand for a period of 8 days at room temperature. Adsorption amount of dye (mg/g) was calculated by the Freundlich equation:

$$X/m = kC^{1/n}$$

$$X = [V(C_1 - C_2)] \quad \text{(mg)}$$

where m is the weight of dry hydrogel (g); V is the volume of solution (L); K and n are constants; C_1 and C_2 are the concentrations (mg/L) of dye solution before and after adsorption, respectively, that were determined by using an UV–visible spectrophotometer at identical dye's absorbance wavelengths; the standard calibration curves were previously determined.

RESULTS AND DISCUSSION

In spite of the availability of the huge number and variety of synthetic vinyl monomers, hydrogels can be prepared from just a few hydrophilic monomers. Among them, 2-hydroxyethyl methacrylate, acrylamide, and N-vinyl-2-pyrrolidone comprise the three most frequently used. Polyethylene oxide and poly (vinyl alcohol) are two polymers preferred in the synthesis of hydrogels.[8] For incorporation of some sensitivity properties to the hydrogels for specific purposes, the above-mentioned monomers or polymers can be used for radiation copolymerization and/or grafting with monomers carrying appropriate functionalities. However, it is a challenge to obtain hydrogels from nonvinyl groups containing monomers. This problem can be overcome by a radiation method, which makes possible the incorporation of such moieties in the hydrogels network structure. To prepare such a system, high-energy radiation (or
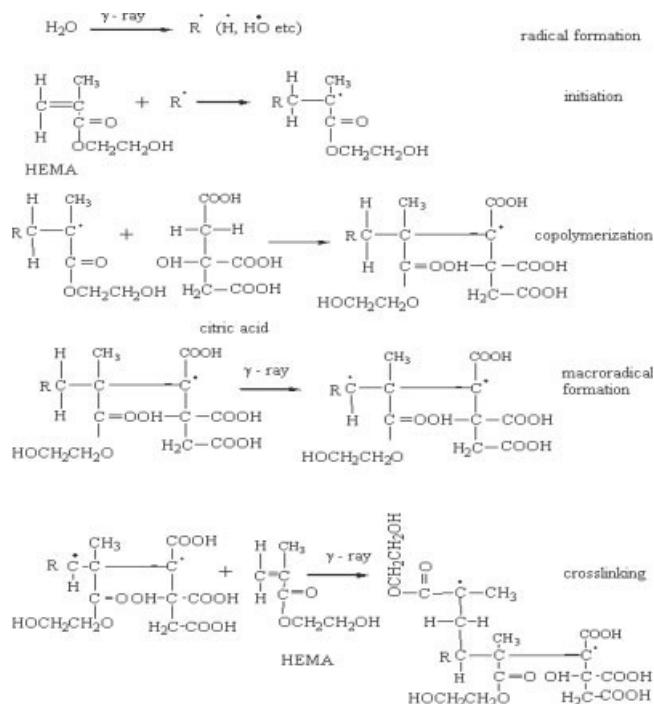
Scheme 1 Possible copolymerization and crosslinking mechanism of HEMA and citric acid.

ionizing radiation), such as γ-rays and electron beams, can be used.

Radiation technique seems viable for the preparation of hydrogels, since monomers or a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. As this hydrogel is not contaminated with foreign additives, crosslinks must be composed of stable C—C bonds, and it is of interest to study the preparation of hydrogels by irradiation.[9,10]

In this connection, HEMA was copolymerized with citric (CAc), tartaric (TA), and succinic (Sc) acids by using γ-rays as initiator to obtain copolymeric hydrogels containing acid groups moiety. The effect of the preparation conditions such as irradiation dose and concentration of di- or tri-protic acid added to HEMA was investigated.

Preparation of radiation-induced hydrogels

A radiation technique was used to copolymerize HEMA with citric (CAc), tartaric (TA), and succinic (Sc) acid. When monomers of HEMA and nonvinyl carboxylic acid are irradiated together with γ-rays, one double bond of CC on HEMA and one or two of CH bonds of acid break up by ionizing radiation and free radicals are generated. These free radicals react with each other, and a copolymeric HEMA/CAc, HEMA/TA, and HEMA/Sc hydrogels are pro-

duced. For the polymerization and crosslinking of poly(HEMA/CAc) by γ-irradiation, a possible mechanism is proposed in Scheme 1. During the irradiation of HEMA, acid, and water ternary mixtures, the polymer chains crosslink and a gel is obtained. It was found that the minimum dose required for gel preparation is 2 kGy. For the polymerization and crosslinking of poly(HEMA/CAc) by γ-irradiation, a possible mechanism is proposed in Scheme 1.[11]

The percent gelation of the investigated hydrogels are presented in Table I. As can be seen from this table, the percent gelation of these hydrogels increases with increasing irradiation doses.

### Characterization and some selected properties of the prepared hydrogel

Swelling behavior

The influence of swelling time on the water uptake percent for hydrogels prepared at various comonomer compositions is shown in Figures 1–3. It can be seen that the water absorbancy of the hydrogels increases as the swelling time increases to reach a maximum value after 400 min (equilibrium swelling degree) (S_{max}). The equilibrium swelling degree increases as the content of acid increases, along side with the introduction of more hydrophilic groups. Citric acid has three carboxyl groups per chain length, whereas tartaric and succinic acid have only two. Therefore, the observed behavior is dependent on the number of ionizable groups on the polymer, which enhance repulsive the forces of —COOH groups with the neighboring chains. This electrostatic repulsion is responsible for the network swelling with the expected reduction of the hydrostatic pressure inside of the network. Additionally, as acid content increases in the system, osmotic pressure inside the network becomes higher resulting in swelling of the hydrogels.

Hydrogen bonding and other secondary valence forces between adjacent polymer chains hold these

TABLE I
Effect of Acid Content on the Value of Gel Fraction Yield for the Different Hydrogels, at Different Doses

| Dose (kGy)	CAc in HEMA/CAc (mg)			TA in HEMA/ TA (mg)			Sc in HEMA/ Sc (mg)		
	40	60	80	40	60	80	40	60	80
2	83	80	78	86	84	80	90	88	82
3	86	82	80	89	86	82.7	92	90.6	84
4	90	86	83	92	89.1	85	94	93	87
5	92.6	90	86	94	92	88	95.6	95	90
6	94.3	92.4	89	95.4	94.3	91.5	97	96	93
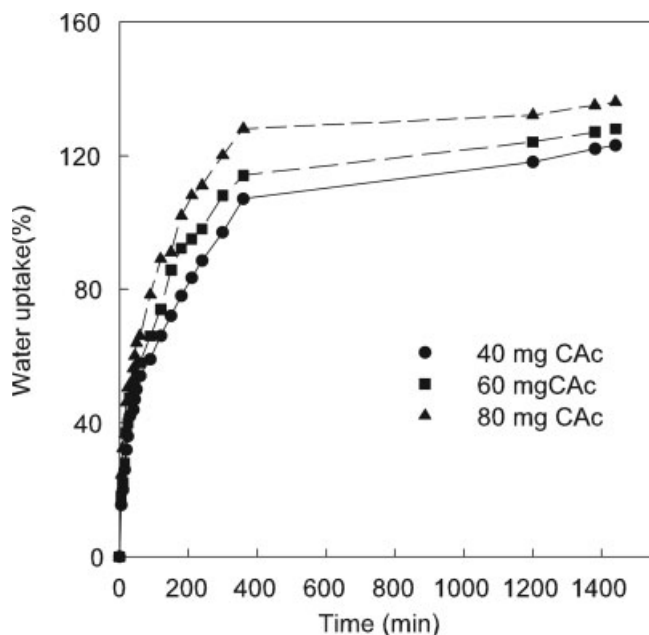
Figure 1 Effect of swelling time (min) on the water uptake % for different HEMA/CAc compositions, at gelation dose of 2 kGy.

HEMA and acid networks together and play an important factor for swelling. Water swells the polymer networks because it penetrates between the chains and breaks interchain secondary valence bonds by forming hydrogen bonding with carboxyl groups of acid and HEMA. This fact permits the polymer networks to expand to accommodate the influx of water through relaxation of the stresses produced by osmotic pressure.[11]
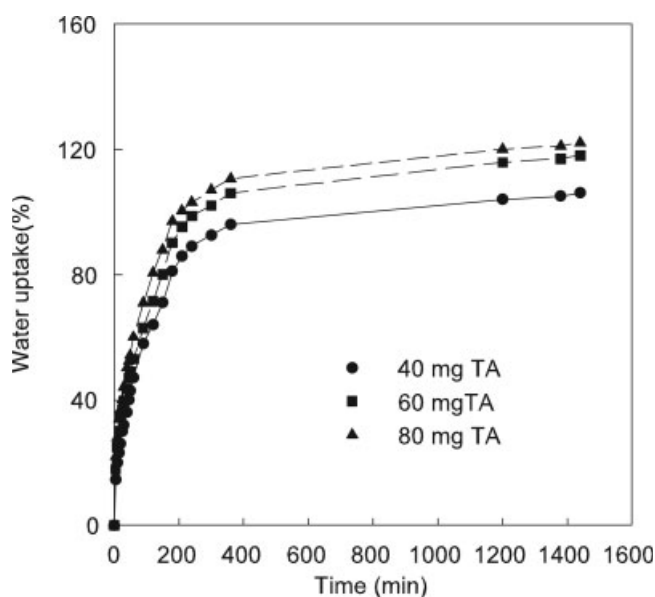
Figure 2 Effect of swelling time (min) on the water uptake % for different HEMA/TA compositions, at gelation dose of 2 kGy.
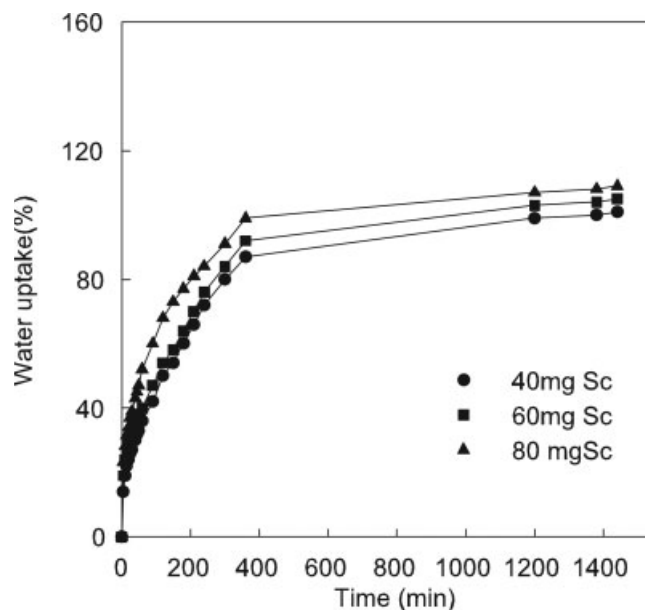
Figure 3 Effect of swelling time (min) on the water uptake % for different HEMA/Sc composition, at gelation dose of 2 kGy.

