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Poly(hydroxamic acid) hydrogels from poly(acrylamide): preparation and characterization

Yasemin Isikver[1], **Dursun Saraydin** [1] (✉), **Nurettin Sahiner**[2]

[1]Cumhuriyet University, Department of Chemistry, Hydrogel Research Laboratory,
58140 Sivas, Turkey
e-mail: saraydin@cumhuriyet.edu.tr
[2] Hacettepe University, Department of Chemistry, 06532 Beytepe/Ankara, Turkey

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Summary

Poly(hydroxamic acid) (PHA) hydrogels from crosslinked poly(acrylamide) (PAAm) hydrogels containing different type crosslinkers such as such as N, N'-methylene bisacrylamide (N) and ethyleneglycol dimethacrylate (E). The effect of crosslinkers on some physical properties was investigated. The structure of hydrogels was characterized spectroscopically and thermally. The swelling parameters of PHA in distilled water, such as percent equilibrium swelling (S_{eq}%), initial swelling rate (r_o), maximum equilibrium swelling (S_{max}), diffusional exponent (n), network parameter (k) and diffusion coefficient (D) were calculated. It has been found that the ionogenity of PHA and the structure of the used crosslinkers during the synthesis have been effective on the swelling behaviour of the hydrogels.

Introduction

Ion exchange resins having chelating functional groups have long been of interest for removal of specific metal ions from water. By appropriate selection of functional groups, resins have been designed to complex with a variety of transition, alkaline earth, and alkali metals. Many of these resins bind several metal ions and thus are somewhat limited in their selectivity [1].

The hydroxamic acid group is well known for its ability to form a stable chelates with various heavy metal ions. A number of chelating polymers, containing hydroxamic acid group, have been prepared from various starting materials using different methods. Several workers attempted to the prepare poly(hydroxamic acid) resins from poly(acrylonitrile), polymethylacrylate, polyethyl acrylate, chloro-methylated styrene, poly(4-vinyl-2'-carboxy benzophenon), poly(acrylonitrile-co-4 vinyl pyridine) cellulose and starch [2-8]. However, there has not been encountered with the preparation of PHA from PAAm hydrogel in the aqueous medium in the literature.

In our previous studies, radiation induced acrylamide based hydrogels were prepared for adsorption and separation purpose [9-11]. Here, in this study poly(hydroxamic acid) hydrogels (PHA) from poly(acrylamide) (PAAm) hydrogels [12] crosslinked with N, N' methylenebis acrylamide (N) or ethyleneglycol dimethacrylate (E) were prepared and characterized for the purpose of metal ion adsorption. The influences of the ionogenity of the hydrogels and the nature of the used crosslinkers on the some physicochemical properties of the obtained hydrogels were examined. N and E type hydrophilic crosslinkers were chosen due to their semiflexible and flexible nature, respectively.

Experimental

Acrylamide (Merck, Darmstadt, Germany) as monomer, N, N' methylenebisacrylamide and ethyleneglycol dimethacrylate (Sigma, St. Louis, US) as crosslinkers, ammonium persulfate (Merck, Darmstadt, Germany) as initiator, N, N, N', N'-tetramethylethylene diamine (Sigma, St. Louis, US) as catalyst, hydroxylamine hydrochloride and sodium hydroxide (Sigma, St. Louis, US) as modifiers were analytical reagent-grade and used as received.

An aqueous solution of acrylamide containing N or E (95:5 in the mole ratio in 0.4 mol water) with 0.01 mmol ammonium persulfate and 2.5 mmol N, N, N', N'-tetramethylethylene diamine (TEMED) were mixed and placed in PVC straws of 3 mm diameter. PAAm hydrogels having hydrophilic crosslinkers were prepared in a thermostated water bath at +4 °C. A gel formed after 20 min of reaction. After 24 h, the hydrogel rods were cut into pieces of 3-4 mm length and washed with distilled water and dried in air and vacuum, and stored. The polymers were named as N-0 and E-0 for N and E, respectively.

For the preparation of H-form of PHA a solution of hydroxylamine hydrochloride (3 M, 100 mL) was added to 20 g crosslinked PAAm in 300 mL distilled water. The resulting mixture was stirred for 2 hours at ambient temperature. The hydrogels were washed with distilled water and dried in air and vacuum, and stored. The polymers were named as N-1 and E-1, respectively.

