

Swelling Characterization of Polyelectrolyte Poly(Hydroxamic Acid) Hydrogels in Aqueous Thiazin Dye Solutions

Erdener Karadağ

Adnan Menderes University, Fen-Edebiyat Faculty, Chemistry Department, Aydın, Turkey

Dursun Saraydın and Yasemin Çaldıran Işıkver

Cumhuriyet University, Chemistry Department, Sivas, Turkey

In this study, swelling behavior of polyelectrolyte poly(hydroxamic acid) (PHA) hydrogels have been investigated in aqueous thiazin dye solutions. PHA hydrogels were prepared by free radical polymerizations of acrylamide with some cross-linkers such as *N,N'*-methylenebisacrylamide (NBisA) and ethylene glycol dimethacrylate (EGDMA); then they were used in experiments on swelling and diffusion of some water-soluble cationic dyes such as methylene blue (MB), thionin (T), and toluidin blue (TB). Swelling experiments were performed in water at 25°C, gravimetrically. The equilibrium swelling percent (S%) values of PHA hydrogels were calculated as 238–2705%. Some swelling kinetic parameters such as initial swelling rate, swelling rate constant, and maximum (theoretical) swelling percent were found. Diffusional behavior of dye solutions was investigated. Dye diffusion into hydrogels was found to be non-Fickian in character. Diffusion exponent (*n*) is over 0.50. For sorption of thiazin cationic dyes, MB, T, and TB to PHA hydrogels were studied by batch sorption technique at 25°C. PHA hydrogels in the dye solutions showed the dark coloration. In the experiments of the adsorption, S-type adsorption in the Giles classification system was found.

Keywords Swelling; Poly(hydroxamic acid); Hydrogel; Dye sorption; Diffusion

INTRODUCTION

Hydrogels are three-dimensional networks of hydrophilic polymer chains in between liquids and solids. One of the most interesting features is their capability to swell and shrink, depending on their surroundings. Hydrogels are cross-linked macromolecules with segments of hydrophilic groups. Cross-linking the polymer chains forms a three-dimensional elastic polymer network. When such a network is in contact with water or an aqueous solution, it increases its volume by absorbing water and solutes. The process is called *swelling*^[1–5].

Polymeric gels (hydrogels) are the objects of intensive studies. Hydrogels have found widespread applications in bioengineering, biomedicine, food industry, and water purification and separation processes. The ability to absorb and to store much water and water solutions makes hydrogels unique materials for a variety of applications^[6–15]. Studies have been reported on the use of hydrogels or hydrophilic characteristic cross-linked polymers or copolymers as adsorbents for the removal of heavy metals, for the recovery of dyes, for removal of toxic or radioactive elements from various effluents, and for metal preconcentration for environmental sample analysis from aqueous solutions^[6–20]. Many methods have been proposed for the removal of dyes and other hazardous materials. Chemical precipitation, membrane extraction, coagulation, complexing, solvent extraction, ion change, and adsorption are some of the commonly used processes, but each has its own merits and demerits in its applications. Adsorption or ion exchange using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment processes for removing dyes from chemical process industries in certain developed countries^[21–23].

Synthetic dyes represent a relatively large group of organic chemicals, which are met in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on man. In order to minimize the possible damages to man and the environment arising from the production and applications of cationic dyes, several studies were made around the world. The potential toxicity of some cationic dyes has been known for many decades. Some cationic dyes have not been used because they are carcinogenic^[24]. The removal of color from textile waste is a major environmental problem because of the difficulty of treating such waters by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and

Address correspondence to Erdener Karadağ, Fax: +90 256 2135379; E-mail: ekaradag@adu.edu.tr

other municipal and agricultural purposes. Some polymeric cross-linked adsorbents were reported for the removal of acidic and basic dyes from aqueous solutions^[21–23].

A number of polymers containing acrylamide and some acidic group, or cross-linked hydrophilic polymers, have been prepared from various starting materials using different methods^[17–21,23,25–31]. The hydroxamic acid group is well known for its ability to form stable chelates with various heavy metal ions. Several workers attempted to the prepare poly(hydroxamic acid) resins from several polymers^[32–35]. The present paper is aimed to investigate the swelling properties of PHA hydrogels in water-soluble cationic thiazin dyes. Water-soluble thiazin dyes such as methylene blue (MB), thionin (T), and toluidin blue (TB) resemble the large molecular dyes found in wastewater.