From Figures 4–6, it can be seen that $S_{eq}\%$ decreased with the increase of irradiation dose, while increasing with CAc content. The increase for dose lessens the number of small chains. Thus, hydrogels exposed to higher doses have higher crosslink density than hydrogel exposed to lower doses. This means that a high amount of adsorbed dose decreases the number–average molar mass between crosslinks, while a low amount of adsorbed
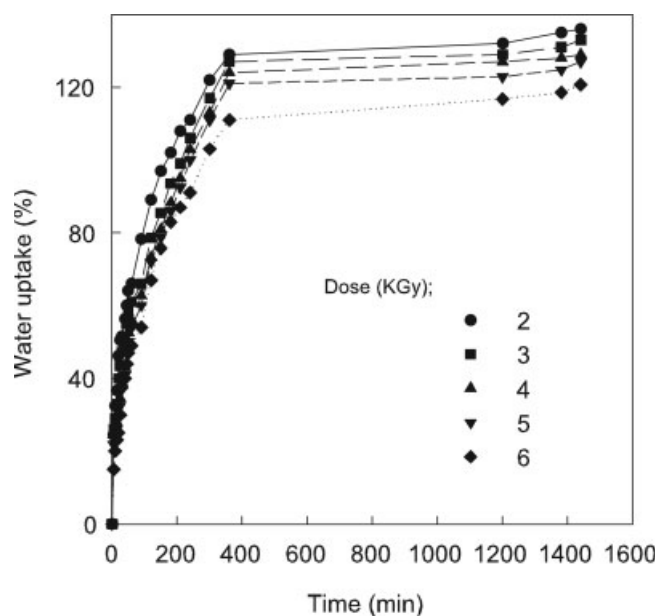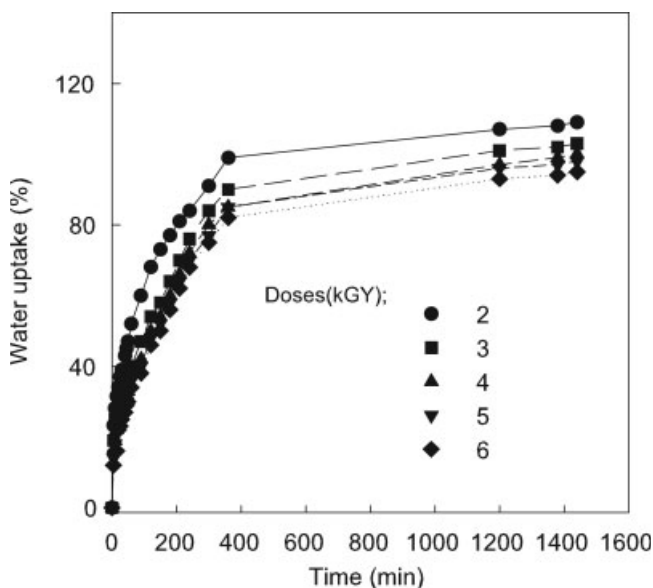

Figure 4 Effect of swelling time (min) on the water uptake % of (HEMA/CAc) hydrogel (80 mg CAc), at different gelation doses.
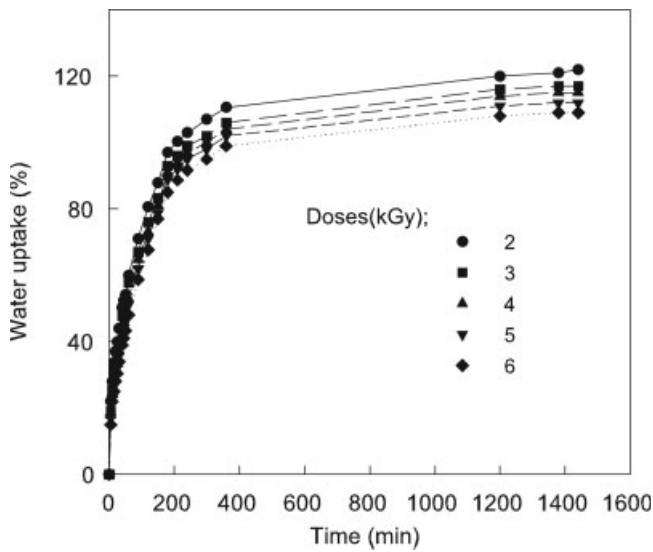
Figure 5 Effect of swelling time (min) on the water uptake % of (HEMA/TA) hydrogel (80 mg TA), at different gelation doses.

dose increase the number–average molar mass between crosslinks.

The equilibrium swelling behaviors of (HEMA/CAc, HEMA/TA, and HEMA/Sc) hydrogels were investigated as a function of pH. The variation of S_{eq}% with pH of solution is an important property for the pH-sensitive hydrogels. Figure 7 illustrates the S_{eq}% of HEMA and 80 mg acid containing hydrogels irradiated to 2 kGy in buffer solutions from pH 1 to 10.5. As can be seen from Figure 7, the

values S_{eq}% of HEMA hydrogels increased gradually with the incorporation of the ionizable acid. It is well known that CAc is a triprotic acid with the dissociation constants $pK_{a,1}$ = 3.14, $pK_{a,2}$ = 4.77, and $pK_{a,3}$ = 6.39; and TA and Sc are diprotic acid with dissosiation constants $pK_{a,1}$ = 3.2, $pK_{a,2}$ = 4.8, and $pK_{a,1}$ = 4.2, $pK_{a,2}$ = 5.6, respectively. The consecutive swelling at around these pH values takes place more or less in a stepwise manner around pK_a values. An increase could be expected in S_{eq}% values around these pK_a value, however, it should not be forgotten that the amount of used acid (CAc, TA, and Sc) is very low when compared to overall composition of hydrogels. Charged groups attached to the polymeric network structure played an essential role in swelling properties.[12]
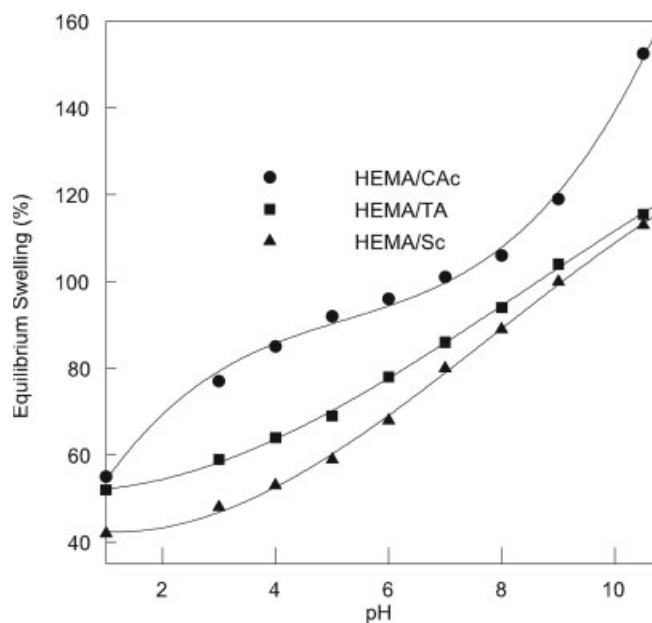
Hence, the ionization of all carboxylic groups in acid increases the S_{eq}% of hydrogel in the basic media as shown in Figure 7.

Kinetic swelling and diffusion

For extensive swelling of hydrogels, the following relation can be written:[13]

$$\frac{t}{S} = A + Bt \qquad 1$$

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = 1/(k_s\, S_{eq}^2)$ is the reciprocal of the initial swelling rate of the gel r_o, and K_s is the swelling rate constant. The relation represents second-order kinetics.[13]

Figure 6 Effect of swelling time (min) on the water uptake % of (HEMA/Sc) hydrogel (80 mg Sc), at different gelation doses.