A solution of NaOH (7.5 M 50 mL) was added to 20 g H-form of PHA in 300 mL distilled water and stirred for 24 h to prepare Na-form of PHA. The polymers were named as N-2 and E-2, respectively.

Hydrogen and sodium capacity were done according to references 13 and 14. For hydrogen capacity, the swollen PHA (0.2 g) was shaken with 50 mL of 0.25 M NaOH solution for 6 h. Determination of the NaOH concentration was done by titrating with 0.25 M hydrochloric acid. Hydrogen capacity of the hydrogel was calculated from the amount of sodium hydroxide reacted with PHA hydrogel. For sodium capacity, the swollen PHA hydrogel (0.25 g) was shaken with 50 mL of 0.125 M sodium bicarbonate solution for 12 h, then the resin was filtered and washed thoroughly with distilled water. The total filtrate was acidified with 50 mL 0.125 M hydrochloric acid, boiled to expel carbon dioxide, and back-titrated with 0.125 M sodium hydroxide. Sodium capacity of the hydrogel was calculated from the amount of sodium bicarbonate reacted with the polymer.

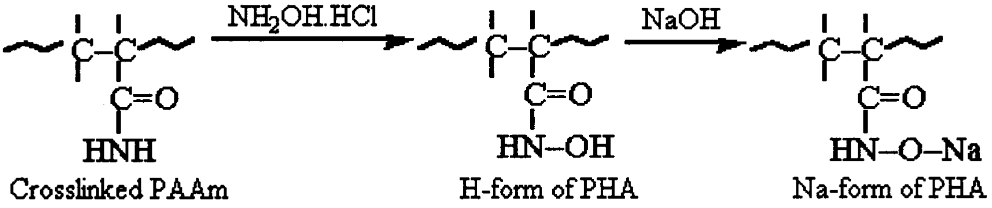
IR spectra of the polymers were taken with Mattson 1000 model Fourier Transform Infrared Spectrophotometer. The thermal characterization was performed by using a Dupont 9900 model thermal analyzer (DSC).

The swelling of gels is done by immersion in doubly distilled water at 25±0.1 °C in the water bath. The absorbed amount of water is determined by weighing the samples, after wiping, at various time intervals. The radii of cylindrical gels were measured by a micrometer.

Results and Discussion

Preparation

In this study, PHA gels were prepared from the reaction of the corresponding crosslinked poly(acrylamide) with hydroxylamine, and hydroxylamine with sodium hydroxide. A schematic presentation of possible reaction between acrylamide gel and hydroxylamine, and between acrylamide gel and hydroxylamine with sodium hydroxide are shown in Scheme 1.



Scheme 1 The chemical modifications of crosslinked poly(acrylamide)

H-forms of crosslinked PHA polymers were formed at the end of the first reaction and Na-forms of crosslinked PHA gels were obtained with the second reaction 2.

Hydrogen ion capacity, a measure of acidic group (hydroxamic and carboxylic) content on the polymers while the sodium-hydrogen exchange from sodium bicarbonate solution is a measure of the carboxylic acid groups by hydrolysis of the amide groups. Ion exchange capacities of poly(hydroxamic acid) hydrogels were calculated and, are summarized Table 1.

Table 1 shows that N-1 and N-2 contain 3.77 and 4.67 mmol g^{-1} hydroxamic groups, and 3.13 mmol g^{-1} carboxylic acid groups with 6.39 and 5.49 mmol g^{-1} unreacted amide groups, respectively, while E-1 and E-2 contain 5.34 and 7.24 mmol g^{-1} hydroxamic groups, and 4.06 mmol g^{-1} carboxylic acid groups with 3.51 and 1.61 mmol g^{-1} unreacted amide groups, respectively. Unreacted amide groups amount of N type hydrogels are higher than unreacted amide groups amount of E type hydrogels. In addition to its more hydrophilic nature, E type crosslinker is flexible while N type crosslinker is semiflexible. Consequently, the chains of E-type crosslinker used hydrogels are more mobile for conversion of amide groups to hydroxamic groups than N type crosslinker used hydrogels.

Characterization

On the addition of a solution of iron (III) or vanadium (V) to the hydrogels having hydroxamic acid groups (14), the colors of hydrogels turns from transparent to bright red-violet. The prepared hydrogels were transferred into a solution of iron (III) or vanadium (V). The polymers of N-1, N-2, E-1 and E-2 were showed the bright red-violet coloration, while N-0 and E-0 hydrogels have not shown any coloration. The formation of coloured polymer complexes shows that the polymers of N-1, N-2, E-1 and E-2 contain hydroxamic acid functional groups.