EXPERIMENTAL

Preparation and characterization of acrylamide (AAm) and PHA superswelling hydrogels were reported in our previous study^[34]. Monovalent cationic thiazin dyes, methylene blue (MB), thionin (T), and toluidin blue (TB) were obtained from Merck (Darmstadt, Germany).

Equilibrium swelling experiments were used to investigate the swelling properties of the materials, which were prepared using the various preparation methods. To measure the parameters of diffusion and swelling, PHA hydrogels were accurately weighed and transferred into aqueous dye solutions of 20 mg L⁻¹ MB, T, and TB in a beaker. Solution uptake with respect to time was obtained by periodically removing a sample from the solution, quickly blot drying, and reweighing. The measurements were conducted at 25 ± 0.1 °C in a water bath.

The swelling percent (S%) of PHA hydrogel in aqueous cationic thiazin dye solutions of 20 mg L⁻¹ of MB, T, and TB were calculated from the following relation:

$$S\% = \frac{w_t - w_o}{w_o} \times 100 \quad (1)$$

where w_t is the mass of the swollen gel at time t , and w_o is the mass of the dry gel at time 0.

The synthetic aqueous solutions of monovalent cationic thiazin dyes were prepared in the following concentration range: 8–80 mg L⁻¹ for MB, T, and TB. Of the dry gel, 0.1 g were transferred into 50 mL of the synthetic aqueous solutions of the dyes and allowed the equilibrate for 48 hours at 25 °C. These aqueous dye solutions were separated by decantation from the superswelling hydrogels. Spectrophotometric measurements were carried out using a Shimadzu 160 model UV-VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at 598 nm for T, at 626 nm for TB^[36], and at 655 nm for MB^[37]. Distilled water was chosen as the reference. The equilibrium concentrations of the monovalent cationic

thiazin dye solutions were determined by means of precalibrated scales.

RESULTS AND DISCUSSION

Equilibrium Swelling Studies

Monovalent cationic dye molecules in aqueous solutions intake of initially dry hydrogels were followed for a period of time, gravimetrically. Swelling isotherms of PHA hydrogels were constructed, and representative swelling curves are shown in Figure 1. The figure shows that swelling increases with time up to certain level, then levels off. This value of swelling may be called the *equilibrium swelling percent* ($S_{eq}\%$). $S_{eq}\%$ of PHA hydrogels is used for the calculation of swelling characterization parameters. $S_{eq}\%$ of PHA hydrogels is given in Table 1. Table 1 shows that the values of $S_{eq}\%$ are 230–253% for poly(hydroxamic acid) hydrogels cross-linked by NBisA (PHA/N) and 2289–2705% for poly(hydroxamic acid) hydrogels cross-linked by EGDMA (PHA/E). Hydrophilicity of PHA/E copolymers becomes greater than that of PHA/N, so the swelling of PHA copolymers is greater than the swelling of acrylamide hydrogels. The more hydrophilic the groups in the PHA/E get, the more the hydrogels of the PHA/N swell.

Diffusion

The following equation is used to determine the nature of diffusion of penetrate into hydrogels:

$$F = k t^n \quad (2)$$

where F is the fractional uptake at time t ; k is a constant incorporating characteristics of the macromolecular network system and the penetrate; and n is the diffusion exponent, which is indicative of the transport mechanism.

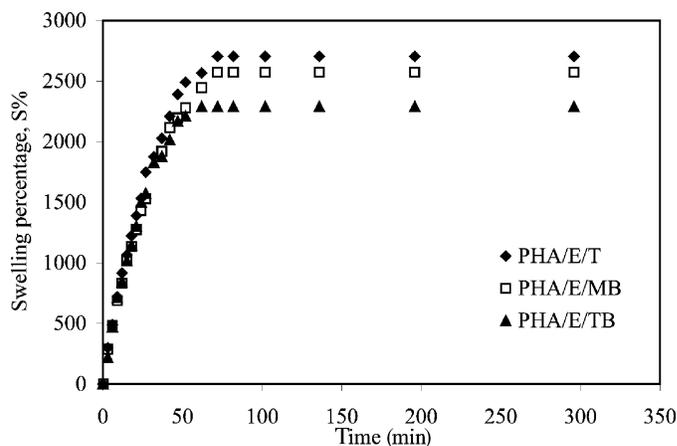


FIG. 1. Swelling isotherms of PHA/E hydrogels in aqueous dye solutions.