Figure 7 Effect of pH on the equilibrium degree of swelling for different hydrogels; dose = 2 kGy.
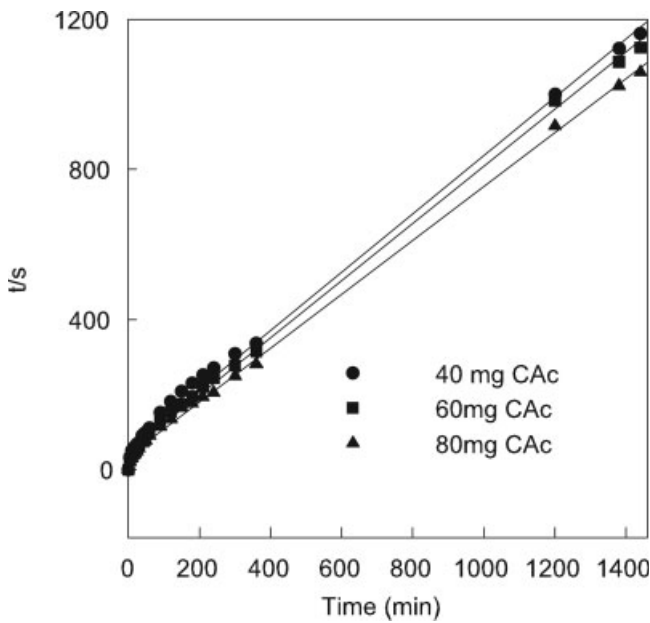
Figure 8 Water uptake kinetics curve of HEMA/CAc hydrogels.

If second-order kinetics are applicable, the plot of t/S against t of eq. (1) should give a linear relationship, from which S_{eq}, k_s, and r_o can be determined from the slope and intercept of the plot in Figures 8–10 and are presented in Table II. The values of maximum swelling and initial swelling rate of the hydrogels suggest similar swelling behavior.

Table II presents the initial swelling rates and equilibrium swelling degrees calculated according to

second-order swelling equation. Although all copolymeric hydrogels possessed an increased amount of acid content, they expectedly swell faster than those possessing lower amount of acid due to the increased extent of hydrophilicity; there could not be any proportionality between them. The swelling degree and rate largely depend on ionization of carboxyl groups of acid, which in turn somewhat differ in the hydrogel than in pure acid.

Dynamic sorption data not only reflect the progress of the swelling process but also provide information about the water-transport mechanisms, as revealed by the equations:

$$F = \frac{W_t}{W_\infty} = kt^n$$

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

For the hydrogels, $\ln F$ versus $\ln t$ plots were drawn and some representative results are shown in Figures 11–13. The swelling exponents n and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table III. The values present in the table were analyzed for the prediction of water-transport mechanisms.

When the hydrophilic polymer (acids) varies in the content range of 40–80 mg, n decreases thereby indicating a shift in the water-transport mechanism from the anomalous (non-Fickian)-type to the Fickian-type. The results can be attributed to the fact
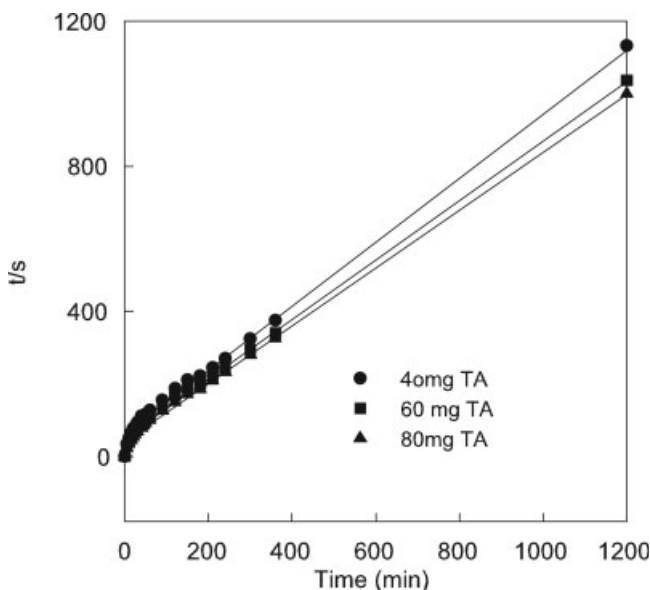
Figure 9 Water uptake kinetics curve of HEMA/TA hydrogels.
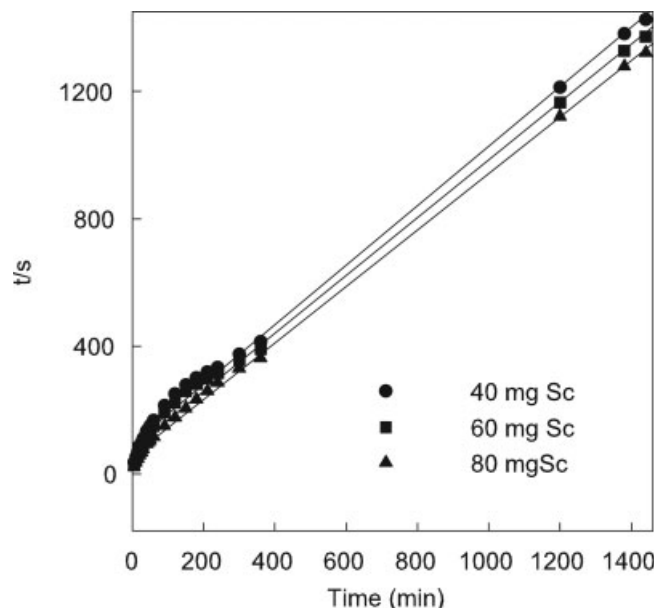
Figure 10 Water uptake kinetics curve of HEMA/Sc hydrogels.

TABLE II
Effect of Acid Content on the Value of Swelling Parameters for the Different Hydrogels, at a dose of 2kGy

Parameter	CAc in HEMA/CAc (mg)			TA in HEMA/TA (mg)			Sc in HEMA/Sc (mg)		
	40	60	80	40	60	80	40	60	80
S_{max} (g_{water}/g_{gel})	1.35	1.39	1.47	1.18	1.3	1.33	1.12	1.16	1.2
r_o (g_{water}/g_{gel}) (min)	0.016	0.021	0.027	0.016	0.021	0.024	0.11	0.013	0.018
K_s (10^{-3}) (g_{gel}/g_{water}) (min)	8.8	10.8	12.3	11.8	12.0	13.8	8.3	9.25	12

that increasing the acid content in the hydrogel results in a network with a greater number of macromolecular chains, and this will lead to a restricted diffusion of water molecules. This obviously makes the swelling process diffusion-controlled, that is, Fickian in nature. A slowed diffusion process indicates a lower degree of swelling and in the aforementioned range of acid concentrations, the swelling ratio decreased as mentioned previously.

For hydrogel, F versus $t^{1/2}$ values are plotted and representative graphs are shown in Figures 14–16. The diffusion coefficients were calculated from the slope of the line.

Table III shows D values for various compositions of the hydrogel. It is clear from the data that the D values vary with the mechanism of water transport.

Thermal gravimetric analysis

Figure 17 shows the thermograms for the different hydrogels at various elevated temperatures. There are three types of the decomposition region on the thermograms of the hydrogels. It is reported that the first region (0–220°C) corresponds to loss of bound water, in the second region (220–380°C) there is a decomposition in the side groups and branches of the hydrogel. The third region (>380°C) represents substantial mass loss and is normally attributed to main chain breakdown. To determine the thermal stabilities of HEMA/CAc, HEMA/TA, and HEMA/Sc hydrogels, the temperatures for the maximum mass loss (T_{max}, °C) were found directly from their thermograms given in Figure 17. The temperatures for the maximum mass loss of HEMA/CAc, HEMA/TA, and HEMA/Sc hydrogels are 450, 435, and 400°C, respectively. It was reported that TGA of pure PHEMA shows that the mass loss of PHEMA begins at ∼ 322°C and reaches maximum at 361°C.[14] It was observed that T_{max} of HEMA hydrogel is lower than that of HEMA/CAc, HEMA/TA, and HEMA/Sc hydrogels. So, it is said that, HEMA poly-
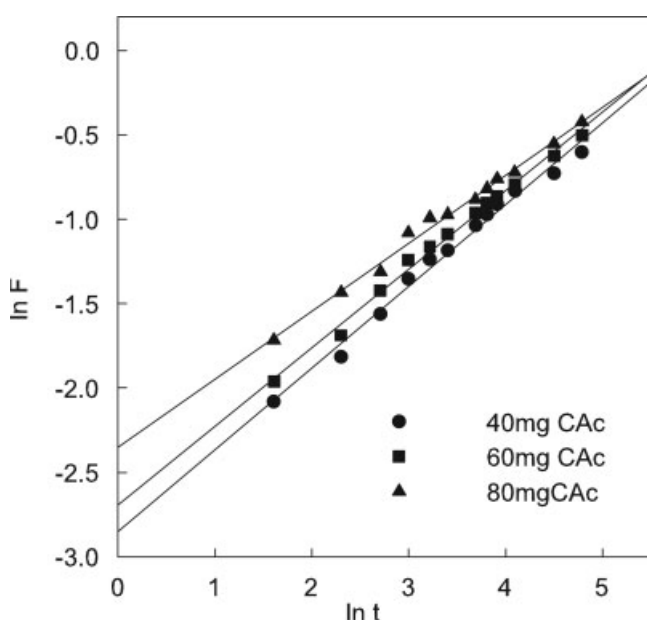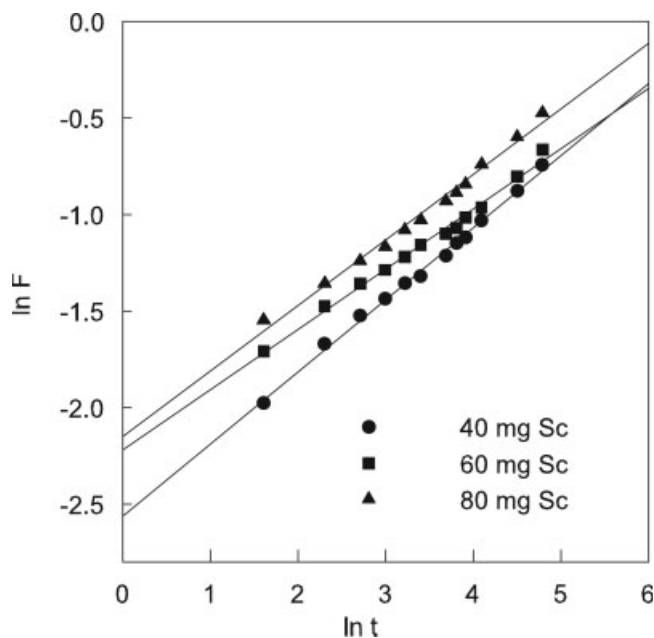

