

# The Usability of (Sodium Alginate/Acrylamide) Semi-Interpenetrating Polymer Networks on Removal of Some Textile Dyes

Dilek Şolpan, Murat Torun, Olgun Güven

Department of Chemistry, Hacettepe University, 06800 Beytepe/Ankara-Turkey

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**ABSTRACT:** In this study, (sodium alginate/acrylamide) interpenetrating polymer networks ((NaAlg/AAm)IPN) have been prepared at definite composition. The aqueous solution of 3% (w/v) sodium alginate and 50% (w/v) acrylamide was irradiated with  $^{60}\text{Co}$ - $\gamma$  rays at a dose rate of 0.07 kGy/h up to 5 kGy. The percent conversion was determined gravimetrically and 100% gelation was achieved at 5 kGy dose. To understand whether the semi-interpenetrating polymer network of sodium alginate is performed, Fourier Transform Infrared (FTIR) spectra of polyacrylamide (PAAm), sodium alginate, and the semi-interpenetrating polymer network were recorded. It is found that the FTIR spectra of PAAm, NaAlg, and the semi-interpenetrating polymer network are different. The thermograms of PAAm, sodium alginate, and the semi-interpenetrating polymer network were recorded for investigating their thermal character. (NaAlg/AAm)IPN hydrogels were immersed to swell in a solution of pH 7, at a temperature of 25°C. The swelling results at pH 7.0 indicated that (NaAlg/AAm)IPN hydrogel, containing 3% NaAlg showed maximum % swelling in water but swelling increased in the order of water > Magenta > Methylene Blue > Safranine-O > Methyl Violet. Diffusion of water and

aqueous solution of dyes within (NaAlg/AAm)IPN hydrogels was found to be of Fickian character at the initial stage of swelling with regard to values calculated for diffusion coefficient of (NaAlg/AAm)IPN hydrogels in water and aqueous solution of dyes. Some diffusion parameters were calculated from swelling of (NaAlg/AAm)IPN in water and dyes and their adsorption isotherms were plotted. In the adsorption experiments, the efficiency of (NaAlg/AAm)IPN hydrogels to adsorb Magenta, Safranine-O, Methylene Blue, and Methyl Violet dyes from water was studied. (NaAlg/AAm)IPN hydrogels showed different adsorption for different aqueous solution of dyes at pH 7.0. Adsorption isotherms were constructed for (NaAlg/AAm)IPN-dye systems. S type adsorption in the Giles classification system was found. Thermal and spectroscopic characterization of semi-interpenetrating polymer network of sodium alginate and acrylamide and dye adsorbed semi-interpenetrating polymer network of sodium alginate and acrylamide was recorded. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3787–3795, 2008

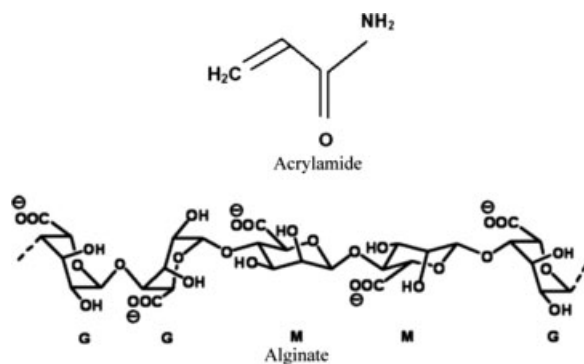
**Key words:**  $\gamma$ -irradiation; semi-interpenetrating polymer networks; adsorption; pollution of dyes in water

## INTRODUCTION

The pollution of natural waters in countries that have the developed textile industry is a great problem. The wastes of dyes give color to the water and are hazardous for human health. Adsorption method is widely used as other methods to remove textile dyes from natural waters. Activated carbon, chitin, chitosan, and some polymeric materials are used for this purpose. Polymeric materials have the superiority on other methods because of reusability. In recent times, some biopolymers such as alginate and chitosan are preferred for adsorption of cationic groups such as metals.<sup>1–3</sup> The semi-interpenetrating polymer network of sodium alginate and acrylamide