TABLE 1
Some swelling parameters of PHA hydrogel systems

Dyes	S_{eq} %	n	$k \times 10^2$	$K_{0.5}$
EGDMA				
MB	2473	0.77	4.76	366.28
T	2705	0.80	4.50	421.76
TB	2289	1.02	3.27	370.27
NBisA				
MB	253	0.64	7.44	32.32
T	230	0.73	5.22	29.92
TB	238	0.57	9.50	29.72

Eq. (2) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1.0, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That are reflected by n between 1/2 and 1^[38].

For PHA hydrogels, $\ln F$ versus $\ln t$ graphs are plotted, and representative results are shown in Figure 2. Diffusion exponents (n) and diffusion constants (k) are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 1. Table 1 shows that the number determining the type of diffusion (n) is over 0.50. They are between 0.57–1.02. Hence, the diffusion of dye solutions into the PHA hydrogels is found to have a non-Fickian character^[38,39]. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately. Diffusion constants of PHA hydrogels are between 3.27×10^{-2} – 9.50×10^{-2} . There is no good relation between the values of diffusion constants of PHA hydrogels.

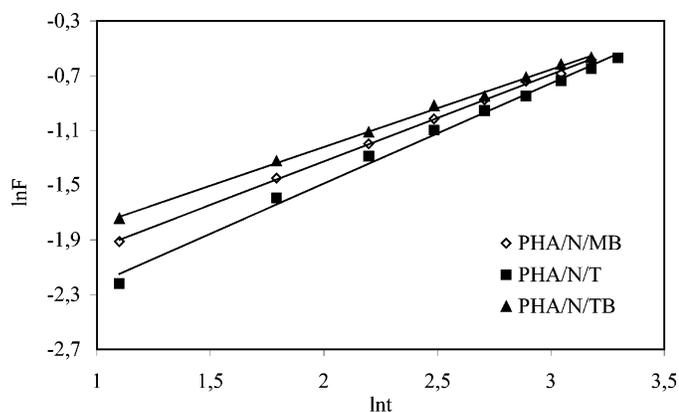


FIG. 2. Plots of $\ln F$ vs $\ln t$ for PHA/N hydrogels in thiazin dye solutions.

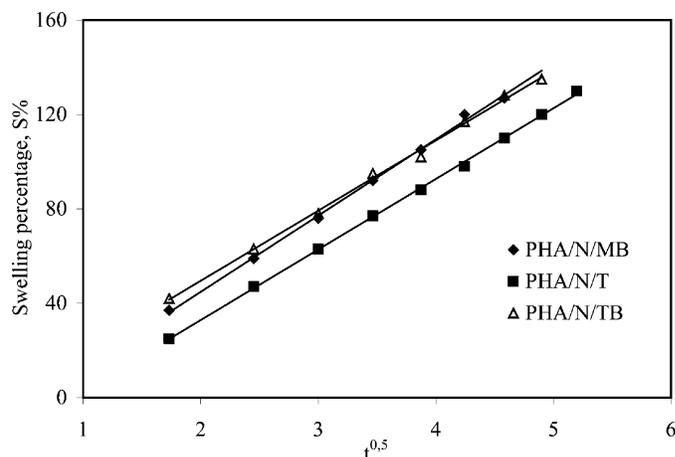


FIG. 3. Plots of swelling rate for PHA/N hydrogels in thiazin dye solutions.

Swelling Rate Coefficients

Swelling characteristics, particularly the rate of aqueous swelling or water and aqueous solutions uptake was followed by some methods.

Figure 3 shows the equilibrium swelling percent, $S\%$, for the PHA hydrogels versus the square root of immersion time for the first 60% of the fractional uptake^[40]. Excellent linear correlations were observed. Linear slopes of all PHA hydrogel systems swelling behaviors in Figure 3 were assumed to represent relative swelling rate coefficients ($K_{0.5}$). The swelling rate coefficients are tabulated in Table 1. Swelling rate coefficients of PHA/E hydrogels are bigger than PHA/N hydrogels. The swelling process of the PHA/E hydrogels is quicker than the swelling rate of the PHA/N hydrogels. Furthermore, it can be said that PHA/E hydrogels swell very good from PHA/N hydrogels.