Figure 11 Plots of ln F versus ln t for different compositions of HEMA/CAc hydrogels, at irradiation dose of 2 kGy.
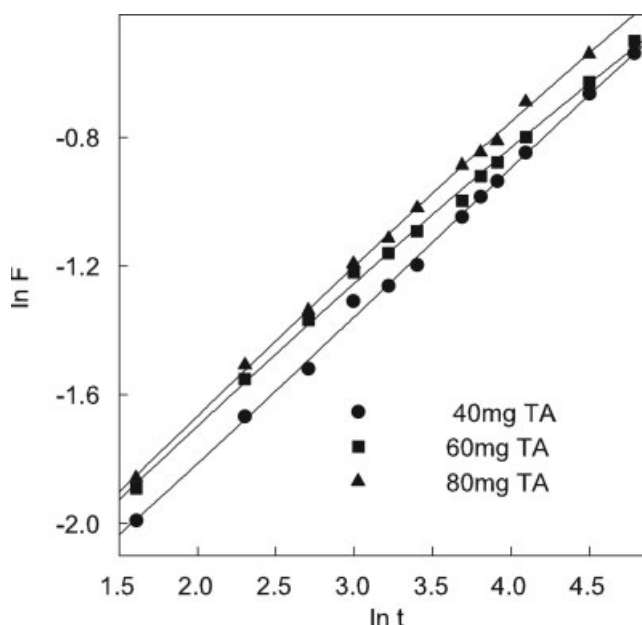
Figure 12 Plots of ln F versus ln t for different compositions of HEMA/TA hydrogels, at irradiation dose of 2 kGy.

Figure 13 Plots of ln F versus ln t for different compositions of (HEMA/Sc) hydrogels; at irradiation dose of 2 kGy.

mers in the case of adding CAc, TA, and Sc rapidly increased with the heating.

Applications of the prepared hydrogels

Waste dyes treatment

To observe the uptake of some dyes, the prepared hydrogels were placed in aqueous solutions of cationic and anionic dyes and allowed to equilibrate for 6 days at room temperature; thereafter, they showed dark coloration to the colors of the original solutions. The concentration of surrounding solution was monitored by using UV–VIS spectrophotometer.

Effect of treatment time

Time needed for the treatment of wastewater dyes is of great importance from the economic point of view. Figures 18 and 19 show the effect of time on

the dye uptake for different dyes using (HEMA/ CAc), (HEMA/TA), and (HEMA/Sc) hydrogels. For all figures, the dye uptake initially increases sharply with time; then reaches its maximum after 6 days. This behavior is observed for all hydrogels investigated here (Isma acid fast yellow G and Maxilon C.I. Basic dyes). Hydrogels in the aqueous solutions of Maxilon C.I. Basic dye showed dark colorations. These hydrogels have many carboxyl groups that can increase the interaction between the cationic groups of cationic dye and carboxyl groups of hydrogels. On the other hand, there will be anionic repulsion between anionic groups of anionic dyes and carboxyl groups on the hydrogels.

The other type of interaction between the hydrogels and the cationic dyes may be due to hydrophobic and hydrogen bond. Hydrophobic effects are specifically aqueous solution interactions, which in the present case involves the aromatic rings and the methyl and methine groups on the dyes molecule and methine groups of the gel. Hydrogen bond will be expected to occur between amine groups and the nitrogen or sulfur atoms on the dye molecules and the carbonyl groups on the monomer units of cross-linked copolymer. But, electrostatic interactions between the dye molecule and the hydrogel are very dominant due to the hydrophobic and hydrogen bonds (Scheme 2).[15]

Effect of pH of dye solution on adsorption

The influence of the pH on the adsorption of basic and acid dye into prepared hydrogels was investigated and shown in Figures 20 and 21. From the results, it may be seen that the dye uptake of the Basic dye decreases with increasing pH up to pH = 7, then it starts to increase at a faster rate beyond pH = 7. This behavior is due to the protonation of the carboxylic acid groups of hydrogels and amine groups of the dye. At pH 5, adsorption decreases since there is less protonation of amine groups of the dye, and the diffusion of dye solution decreases. For acid dye, the dye uptake decreases with pH increase.

TABLE III
Effect of Acid Content on the Value of Swelling Exponents and Swelling Constant for the Different Hydrogels, at a dose of 2 kGy
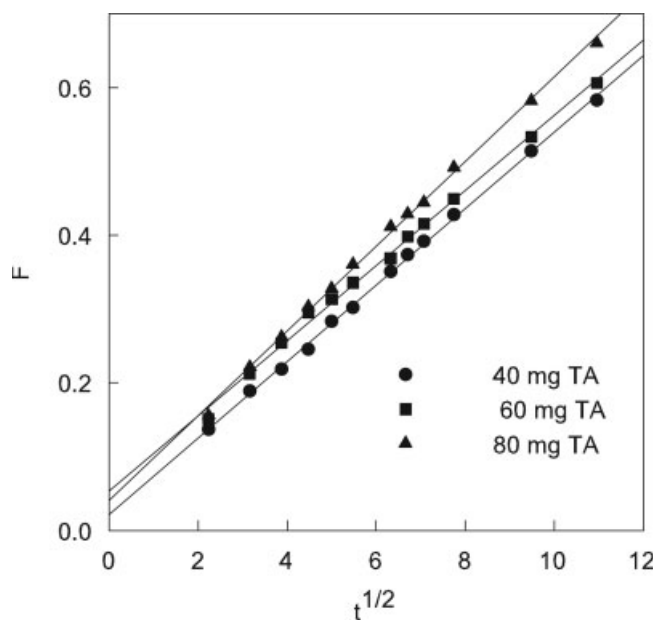
Parameter	CAc in HEMA/CAc (mg)			TA in HEMA/TA (mg)			Sc in HEMA/Sc (mg)		
	40	60	80	40	60	80	40	60	80
Swelling exponents (n)	0.64	0.52	.46	0.62	0.5	0.48	0.61	0.49	0.48
Swelling constants (K) (10^{-2})	6.3	10.3	11.6	13.1	15.9	17.5	7.6	10.9	11.7
Diffusion coefficient, D (10^{-5}) (cm^2/s)	49.7	57.5	74.4	50	85	87.3	40.1	38.5	41.7
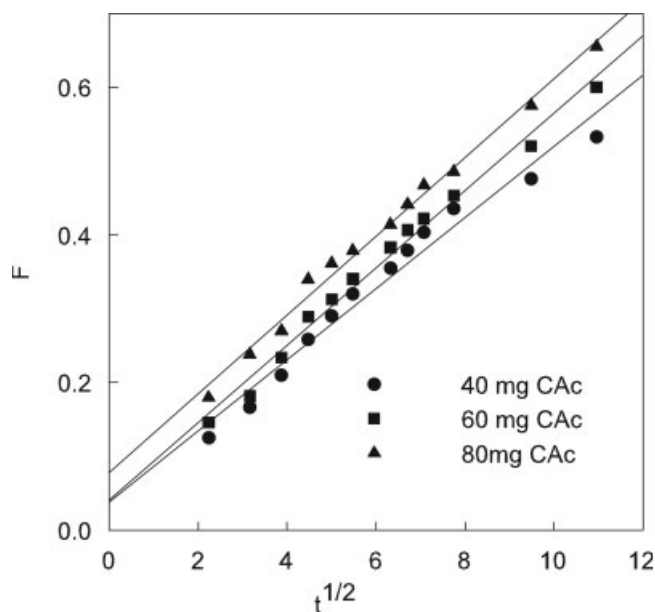
Figure 14 Plots of F versus $t^{1/2}$ for HEMA/CAc hydrogel at different compositions, at radiation dose of 2 kGy.

Effect of initial feed concentration
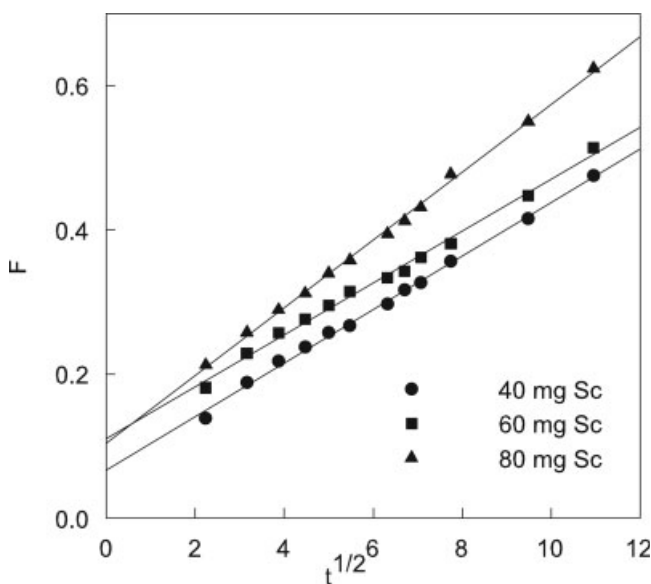
The effect of initial feed concentration of the dyes was investigated and shown in Figures 22 and 23. It can be seen that the dye uptake initially increases with the feed concentration up to 200 mg/L. Thereafter, it tends to level-off. This behavior is observed for all types of dyes investigated, and also for different hydrogels.