Table 1 Ion exchange capacities of PHA polymers

Hydrogel	Hydrogen capacity / mmol g $^{-1}$ (carboxylic and hydroxamic acid)	Sodium capacity/mmol g $^{-1}$ (carboxylic acid)	Hydroxamic acid / mmol g $^{-1}$
N-1	6.9	3.13	3.77
N-2	7.8	3.13	4.67
E-1	9.4	4.06	5.34
E-2	11.3	4.06	7.24

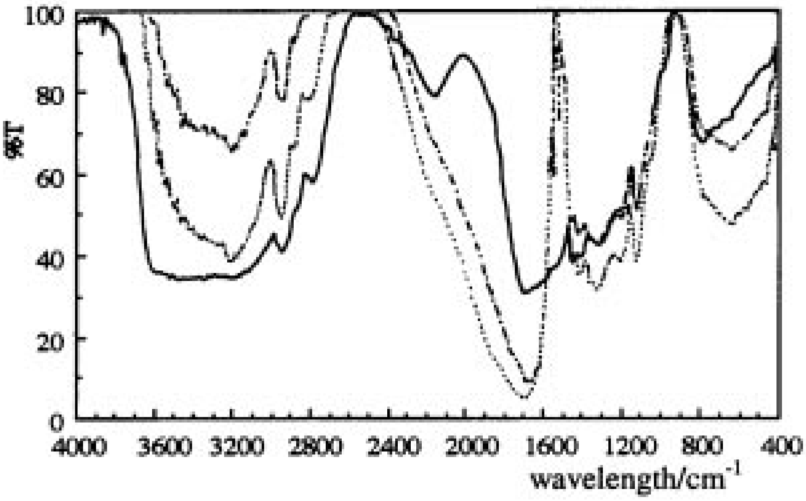


Fig. 1a FTIR spectra of the polymers having N, ——; N-0, –·–; N-1, ···; N-2

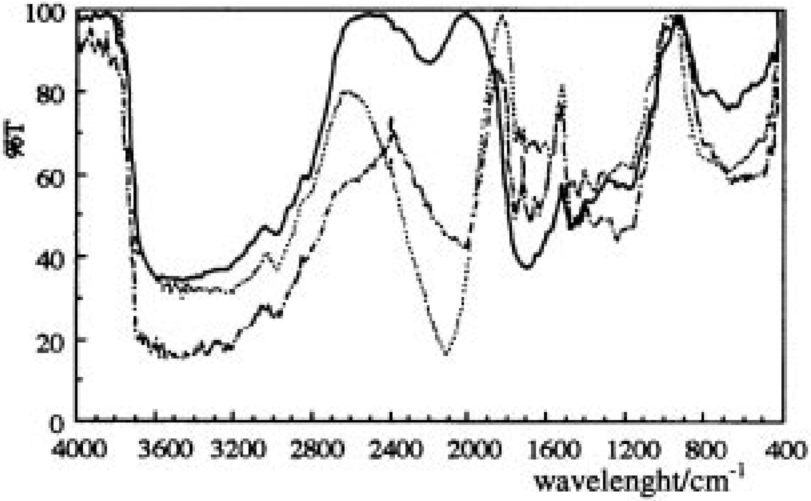


Fig. 1b FTIR spectra of the polymers having E, ——; E-0, –·–; E-1, ···; E-2.

Fig. 1a-b shows the typical FTIR spectra of the polymers. In crosslinked poly(acrylamide), the absorption of carbonyl groups is observed at around 1700 cm^{-1}.

However, for the hydroxamic acid derivatives, the absorption of hydroxamic acid type carbonyl groups is observed at 1680 cm^{-1} [4,7,15]. The peak at 1523 cm^{-1} is related to the deformations in amide groups. In E-1 and E-2 hydrogels, the absorption peaks in the region of 2008 and 2850 cm^{-1} are related to C=N groups in the enol form of hydroxamic acid. Thus it can be said that, poly(hydroxamic acid) hydrogels were obtained by the chemical it can be said that, poly(hydroxamic acid) hydrogels were obtained by the chemical modifications of modifications of the crosslinked poly(acrylamide) with hydroxylamine hydrochloride or hydroxylamine hydrochloride and sodium hydroxide.