Swelling Kinetics

In order to examine the controlling mechanism of the swelling processes, several kinetic models are used to test experimental data. The large number and array of different chemical groups on the polymeric chains (e.g., amine, amide, carbonyl, carboxyl or hydroxyl) imply that there are many types of polymer-solvent interactions. Any kinetics are likely to be global. From a system-design viewpoint, a lumped analysis of swelling rates is thus sufficient to the practical operation.

A simple kinetic analysis is a second-order equation in the form of

$$\frac{dS}{dt} = k_{2,S}(S_{eq} - S)^2 \quad (3)$$

where $k_{2,S}$ is the rate constant of swelling, and S_{eq} (or $S_{eq}\%$) denotes the swelling percent at equilibrium. After

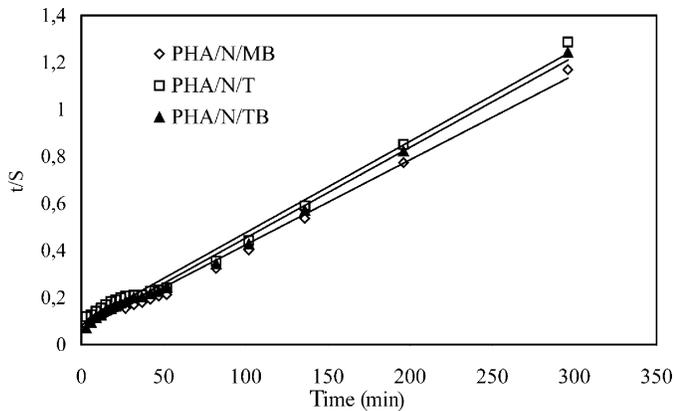


FIG. 4. Swelling kinetics curves of PHA/N hydrogels in thiazin dye solutions.

definite integration by applying the initial conditions $S = 0$ at $t = 0$ and $S = S$ at $t = t$, Eq. (3) becomes

$$\frac{t}{S} = A + Bt \quad (4)$$

where A is reciprocal of initial swelling rate r_0 or $1/k_{2,S}S_{eq}^2$ and B is inverse of the degree of swelling at equilibrium^[41].

To test the kinetics model, t/S versus t graphs are plotted, and representative graphs are illustrated in Figure 4. The calculated kinetic parameters are tabulated in Table 2. As can be seen from Table 2, the kinetics model is in agreement with swelling experiments, since $S_{eq}\%$ (theoretical) or $S_{eq}\%_{max}$ is changed only, with cross-linker type.

Binding Characterization

To observe the dye sorption, PHA hydrogels were placed in aqueous solutions of MB, T, and TB, and all dye solutions showed the (dark) coloration. In the sorption

system at equilibrium, the total solute (dye solutions) concentration; C_0 is

$$C_0 = C_b + C \quad (5)$$

where C_b is the equilibrium concentration of the dye solutions on the sorbent per liter solution (bound solute concentration) and C is the equilibrium concentration of the solute in the solution (free solute concentration). The value of the bound concentration may be obtained by using Eq. (5). For a fixed free solute concentration, C_b is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio, r , defined by

$$r = \frac{C_b}{P}. \quad (6)$$

Thus, with C_b in mol liter, and P is base mol (moles of monomer units) per liter solute represents the average number of molecules of solute bound to each monomer unit at that free solute concentration^[42]. To determine the binding properties of thiazin dyes into PHA hydrogels, a plot of the binding ratio (r) against the free concentration of dye solutions is shown in Figure 5 for PHA/N hydrogels as representative binding isotherms. Sorption of thiazin dyes, MB, T, and TB within PHA hydrogels corresponds to S-type sorption isotherms in the Giles classification system for sorption of the dyes from its solution^[43].

There can be some reasons for noncovalent interactions in the binding of dye molecules by PHA hydrogels. The main interactions between the hydrogel and dyes may be hydrogen bonding. Specifically, hydrogen bonding will be expected to occur between dye molecules and sulfur and between nitrogen atoms and carbonyl groups on the repeating monomeric unit of the cross-linked polymer.