Effect of temperature of dye solution on adsorption

One of the important parameters that affect adsorption capacity is temperature. The effect of temperature on the adsorption of dyes on different hydrogels are shown in Figures 24 and 25. It can be seen that the dye uptake decreases with the increase in the temperature of the aqueous dye solution. These changes are due to volume collapse upon warming. It has been shown that a number of hydrogels demonstrate nearly continuous volume transition from low temperature, highly swollen gel network to a collapsed, high temperature phase near their critical points.

Metal ions treatment

Citric, tartaric, or succinic acid in aqueous solution presents some characteristics such as three- and two-step dissociation process of three and dicarboxyl groups, binding of counter ions, etc. These characteristics are attributed to the hydrophobic interaction of nonpolar side chains and the short-range electrostatic interaction of carboxyl group pairs. The presence of these carboxyl groups is responsible for metal absorption from aqueous solutions. Metal absorption is in agreement with the exchange between metal ion in the external solution and H^+ from the polar groups in the polymer chain, considering that carboxyl groups in the hydrogel bind with metal ion due to the electrical charge.

The kinetics of metal ion uptake process is relatively slow, the diffusion of ion inside the hydrogel is likely the rate-limiting factor. In metal ion solutions,

Figure 15 Plots of F versus $t^{1/2}$ for HEMA/TA hydrogel at different compositions, at radiation dose of 2 kGy.


Figure 16 Plots of F versus $t^{1/2}$ for HEMA/Sc hydrogel at different compositions, at radiation dose of 2 kGy.
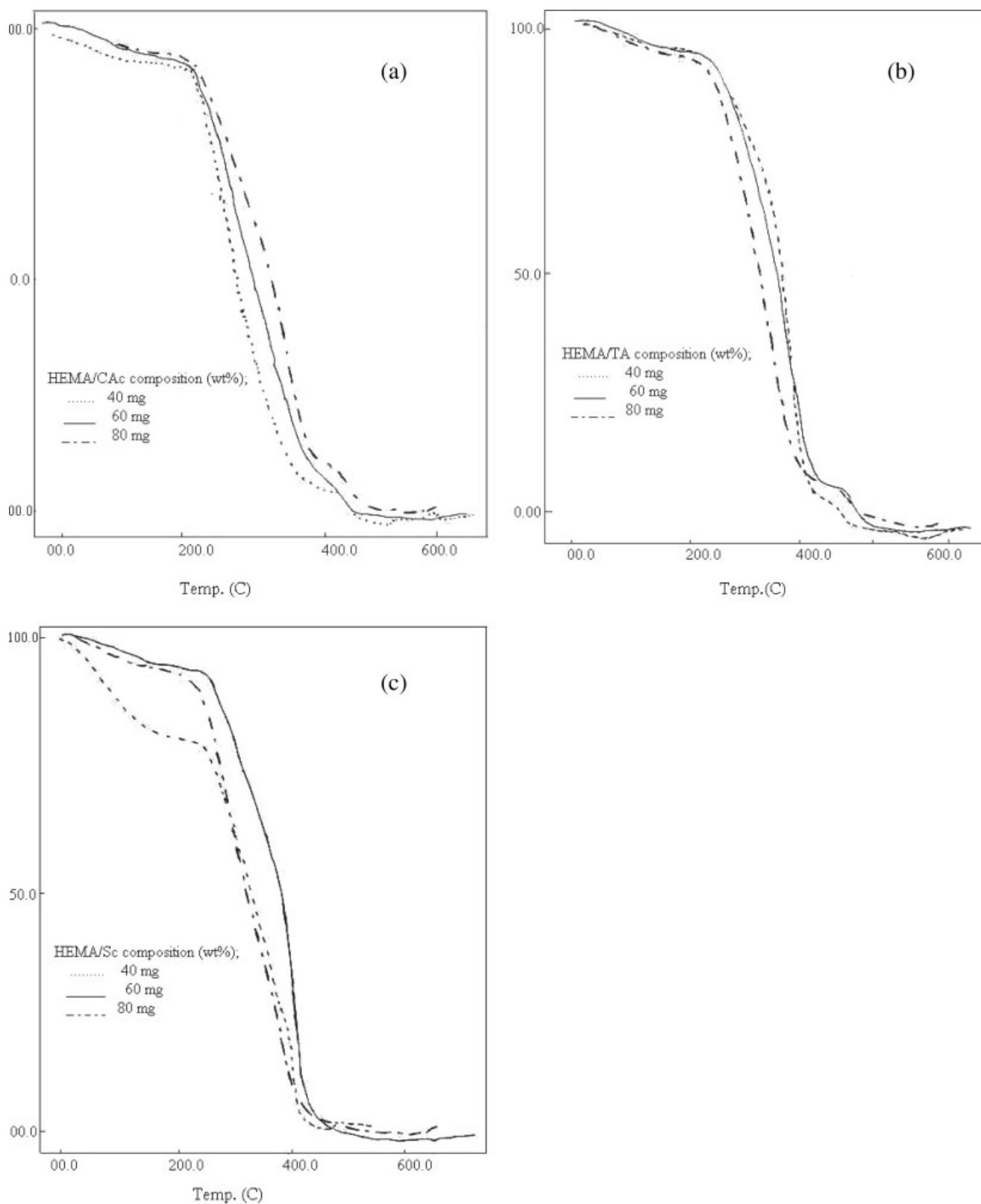
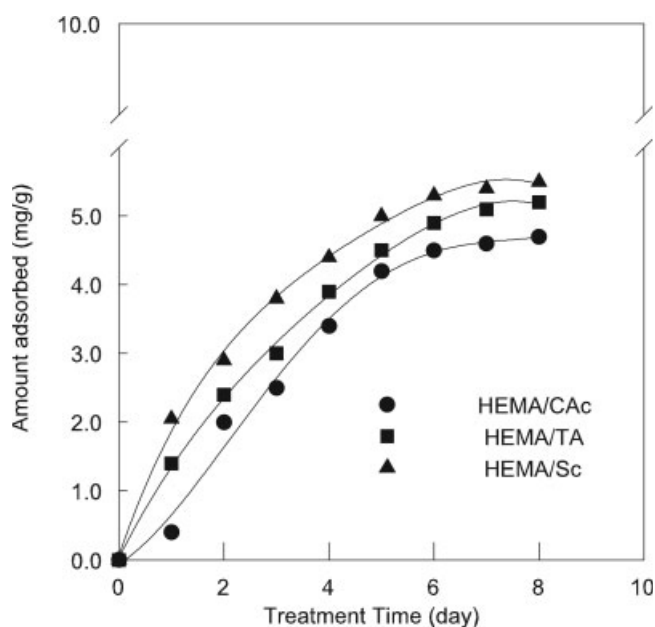**Figure 17** TGA thermograms for different hydrogel composition; (a) HEMA/CAc, (b) HEMA/TA, (c) HEMA/Sc.

the polymer network first swells but, because of the neutralization of electric charge by metal ion binding to the carboxylate anions, it quickly deswells.

A theory for the elucidation of the swelling mechanism of ionic hydrogels identified three forces acting on the ionic hydrogels: the rubber elasticity, the
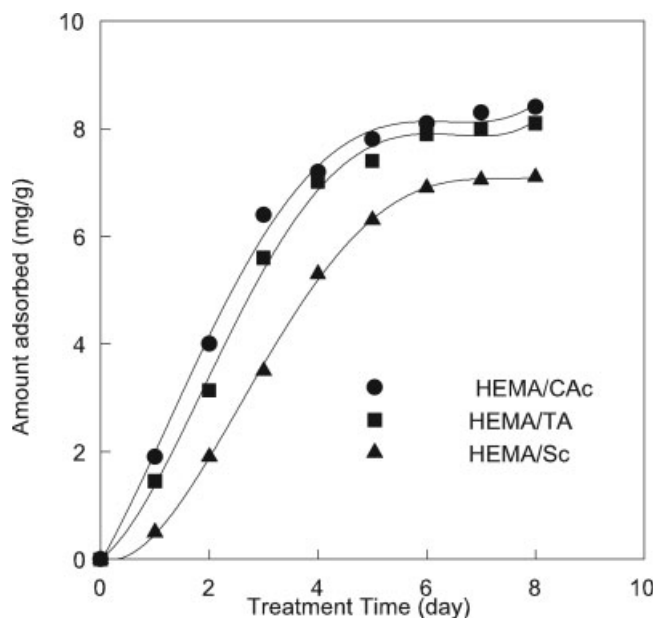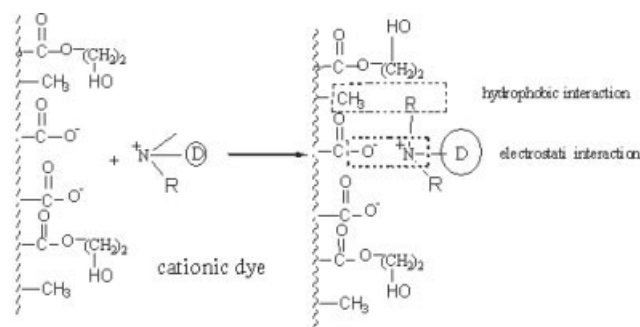
Figure 18 Effect of treatment time on the Maxilon C.I. Basic Dye uptake for different hydrogels, initial feed concentration = 100 mg/L.
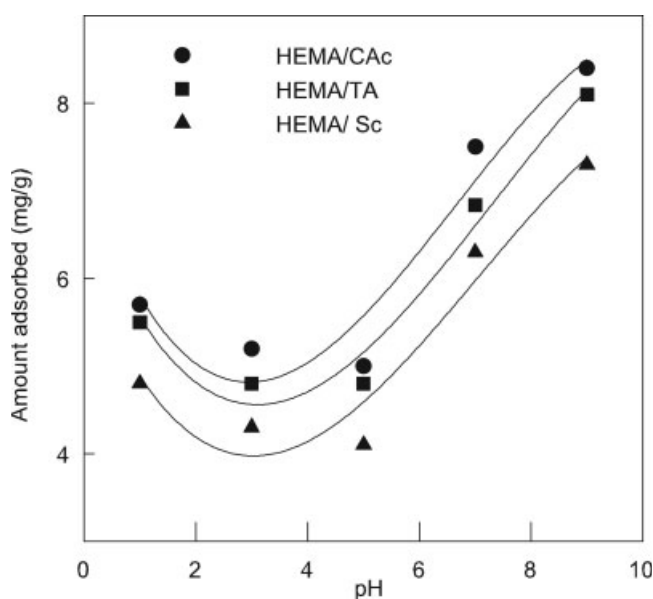

HEMA/TA hydrogel

Scheme 2 Possible complexation process between HEMA/TA hydrogel and dye molecule.

interaction force between polymer strands and solvent, and the dissociated ion pressure. The latter has been recognized as the determining factor in the swelling degree of ionic hydrogels.[16] They called the sum of these forces the osmotic pressure of the hydrogel, and concluded that hydrogels adjust their volume so that the osmotic pressure becomes zero.