is synthesized with  $\gamma$ -irradiation to avoid dissolution of sodium alginate in water. The efficient removal of textile dyes from water is an important and widely studied research area. A technique which has been used is the use of (sodium alginate/acrylamide) interpenetrating polymer networks to remove the textile dyes from water. The (Sodium Alginate/Acrylamide) semi-interpenetrating polymer networks were prepared and were used for adsorption of Magenta, Safranine-O, Methylene Blue, and Methyl Violet. The alginate in the polymeric network supplies the adsorption and acrylamide increases the stability of the structure. The polymeric network was synthesized with  $\gamma$ -irradiation and the aroused crosslinks prevent the solubility of the structure in aqueous solutions. Interpenetrating polymer networks (IPNs) are composed of two or more polymer networks synthesized or crosslinked at the immediate presence of each other. Environmentally sensitive biocompatible hydrogels have been used to make IPNs.<sup>4</sup>

Correspondence to: D. Şolpan (solpan@hacettepe.edu.tr).



**Figure 1** Chemical formula of acrylamide and alginate.

## EXPERIMENTAL

### Materials

Medium viscosity sodium salt of alginic acid (NaAlg) (A-2023, Sigma Chemical Co., St Louis, MO), obtained from *Macrocystitis pyrifera* was used in all studies. The monomer used in this study, namely, acrylamide (AAm) was obtained from BDH (British, Drug House, Poole, Dorset, UK). Sodium phosphate, disodium hydrogen phosphate-2-hydrate, and phosphoric acid used to prepare phosphate buffer solutions were obtained from BDH. Magenta, Safranin-O, Methylene Blue, and Methyl Violet were supplied from Allied Chemical and was used without any further purification. Chemical formula of the used materials is given in Figure 1.

### Preparation of IPN hydrogels

The concentration of alginate solution was 3% (w/v) in 50% (w/v) acrylamide solution. These solutions were placed in polyvinylchloride straws of 3-mm diameter and irradiated in air at ambient temperature in a Gammacell 220 type  $\gamma$ -irradiator. Irradiation dose (5 kGy) was applied at a fixed dose rate of 0.07 kGy/h. IPN hydrogels obtained in long-cylindrical shapes were cut, washed with distilled water for removal of unreacted monomers (if any), and dried in air and in vacuum and stored for later evaluations. The percent conversion was determined gravimetrically. Hundred percent gelation was achieved for all mixtures at 5 kGy dose.

### Swelling studies

Dried IPN hydrogels were weighed. Then they were immersed to swell in a solution of desired pH 7, at a temperature of 25°C. Periodically, the IPN hydrogels were withdrawn from the solution and weighed after removing the excess surface water. This procedure was continued until the weights of IPN hydrogels reached a constant value. The percent swelling

of each IPN hydrogel was calculated from the following relation:

$$\% \text{ Swelling} = [(m_t - m_0)/m_0] \times 100 \quad (1)$$

where  $m_t$  is the mass of swollen IPN at time  $t$ , and  $m_0$  is the initial mass of dry IPN. Some parameters (diffusion characters, equilibrium water content, etc.) were calculated by using swelling data.

### Spectroscopic analysis

Fourier Transform Infrared (FTIR) spectra of the homopolymers, IPN hydrogels, dyes, and IPN hydrogels which contain dyes were recorded between 4000 and 400  $\text{cm}^{-1}$  on a Nicolet 520 FTIR spectrometer as KBr pellets. The IPN hydrogels were characterized by comparing the FTIR spectra of homopolymers and IPN hydrogel, Magenta, Safranin-O, Methylene Blue, Methyl Violet, and IPN-dye systems.

### Thermal analysis

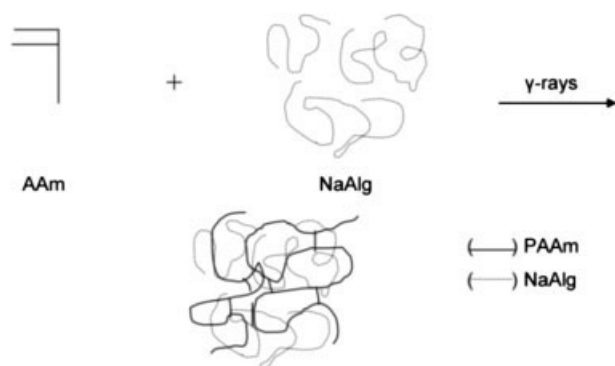
Schimadzu DTG-60H model thermogravimetric analyzer was used for determination of the thermal stabilities of homopolymers and IPN hydrogels. Samples weighing 5–10 mg were heated in dynamic nitrogen atmosphere from 20 to 800°C at a heating rate of 10°C  $\text{min}^{-1}$ .