DSC thermograms of the hydrogels shown in Fig. 2 were obtained after keeping hydrogels for two weeks in a vacuum oven until constant weights have achieved. T_g of the polymers of N-0 and E-0 are 106 and 120 °C, while T_g of N-1 and N-2 are 92 and 89 °C and, T_g of E-1 is 133 °C (for E-2, DSC thermogram has not obtained). It is seen that T_g of E-0 hydrogel is higher than N-0. The carboxyl groups in the chemical structure of E can cause to this increase at the glass transition temperatures of PAAm. For N type hydrogels, T_g of N-0 is higher than T_g values of H- and Na - form of PHA derivatives. The reason of this decrease of T_g can be due to the plasticizer effect of hydroxamic acid groups in these polymers. On the other hand, T_g of E-0 is lower than T_g of E-1. The interactions of carboxyl groups in E and hydroxyl group of hydroxamic acid in E-1 have caused to this increase of T_g.

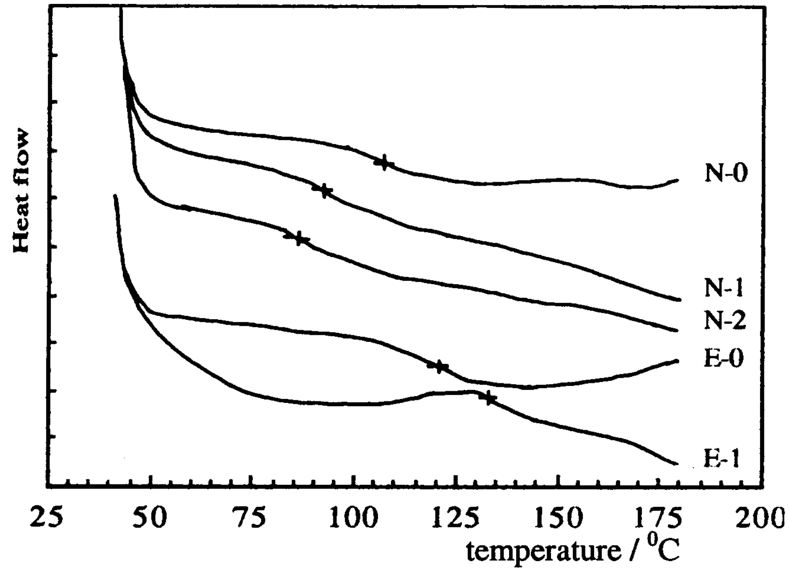


Fig. 2 DSC thermograms of the crosslinked polymers

Swelling and diffusion

The swelling S% is calculated from the following relation

$$S\% = \frac{m_t - m_0}{m_0} x100$$

Where m_o is the mass of dry gel at time 0, m_t is the mass of swollen gel at time *t*. [16, 17].

The water intakes of initially dry polymers were followed for a period of time. Swelling curves of the hydrogels were plotted and, the curves are shown in Fig. 3a. The polymers can be defined as a hydrogel, because they swell higher than 20% of their mass.

The hydrogels show similar swelling behavior in all cases. The swelling curves are similar in shape but differ in size and position. If Fig. 3a is investigated, it is shown that swelling is increased by time, but then it levels off. This value may be named equilibrium swelling (S_{eq}%). These S_{eq}% values are given Table 2.

Table 2 shows that the values of S_{eq}% of the polymers having N are changed among 160-335%, while the values of S_{eq}% of the hydrogels having E are changed among 755%-2150%. The number of hydrophilic groups of E is higher than N, so, the swelling of the polymers having E is higher than swelling of the polymers having N. The swelling degrees of the polymers were increased in following order; Na-form of PHA>H-form of PHA>PAAm.

Since type-2 is the sodium salt form of hydroxamic acid, it is the most ionogenic form of all other types. Thus, type-1 (poly(hydroxamic acid)) contains as only as the ionizing degree of PHA while polyacrylamide has non-ionogenic groups. It is evident that, the more the ionogenic content of a hydrogel the more the swelling degree gets.

For extensive swelling of polymers, it can be written following relation [18];

$$\frac{t}{S} = A + B\,t \qquad (2)$$

here $B=1/S_{max}$ is the inverse of the maximum or equilibrium swelling, $A=1/(dS/dt)_o$ or the reciprocal of the initial swelling rate of a gel (r_o). The relation represents second order kinetics.