According to their interpretation, the decrease of water absorption capacity in electrolyte solutions is considered to be due to the decrease in osmotic pressure difference between the inside and the outside of the hydrogel. All investigated hydrogels have —COOH groups fixed on the hydrogel network as functional groups; so they can be substantial like weak acid type cation exchange resins. When it is immersed in electrolyte solutions, ion exchange takes place during the swelling.

In the metal ion/hydrogel system, metal ion has a cationic character and can interact by electrostatic forces with the anionic carboxyl groups of acid in the hydrogel. Possible interactions between metal

Figure 19 Effect of treatment time on the Acid fast yellow G dye uptake for different hydrogels, initial feed concentration = 100 mg/L.

Figure 20 Effect of pH on the Maxilon C.I. Basic dye uptake for different hydrogels, initial feed concentration = 100 mg/L.
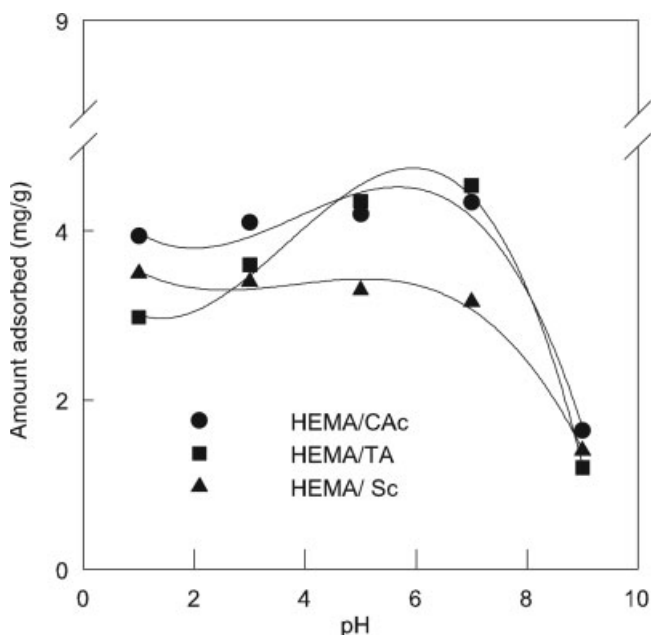
Figure 21 Effect of pH on the Acid fast yellow G dye uptake for different hydrogels, initial feed concentration = 100 mg/L.
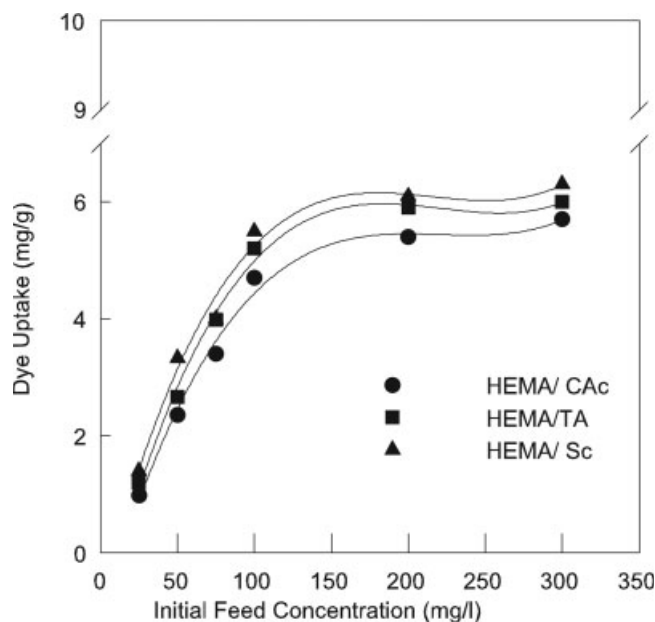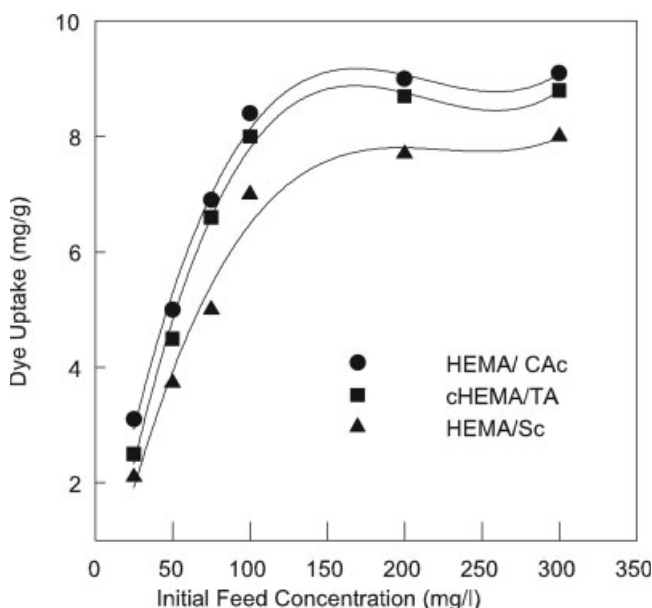

Figure 23 Effect of initial concentration on the Acid fast yellow G dye for different hydrogels, time = 6 days.

ion and acidic groups can be designated as follows (Scheme 3):

Capacity of hydrogels and maximum uptake of different metals

The maximum metal uptake of different metals by ionic hydrogels is plotted in schematic diagrams and

shown in Figure 26. Studying the sorption capacity of the sorbent toward various metal ions is carried out by equilibrating a fixed amount of the sorbent with different metal ion solutions of 1000 ppm concentration for 5 h. The metal uptake is expressed in mmole/g. The HEMA/TA hydrogel shows good

Figure 22 Effect of initial concentration on the Maxilon C.I. Basic dye for different hydrogels, time = 6 days.
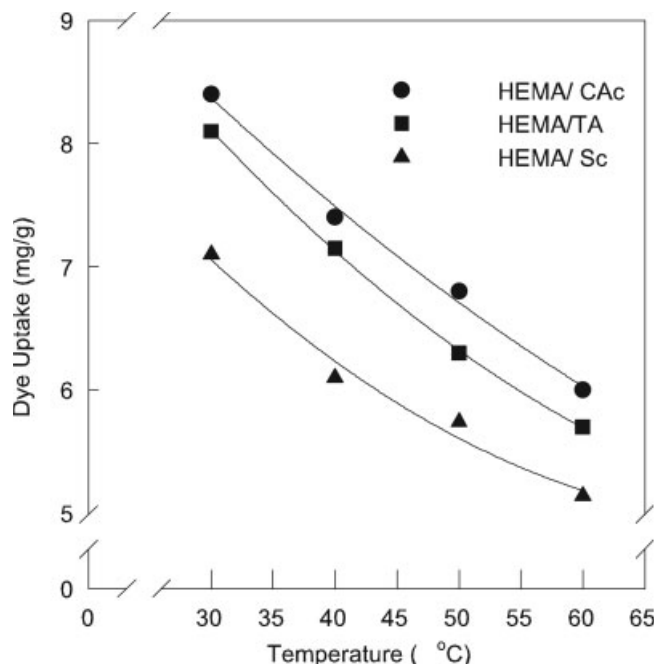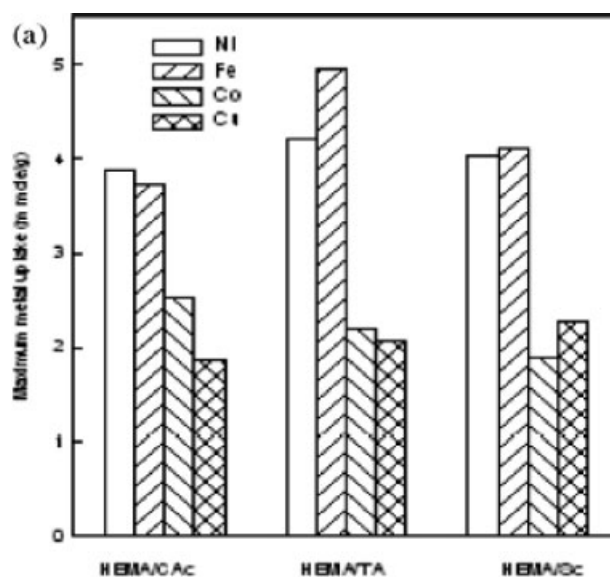

Figure 24 Effect of temperature on the Maxilon C.I. Basic dye uptake for different hydrogels; initial concentration = 100 ppm.
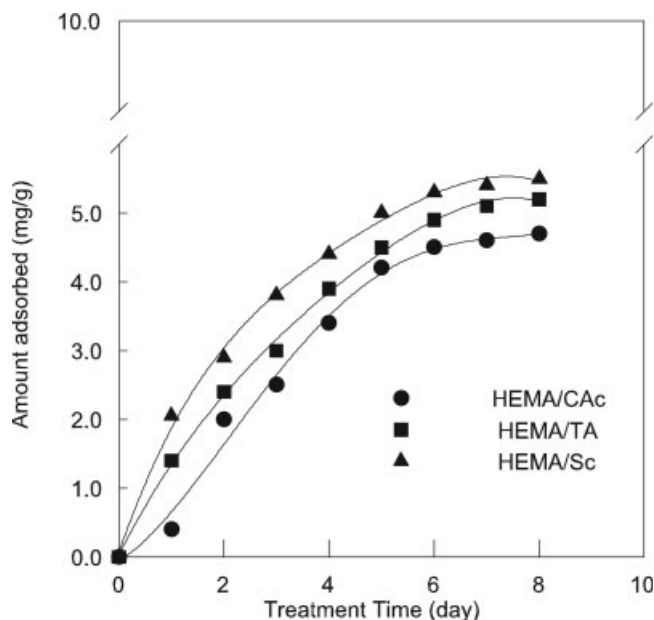
Figure 25 Effect of temperature on the Acid fast yellow G dye uptake for different hydrogels; initial concentration = 100 ppm.