TABLE 2
Swelling kinetics parameters of PHA hydrogel systems

Dyes	EGDMA	NBisA
Initial swelling rate, r_0 , (dS/dt) ₀		
MB	136.70	15.79
T	150.21	11.52
TB	157.26	14.96
Swelling rate constant, $k \times 10^4$		
MB	16.54	2.06
T	16.57	1.74
TB	25.11	2.23
The maximum (theoretical) swelling percent, $S\%_{max}$		
MB	2874	276
T	3010	256
TB	2502	258

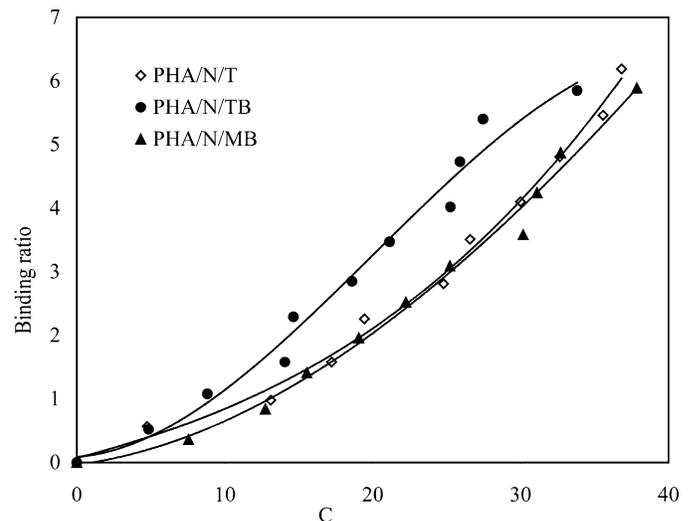


FIG. 5. Binding isotherms of PHA/N hydrogels in thiazin dye solutions.

The results of sorption swelling studies are parallel to the results of swelling studies. The ionic charge content in the polymeric structure is important. The swelling degree of the hydrogels increases due to an increase of the hydrophilic units on hydrogel structure^[34]. Therefore, PHA hydrogels have many ionic groups that can increase interaction between the dye molecules and anionic groups of hydrogels. So, it can be seen that swelling or the sorption capability of PHA hydrogels is increased. The most important effect is hydrophilicity of copolymeric gels.

CONCLUSION

The present work has given the quantitative information on the swelling and binding characteristic of some monovalent cationic thiazin dyes such as methylene blue (MB), thionin (T), and toluidin blue (TB) with PHA hydrogels. Some swelling parameters have been calculated. The values of equilibrium swelling percentage, S_{eq} %, are 238–253% for poly(hydroxamic acid) hydrogels cross-linked by NBisA (PHA/N) and are 2289–2705% for poly(hydroxamic acid) hydrogels cross-linked by EGDMA (PHA/E). The diffusion exponents (n) are over 0.50. They are between 0.57 and 1.02. So, diffusion type of dye solutions into PHA hydrogels has been found as non-Fickian in character.

PHA hydrogels have sorbed the monovalent thiazin cationic dyes. An S-type sorption isotherm in the Giles classification system was found.

At the end of this study, it can be said that PHA hydrogels shows good swelling characteristics with aqueous dye solutions. On the other hand, PHA hydrogels may be used as a sorbent for removal of some agents (such as organic molecules) and dye molecules. The utilization of these types of hydrogels in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization, and enrichment of some species makes hydrogel more popular.