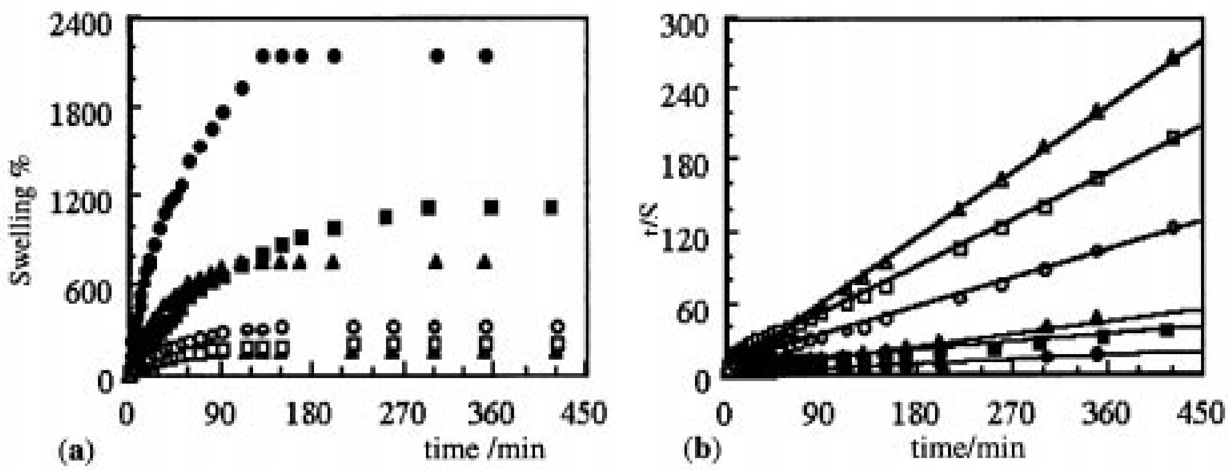


Fig. 3 (a)Time depending swelling and (b) swelling rate curves of the crosslinked polymers, ◊; N-0, □; N-1, ○; N-2, ▲; E-0, ■; E-1, ●; E-2

Fig. 3b shows the linear regression of the representative swelling curves obtained by means of eq. 2. The values of r_o [g water (g gel)$^{-1}$ min^{-1}] and S_{max} [g water (g gel^{-1})] were calculated from the slope and intersection of the lines and, are presented in Tab2.

Table 2 shows that the values of S_{max} of the polymers are parallel with respect to the results of swelling of the gels. Swelling processes of the polymers having E is quicker than the swelling rate of the hydrogels having N in distilled water. These results are in accordance with conversion of PAAm hydrogels to PHA hydrogels. Thus, E type PAAm conversion amount to PHA is higher than that of N type PAAm hydrogels.

The following equation was used to determine the nature of diffusion of water into hydrogels

$$F = kt^{n} \tag{3}$$

where F is the fractional uptake at time t. k is a constant incorporating characteristic of the macromolecular network system and the penetrant and *n* is the diffusional exponent, which is indicative of the transport mechanism. Equation 3 is valid for the first 60% of the fractional water uptake. Fickian diffusion and Case II transport are defined by n equal to 1/2 and 1, respectively. Anomalous transport behaviour (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected by anomalous behaviour defined by values of *n* between 1/2 and 1 [16, 19].

For the polymers, ln F *vs*. ln t graphs is plotted and representative results are shown in Fig. 4a. n exponents and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 2.

Table 2 shows the number determining type of diffusion (n) is over 0.50. Hence the diffusion of water into the hydrogels is generally taken as a *non-Fickian* character [20]. When diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

Table 2 Swelling and diffusion parameters of the hydrogels in distilled water

Polymer	S_{eq} %	r_o x10^2	S_{max}	n	k x10^3	Dx10^7
N-0	160	23.6	1.62	0.56	9.4	31.4
N-1	210	7.5	2.32	0.57	9.1	8.5
N-2	335	11.0	3.75	0.59	8.3	13.8
E-0	755	31.3	8.43	0.68	8.7	32.7
E-1	1125	12.5	14.89	0.87	2.2	10.4
E-2	2150	61.5	24.98	0.69	21.1	37.5