Figure 26 Schematic diagram for the maximum uptake of different metals by different hydrogel.

affinity toward the adsorption of different metals investigated here. The chemisorption capacities of the sorbents toward Fe(III), Ni(II), Cu(II), and Co(II) is found to be different with various chelating groups. For HEMA/TA hydrogel, the sorption of Fe(III) and Ni(II) ions is higher than other metals. However, in the case of HEMA/CAc, the sorption of Co(II) is higher than other metals under investigation. Meanwhile, for HEMA/Sc, the chemisorption of Cu(II) is higher than other metals. The aforementioned results can be explained according to the ligand-type and the structure of chelate. From the diagrams, it is obvious that all the hydrogels have a great affinity toward Fe(III) than other metals. These results can be explained by considering the valence of metals. The trivalent Fe(III) forms a more stable

and strong complex with functional groups of the hydrogels.

Effect of initial concentration of metals in the feed solution

Figures 27–29 show the metal uptake as a function of initial feed concentration for different metals using the prepared hydrogels. It can be seen that, increasing in concentration of metal ions results in increasing the mount of metal uptake. These results revealed that the chelating sites of the sorbent become saturated when the concentration of the feed solution reaches 1000 ppm, above which no more metal ion uptake occurred.

The weakness of the adsorbent–adsorbate forces will cause the uptake at low concentrations to be small but once a molecule has become adsorbed, the
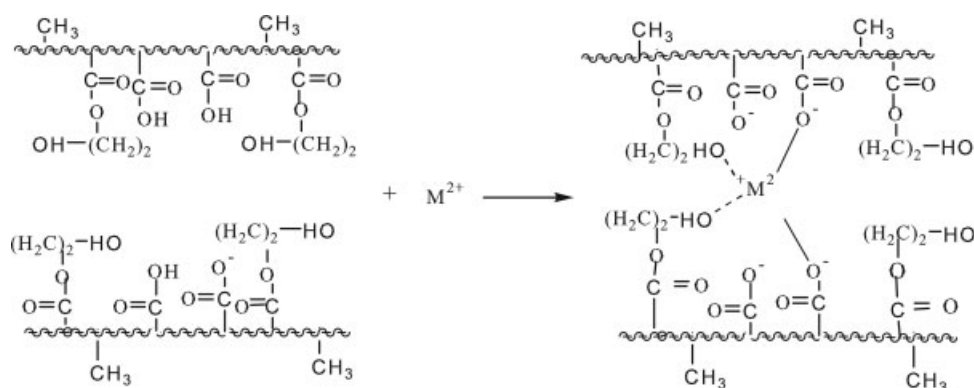
Scheme 3 Possible electrostatic interaction between metal ions and HEMA/TA hydrogel.
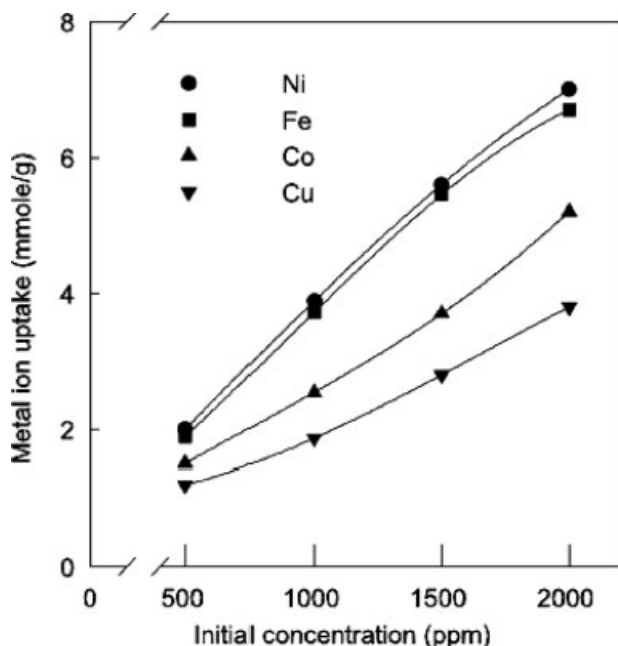
Figure 27 Effect of initial concentration on metal uptake for HEMA/CAc hydrogel, swelling time = 5 h, pH = 5.

adsorbate–adsorbate forces will promote the adsorption of further molecules. The adsorption of either nonpolar molecules or polar molecules always provided that the adsorbent–adsorbate force is relatively weak. A polar adsorbate of particular interest in this context is water, because the dispersion contribution to its overall interaction energy is unusually small compared with the polar contribution. The hydrogel
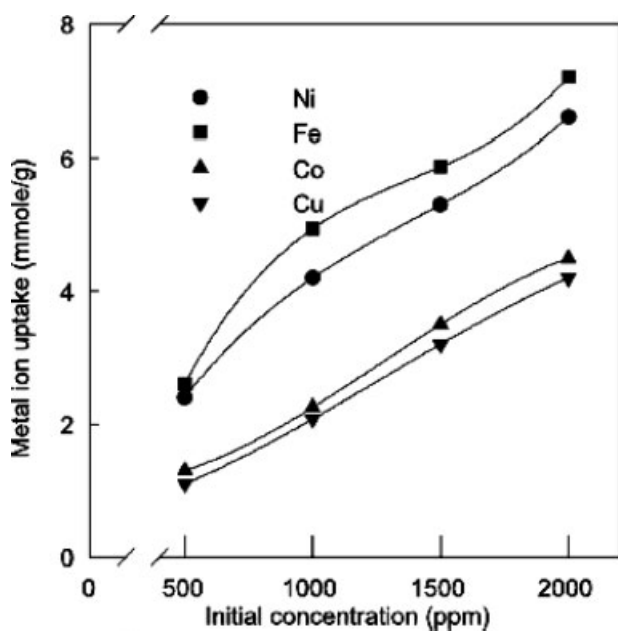

Figure 28 Effect of initial concentration on metal uptake for HEMA/TA hydrogel, swelling time = 5 h, pH = 5.
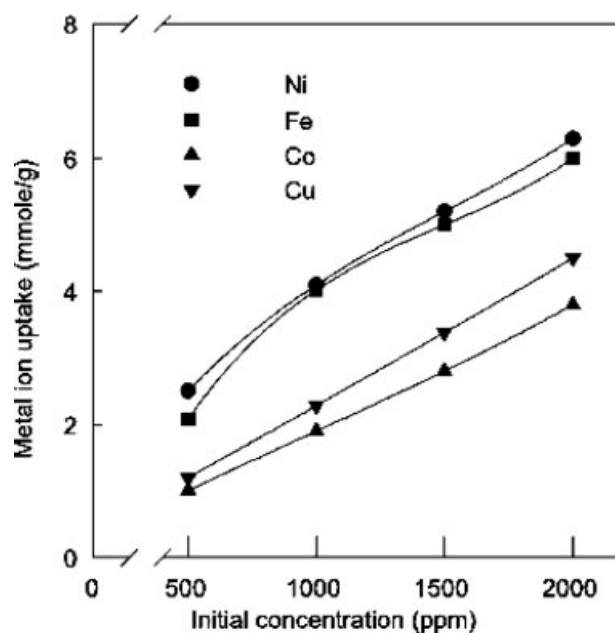

Figure 29 Effect of initial concentration on metal uptake for HEMA/Sc hydrogel, swelling time = 5 h, pH = 5.

is covered with a layer of adsorbed water; however, the adsorbent–adsorbate interaction would be virtually reduced to the weak dispersion energy of water with metals, multiple layers are built up on some parts of the surface while a monolayer is still incomplete on other parts.

Effect of pH of feed solution

Metal ion absorption is pH-dependent as governed by the carboxylic proton–metal ion exchange process. By increasing the pH of salt solutions, the ion swelling pressure will increase due to increasing production of free counter ions due to dissociation of —COOH groups on the hydrogel.

Experiments at pH 1.0 and 2.0 were carried out, but in this case metal absorption was not observed. At this pH, the equilibrium with the exchange ions yields low absorption of metals; ionization degree is very low and the resulting hydrogels are uncharged (entirely protonated) and shrink. The swelling is affected above pH 4.0, in relation with carboxylic acid dissociation. Increasing pH increases the hydrogel ionization and upper values of metal absorption are reached. Uptake of metal ions onto the investigated hydrogels are given in Figures 30–32.