REFERENCES

- Omidian, H.; Rocca, J.G.; Park, K. Advanced in superporous hydrogels. *J. Controlled Release* **2005**, *102*, 3–12.
- Fernandez, E.; Lopez, D.; Lopez-Cabarcos, E.; Mijangos, C. Viscoelastic and swelling properties of glucose oxidase loaded polyacrylamide hydrogels and the evaluation of their properties as glucose sensors. *Polymer* **2005**, *46*, 2211–2217.
- Gupta, P.; Vermani, K.; Garg, S. Hydrogels: From controlled release to pH-responsive drug delivery. *Drug Discovery Today* **2002**, *7* (10), 569–579.
- Evmenenko, G.; Alexev, V.; Budtova, T.; Buyanov, A.; Frenkel, S. Swelling-induced changes of polyelectrolyte gels. *Polymer* **1999**, *40*, 2975–2979.
- Byrne, M.E.; Park, K.; Peppas, N.A. Molecular imprinting within hydrogels. *Adv. Drug Delivery Rev.* **2002**, *54*, 149–161.
- Crini, G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **2005**, *30*, 38–70.
- Gombotz, R.W.; Hoffmann, A.S. Immobilization of Biomolecules and Cells on and within Synthetic Polymeric Hydrogels. In: *Hydrogels in Medicine and Pharmacy*, Vol. 5, Peppas, N.A., Ed., Fundamentals, CRC Press: Florida, 1986.
- Peppas, N.A.; Mikos, A.G. Preparation Methods and Structure of Hydrogels. In: *Hydrogels in Medicine and Pharmacy*, Vol. 1, Peppas, N.A., Ed., Fundamentals, CRC Press: Florida, 1986.
- Güven, O.; Şen, M.; Karadağ, E.; Saraydın, D. A review on the radiation synthesis of copolymeric hydrogels for adsorption and separation purposes. *Radiat. Phys. Chem.* **1996**, *56*, 381–386.
- Denizli, A.; Say, R.; Garipcan, B.; Patir, S. Methacryloylamidoglutamic acid functionalized poly(2-hydroxy methacrylate) beads for UO_2^{2+} removal. *Reactive & Functional Polymers* **2004**, *58*, 123–130.
- Zhang, A.; Asakura, T.; Uchiyama, G. The adsorption mechanism of uranium(VI) from seawater on a macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group. *Reactive & Functional Polymers* **2003**, *57*, 67–76.
- Şahiner, N.; Pekel, N.; Güven, O. Radiation synthesis of *N*-vinyl-2-pyrrolidone/acrylonitrile interpenetrating polymer networks and their use in uranium recovery from aqueous systems. *Radiat. Phys. Chem.* **1998**, *52* (1–6), 271–276.
- Kioussis, D.R.; Wheaton, F.W.; Kofinas, P. Reactive nitrogen and phosphorus removal from aquaculture wastewater effluents using polymer hydrogels. *Aquaculture Engineering* **2000**, *23*, 315–332.
- Kara, A.; Uzun, L.; Beşirli, N.; Denizli, A. Poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) beads for heavy metal removal. *J. Hazard. Mater.* **2004**, *106B*, 93–99.
- El-Hag Ali, A.; Shawky, H.A.; Abd El Rehim, H.A.; Hegazy, E.A. Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution. *Eur. Polym. J.* **2003**, *39*, 2337–2344.
- Rifi, E.H.; Rastegar, F.; Brunette, J.P. Uptake of cesium, strontium and europium by a poly(sodium acrylate-acrylic acid) hydrogel. *Talanta* **1995**, *42* (6), 811–816.
- Karadağ, E.; Saraydın, D.; Güven, O. Behaviors of acrylamide/itaconic acid hydrogels in uptake of uranyl ions from aqueous solution. *Sep. Sci. & Technol.* **1995**, *30* (20), 3747–3760.
- Saraydın, D.; Karadağ, E.; Güven, O. Adsorption of some heavy metal ions in aqueous solutions onto acrylamide-maleic acid hydrogels. *Sep. Sci. & Technol.* **1995**, *30* (17), 3287–3298.
- Manju, G.N.; Anoop-Krishnan, K.; Vinod, V.B.; Anirudhan, T.S. An investigation into the sorption of heavy metal from wastewaters by polyacrylamide-grafted iron(III) oxide. *J. Hazard. Mater.* **2002**, *B91*, 221–238.
- Li, W.; Zhao, H.; Teasdale, P.R.; John, R.; Zhang, S. Synthesis and characterisation of a polyacrylamide-polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd. *Reactive & Functional Polymers* **2002**, *52*, 31–41.
- Karadağ, E.; Üzümlü, Ö.B.; Saraydın, D. Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels. *Eur. Polym. J.* **2002**, *38*, 2133–2141.
- Ekici, S.; Işıtkver, Y.; Şahiner, N.; Saraydın, D. Adsorption of some textile dyes onto crosslinked poly(*N*-vinylpyrrolidone). *Adsorption, Science and Technology* **2003**, *21* (7), 651–659.
- Şolpan, D.; Duran, S.; Saraydın, D.; Güven, O. Adsorption of methyl violet in aqueous solutions by poly(acrylamide-co-acrylic acid) hydrogels. *Radiat. Phys. Chem.* **2003**, *66* (2), 117–127.
- Zollinger, H. *Color Chemistry*, 2nd Ed., VCH, Verlagsgesellschaft mbH, Weinheim, Germany, 1991.
- Durmaz, S.; Okay, O. Phase separation during the formation of poly(acrylamide) hydrogels. *Polymer* **2002**, *41*, 5729–5735.
- Hennink, W.E.; van Nostrum, C.F. Novel crosslinking methods to design hydrogels. *Adv. Drug Delivery Rev.* **2002**, *54*, 3–36.