### Adsorption studies

Effect of the initial concentration of Magenta, Safranin-O, Methylene Blue, and Methyl Violet on the adsorption rate and capacity were studied. Aqueous solutions of Magenta, Safranin-O, Methylene Blue, and Methyl Violet were prepared at (4–40 ppm) concentrations. (Sodium alginate/acrylamide)interpenetrating polymer networks (NaAlg/AAm)IPN hydrogels were added to 20 mL of dye solutions at different pH 7.0. The solutions were shaken in closed flasks at  $(25 \pm 1)^\circ\text{C}$  for 48 h. During the shaking process, aliquots of the solution were collected periodically, for the determination of remaining Magenta, Safranin-O, Methylene Blue, and Methyl Blue concentrations. The dye concentrations in the liquid phase were determined with UV-vis spectrophotometer (Varian, Cary 100). The amount of adsorption per unit mass of (NaAlg/AAm)IPN hydrogels was evaluated by using the following expression:

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

where,  $q_e$  is the amount of dye adsorbed onto unit dry mass of the (NaAlg/AAm)IPN hydrogels ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C_e$  are the concentrations of dye solutions in the initial solution and in the aqueous phase



**Figure 2** Possible reaction mechanism of acrylamide with sodium alginate by irradiation.

after treatment for a certain period of time, respectively, ( $\text{mg L}^{-1}$ ),  $V$  is the volume of the aqueous phase (L), and  $W$  is the amount of dry (NaAlg/AAm)IPN hydrogels used (g).

## RESULTS AND DISCUSSION

### Preparation of IPN hydrogels

Radiation technique can provide a useful method for degradation of different natural polymers.<sup>5</sup> Incorporation of sodium alginate (NaAlg) into a water insoluble matrix increases the mechanical stability. We prepared (sodium alginate/acrylamide) (NaAlg/AAm)IPN hydrogels which are durable and reusable. Modification by crosslinking, grafting, and degradation of natural polymers are expected to expand its application field. Degradation and crosslinking of polymers are affected by the atmosphere of irradiation conditions. A possible reaction mechanism of acrylamide with sodium alginate by  $\gamma$ -rays irradiation is shown in Figure 2. When a solution of acrylamide was irradiated, a bond in the double bond of acrylamide was broken and monomer radicals were formed. If irradiation was continued, crosslinking reaction started, chains were crosslinked to each other, and gelation occurred in the system.