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. The short time approximation method is used for calculation of diffusion coefficients of the hydrogels [21]. The diffusion coefficients of the cylindrical hydrogels were calculated from the following relations:

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} \tag{4}$$

Where *D* in cm^2 s^{-1}, t in second and r is the radius of cylindrical polymer sample. A graphical comparation of equations (3) and (4) shows the semi-empirical equation (3) with n=0.5 and $k = 4\,(D / \pi r^2)^{1/2}$. For the hydrogels, F versus √t plots is plotted and representative results are shown in Fig. 4b. The diffusion coefficients were calculated

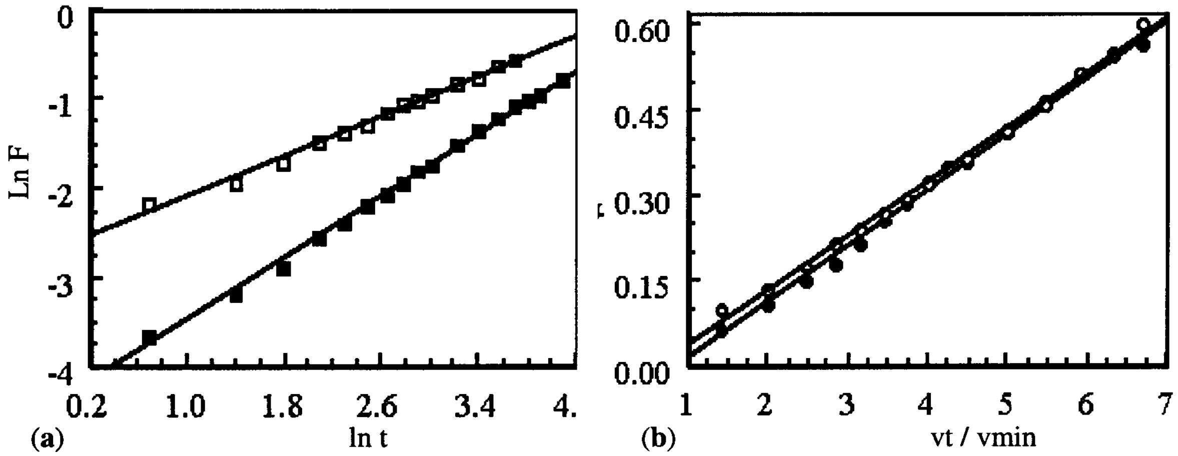


Fig. 4 (a) Plots of ln F vs. ln t and (b) F vs. vt of PHA hydrogels, □; N-1; ■ E-1.○; N-2,●; E-2.

from the slope of the lines and, are listed in Table 2. Table 2 shows that the values of the diffusion coefficient of the hydrogels vary from 8.5x10^{-7} cm^2 s^{-1} to 37.5x10^{-7} cm^2 s^{-1}.

Binding of heavy metal ions and dyes onto PHA

To observe uptake of the some heavy metal ions such as UO_2^{2+}, Cu^{2+}, Ni2+, Co^{2+}, Cr^{3+} and dyes such as cationic azin, thiazin, oxazin and triphenyl arin dyes, PHA hydrogels were placed in the aqueous solutions of the heavy metal ions and dyes and allowed to equilibrated for two days. At the end of this time, H- and Na-forms of PHA hydrogels in the solutions showed the dark coloration of the original solutions, but PAAm do not show any coloration.

Conclusion

It has been that a neutral polymeric hydrogels such as PAAm can be converted to an ionic poly(hydroxamic acid) hydrogels. The ionogenity of a hydrogel together with the nature of crosslinker have a great effect on swelling degree of hydrogels in the water. It is possible to check the swelling ratio of a hydrogel by controlling the amount of ionogenic groups on the network. To impart metal ion adsorption property it has also proven that hydrogels can be modified for recovery and enrichment purposes of some metal ions. There are many studies for the adsorption of metal ions with hydroxamic acid functional groups containing polymer and/or copolymers, yet this study is interesting in the aspect of the first time used modified hydrogels which was originally can not be used as an adsorbent alone itself.

As a result, it was shown that the PHA hydrogels could be used as a sorbent, metal chelator or ion exchanger for the heavy metal ions or the dyes and so immobilization of some of the contaminants in the hydrogels give rise to cleaning of waste water which is one of the most important problems of environmental chemistry.

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