Hydrogels swell at high pH values due to ionization and subsequent electrostatic repulsions of ionized groups, and shrink at low pH values with protonation.[17]

By lowering the initial pH of the solution, the amount of released hydrogen ions increases, and
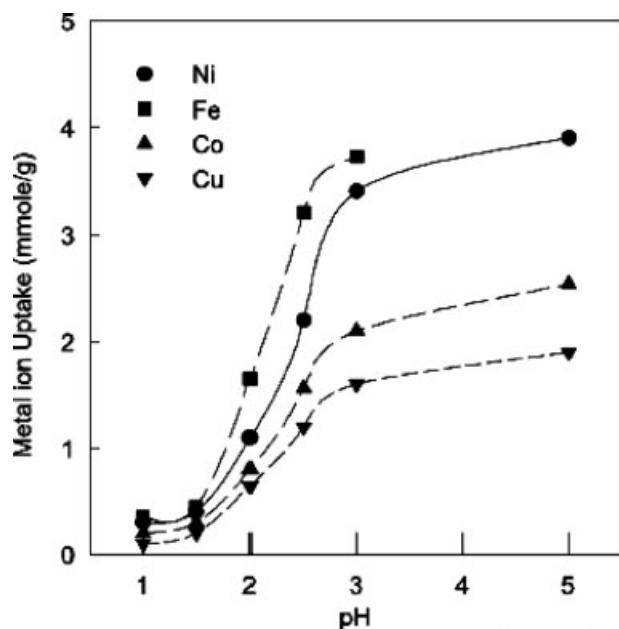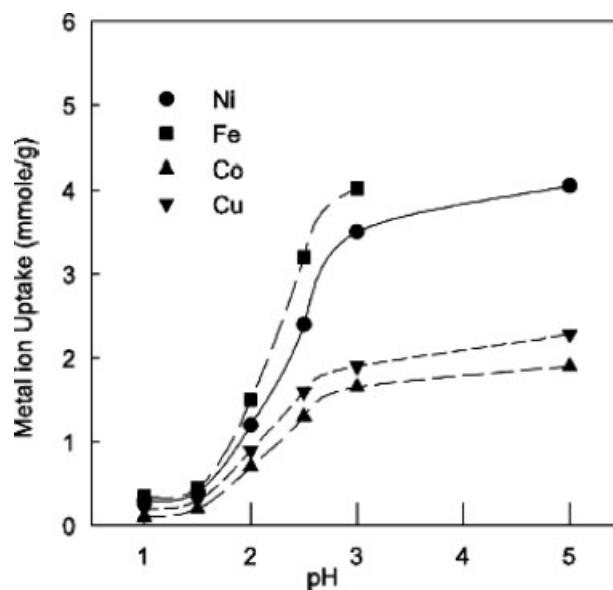
Figure 30 Effect of pH on the metal ion uptake for HEMA/CAc hydrogel at initial metal ion concentration of 1000 ppm, swelling time = 5 h.

hydrogel volume, normalized to the initial swollen volume, decreases. These results suggest that the —COOH groups fixed on the network were partially changed. Even if the salt concentration is sufficiently high, a decrease in pH in the outer solution, which is associated with the ion exchange, must be taken into account.
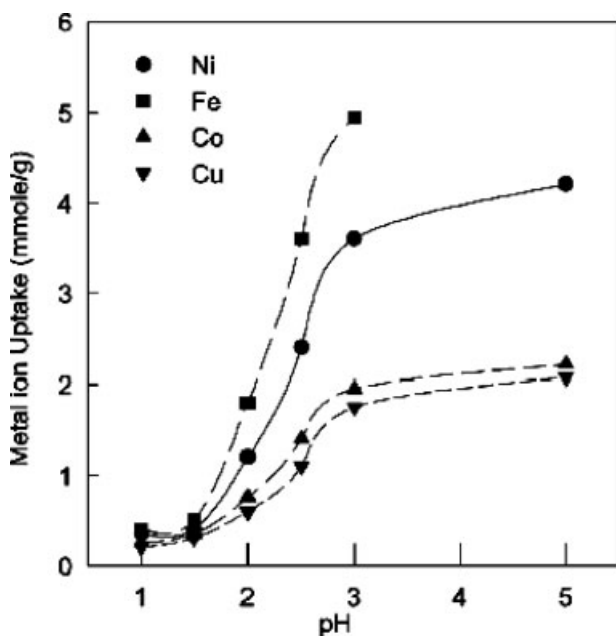
Figure 31 Effect of pH on the metal ion uptake for HEMA/TA hydrogel at initial metal ion concentration of 1000 ppm, swelling time = 5 h.

Figure 32 Effect of pH on the metal ion uptake for HEMA/Sc hydrogel at initial metal ion concentration of 1000 ppm, swelling time = 5 h.
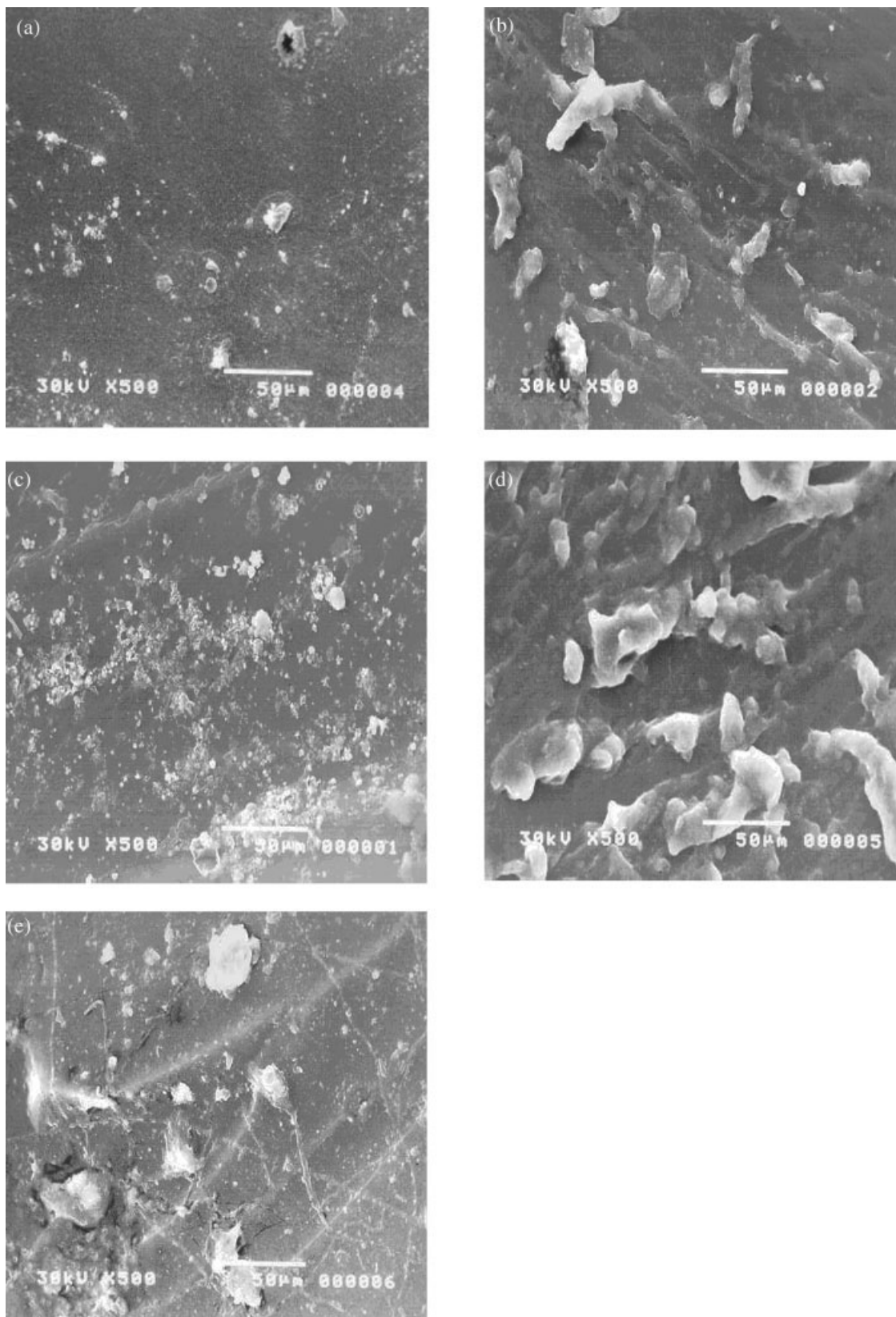
Scanning electron microscopy

Scanning electron micrographs of HEMA/CAc hydrogel before and after dyes and metals uptake are shown in Figure 33. It is shown that the surface of HEMA/CAc hydrogel before uptake is smooth, but the surface of hydrogel after uptake of dyes and metals becomes tough. The dyes and metals appearance as small white spots adsorbed on the hydrogel indicate the existence of dyes or metals by the hydrogel via adsorption process.

CONCLUSIONS

Hydrogels composed of HEMA and citric, tartaric, or succinic acid have been prepared by using γ-radiation. Some properties of importance of the gels were investigated as functions of the concentration of the acids and the irradiation dose. The gelation % increases with the irradiation dose, and decreases as the added acid amount rises. Equilibrium swelling becomes higher with increasing acid concentration, and lower with the increase of the irradiation dose. When the hydrophilic polymer (acids) varies in the content range of 40–80 mg, n decreases thereby indicating a shift in the water-transport mechanism from the non-Fickian-type to the Fickian-type. The prepared gels show good ability to uptake metal ions and dyes from aqueous solutions. Adsorption capacity of the investigated hydrogels was found dependent on the pH of the aqueous metal or dye solution.

Figure 33 Scanning electron micrographs (SEM) of HEMA/CAc copolymer hydrogel before and after uptake of metals and dyes. (a) HEMA/CAc hydrogel free; (b) Co; (c) Fe; (d) Maxilon C.I. Basic; (e) Isma acid fast yellow G.

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