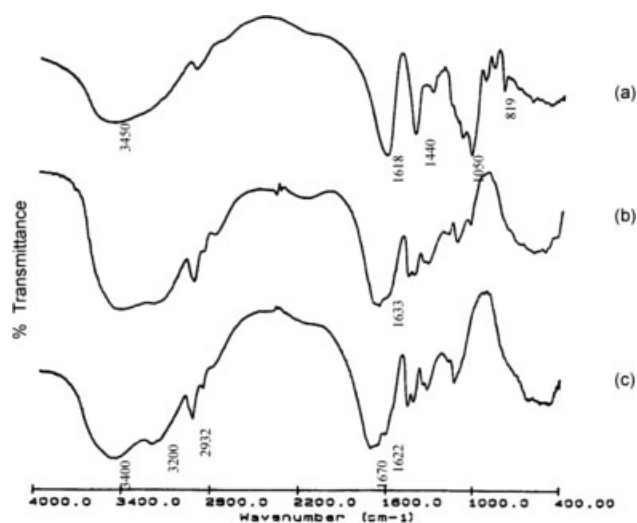
### Spectroscopic analysis

To understand the formation of (NaAlg/AAm)IPN hydrogel, obtained from AAm and NaAlg, Figure 3 shows the FTIR spectra of NaAlg, (NaAlg/AAm)IPN, PAAm in the wavelength range of  $4000\text{--}400\text{ cm}^{-1}$ . For the IR spectra, it is obvious that sodium alginate shows a broad peak at  $3450\text{ cm}^{-1}$  for  $\text{—OH}$  group, two peaks at  $1618$  and  $1440\text{ cm}^{-1}$  for the  $\text{—COO}^-$  group, and one sharp peak at  $1050\text{ cm}^{-1}$ , which is for the  $\text{C—O}$  group. The characteristic peak of sodium alginate appeared at  $819\text{ cm}^{-1}$  ( $\text{Na—O}$ ). The IR spectrum of PAAm exhibiting bands at  $3400\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  were assigned to

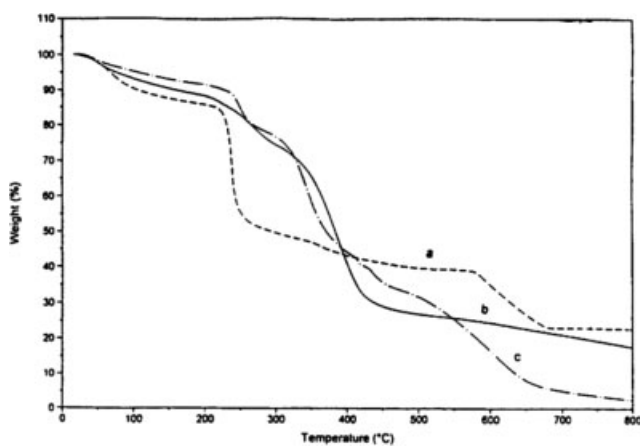
a stretching vibration of  $\text{N—H}$ ,  $1670\text{ cm}^{-1}$  ( $\text{C=O}$  stretching) and  $1622\text{ cm}^{-1}$  ( $\text{NH}$  bending). The bands at  $2932\text{ cm}^{-1}$  ( $\text{CH}$  stretching) and  $1500\text{--}1300\text{ cm}^{-1}$  (various  $\text{CH}$  bending) were also detected. The spectra of the (NaAlg/AAm)IPN hydrogel are characterized by the presence of the absorption bands typical of the pure components. The characteristic peak of sodium alginate appearing at  $819\text{ cm}^{-1}$  was not observed in all the spectra of (NaAlg/AAm)IPN hydrogel. The absorption peaks at  $1633\text{ cm}^{-1}$  assigned to the asymmetrical stretching vibration of  $\text{—COO}^-$  groups coupled with the peaks at  $1670\text{ cm}^{-1}$ ,  $1622\text{ cm}^{-1}$  of PAAm and shifted to  $1633\text{ cm}^{-1}$ , suggested that the new hydrogen bonds formed between  $\text{—COO}^-$  groups of sodium alginate and  $\text{—CONH}_2$  groups of PAAm. Furthermore, the bands of PAAm centered at about  $3400$  and  $3200\text{ cm}^{-1}$ , which were the stretching vibration of  $\text{—NH}_2$  groups involved in both inter and intramolecular hydrogen bonds, broadened, and coupled with  $\text{—OH}$  band of sodium alginate at  $3450\text{ cm}^{-1}$ , included by the addition of sodium alginate to PAAm, implying the occurrence of hydrogen bonds between  $\text{—OH}$  groups of sodium alginate and  $\text{—NH}_2$  groups of PAAm molecules.<sup>6,7</sup>

### Thermal analysis of (NaAlg/AAm)IPN hydrogels

To investigate the thermal properties of NaAlg, PAAm, and (NaAlg/AAm)IPN hydrogels, their thermograms were recorded, and they are given in Figure 4. To determine the thermal stability of NaAlg, PAAm and (NaAlg/AAm)IPN hydrogels, the temperature for the maximum weight loss ( $T_{\text{max}}$ ) and the temperature for half-life ( $T_{1/2}$ ) were found directly from its dynamic thermograms given in