27. Saraydin, D.; Karadağ, E.; Işıkver, Y.; Şahiner, N.; Güven, O. The influence of preparation methods on the swelling and network properties of acrylamide hydrogels with crosslinkers. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2004**, *441* (4), 421–433.
28. Karada, E.; Saraydin, D. Swelling studies of super water retainer acrylamide/crotonic acid hydrogels crosslinked by trimethylolpropane triacrylate and 1,4-butanediol dimethacrylate. *Polym. Bull.* **2002**, *48*, 299–307.
29. Karada, E.; Saraydin, D. Swelling of superabsorbent acrylamide/sodium acrylate hydrogels prepared using multifunctional crosslinkers. *Turk. J. Chem.* **2002**, *26*, 863–875.
30. Tanaka, T. *Gels. Sci. Am.* **1981**, *224* (1), 110–123.
31. Yao, Ke-J.; Zhou, Wen-J. Synthesis and water absorbency of the copolymer of acrylamide with anionic monomers. *J. Appl. Polym. Sci.* **1999**, *53*, 1533–1538.
32. Maekawa, E.; Koshijima, T. Preparation of hydroxamic acid derivative and its metal complexes derived from cellulose. *J. Appl. Polym. Sci.* **1990**, *40*, 1601–1613.
33. Domb, A.J.; Cravalho, E.G. The synthesis of poly(hydroxamic acid) from poly(acrylamide). *J. Appl. Polym. Sci.* **1988**, *26*, 2623–2630.
34. Işıkver, Y.; Saraydin, D.; Şahiner, N. Poly(hydroxamic acid) hydrogels from poly(acrylamide): Preparation and characterization. *Polym. Bull.* **2001**, *47*, 71–79.
35. Saraydin, D.; Işıkver, Y.; Şahiner, N. Uranyl ion binding properties of poly(hydroxamic acid) hydrogels. *Polym. Bull.* **2001**, *47*, 81–89.
36. Karadağ, E.; Saraydin, D.; Güven, O. Interaction of some cationic dyes with acrylamide/itaconic acid hydrogels. *J. Appl. Polym. Sci.* **1996**, *61*, 2367–2372.
37. Saraydin, D.; Karadağ, E.; Güven, O. Adsorption of some basic dyes by acrylamide/maleic acid hydrogels. *Separ. Sci. Technol.* **1996**, *31* (3), 423–434.
38. Peppas, N.A.; Franson, N.M. The swelling interface number as a criterion for prediction of diffusional solute release mechanisms in swellable polymers. *J. Polym. Sci.* **1983**, *21*, 983–997.
39. Am Ende, M.T.; Peppas, N.A. Transport of ionizable drugs and proteins in crosslinked poly(acrylic acid) and poly(acrylic acid-co-2-hydroxyethyl methacrylate) hydrogels. II. Diffusion and release studies. *J. Controlled Release* **1997**, *48*, 47–56.
40. Uruzizaki, F.; Yamaguchi, H.; Nakamura, K.; Numajiri, S.; Sugibayashi, K.; Morimoto, Y. Swelling and mechanical properties of poly(vinyl alcohol) hydrogels. *Int. J. Pharm.* **1990**, *58*, 135–142.
41. Peniche, C.; Cohen, M.E.; Vazquez, B.; Roman, J.S. Water sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copolymers. *Polymer* **1997**, *38*, 5977–5982.
42. Molyneux, P.; Vekavakayanondha, S. The interaction of aromatic compounds with poly(vinylpyrrolidone) in aqueous solution. *J. Chem. Soc. Faraday Trans. L.* **1986**, *82*, 291–317.
43. Giles, C.H.; Smith, D.; Huitson, A. A general treatment and classification of the solute adsorption isotherm. I Theoretical. *J. Colloid Interface Sci.* **1974**, *47* (3), 755–765.