**Figure 3** FTIR spectra of (a) NaAlg, (b) (NaAlg/AAm)IPN, (c) PAAm.



**Figure 4** The thermograms of (a) NaAlg, (b) PAAm, (c) (NaAlg/AAm)IPN.

Figure 4. PAAm gave 25% residue at 600°C. The temperature for maximum weight loss of PAAm is  $T_{\max} = 396^\circ\text{C}$  and  $T_{1/2} = 418^\circ\text{C}$ . There are three decomposition stages at 60–100°C, 259°C, and 396°C, the former being attributed to moisture loss. Weight loss at 259°C could be related to thermal processes involving the degradation of PAAm chains. The third stage at 396°C was indicative of the occurrence of more extensive thermal degradation processes. For NaAlg, the temperature for maximum weight loss is  $T_{\max} = 238^\circ\text{C}$  and the temperature for half-life is  $T_{1/2} = 300^\circ\text{C}$ , and NaAlg gives 30% residue at 600°C. NaAlg shows a peak at 95°C attributed to the loss of water absorbed. The peak at 238°C indicates the occurrence of thermal degradation of intermolecular side chain. The thermogram of NaAlg shows two stages of weight loss. The first weight loss at ~60–120°C was due to the loss of water, the second weight loss started at about 238°C, implying that the occurrence of different extent of thermal degradation of NaAlg. The third weight loss at 578°C may be due to a more extensive thermal degradation. The greatest thermal degradation peak shifted to the higher temperature, resulting from the addition of PAAm to NaAlg. TGA curve of (NaAlg/AAm)IPN hydrogel shows the greatest weight loss at 346°C. As shown in Figure 4, it is understood that the thermal stability and the temperature for maximum weight loss of (NaAlg/AAm)IPN hydrogel is between those of NaAlg and PAAm. When a less stable species combined with a species of higher thermal stability, (NaAlg/AAm)IPN hydrogels gained new thermal characteristics.  $T_{\max}$  for (NaAlg/AAm)IPN hydrogel is 346°C and  $T_{1/2}$  is 384°C.

### Swelling and diffusion studies

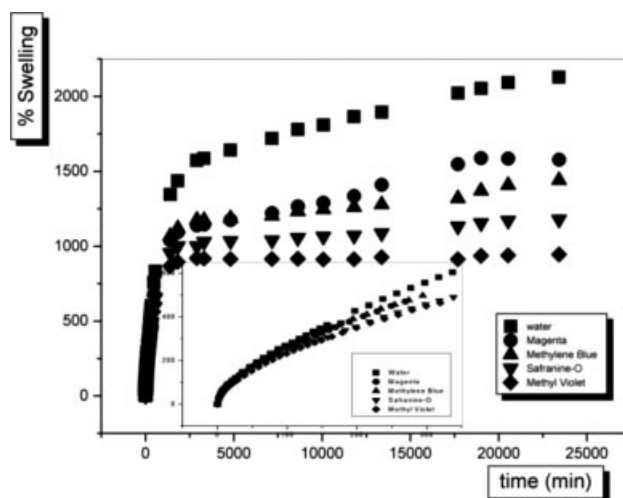
The equilibrium swelling of the (NaAlg/AAm)IPN hydrogels was investigated at pH 7.0 and 0.1M ionic

strength. Figure 5 shows a typical diagram of swelling behavior of (NaAlg/AAm)IPN at 25°C in water. The swelling was fast at the beginning and became slower and slower until the hydrogels reached their maximum swelling ratios.

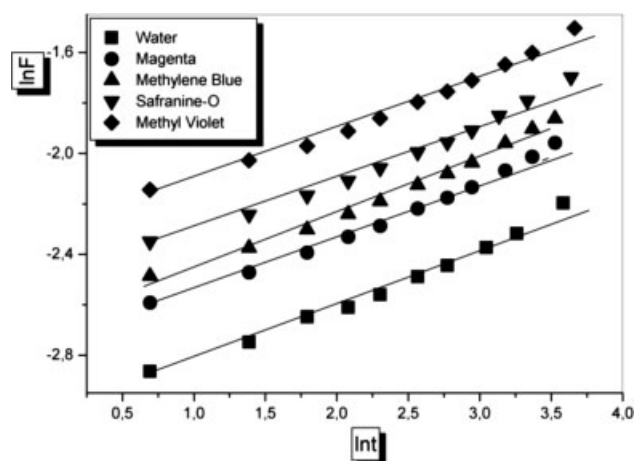
Analysis of the mechanisms of diffusion in swellable polymeric systems has received considerable attention in recent years because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.<sup>8</sup> The following equation is used to determine the nature of diffusion of water into hydrogels:

$$F = M_t/M_\infty = kt^n \quad (3)$$

where  $M_t$  and  $M_\infty$  denote the amount of solvent diffused into the gel at time  $t$  and infinite time (at equilibrium), respectively,  $k$  is a constant related to the network, and the exponent  $n$  is a number to determine the type of diffusion. For Fickian kinetics in which the rate of penetrant diffusion is rate limiting,  $n$  equals 0.5. If during the swelling, a non-Fickian process occurs,  $n$  will have a value between 0.5 and 1.0. To obtain  $n$ ,  $\ln F$  was plotted versus  $\ln t$  (values of  $t$  should be expressed in seconds) and the slope is the value of  $n$ . This equation was applied to the initial stage of swelling, and plots of  $\ln F$  versus  $\ln t$  are displayed in Figure 6, and the values of  $n$  are shown in Table I. From these values, it can be seen that  $n$  values are lower than 0.5 depending on the interaction between (NaAlg/AAm)IPN and water, (NaAlg/AAm)IPN and dyes. Thus, the swelling process seemed to be of Fickian character at the initial stage of swelling. The presence of  $-\text{NH}_2$  and  $-\text{COO}^-$  groups in these IPN hydrogels strongly affects the swelling ratio. The values given in this table show



**Figure 5** The swelling behavior of (NaAlg/AAm)IPN hydrogel in water and dyes solutions at 25°C.  $I = 0.1$ , dose: 5.0 kGy.



**Figure 6** Linear fit line  $\ln F$  versus  $\ln t$  at pH 7.0 for (NaAlg/AAm)IPN hydrogel in water and in 10 ppm dye solutions at 25°C.  $I = 0.1$ , dose: 5.0 kGy.

that  $n$  takes values between 0.21 and 0.23. This is generally explained as a consequence of the slow relaxation rate of the hydrogel.

One of the important parameters in swelling kinetics is diffusion coefficient. The diffusion coefficient ( $D$ ) can be determined by different methods.<sup>4,9</sup> The short time approximation method is used for the calculation of diffusion coefficients of hydrogels. The diffusion coefficient of the cylindrical hydrogels is calculated from the following relation:

$$F = M_t/M_\infty = (Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2) - \pi/3(\pi)^{3/2} + \dots \quad (4)$$

where  $D$  is in  $\text{cm}^2 \text{s}^{-1}$ ,  $t$  in sec, and  $r$  is the radius of cylindrical polymer sample. In hydrogel characterization, diffusion coefficients were calculated from the following relation:

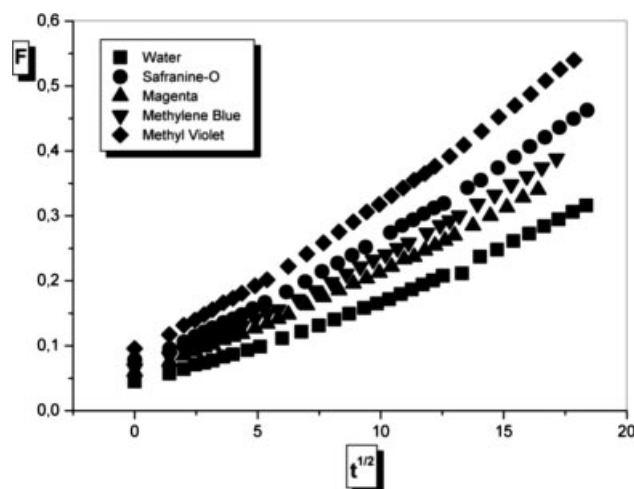
$$D = 0.049/(t/4r^2)^{1/2} \quad (5)$$

$t$  is the time at which the swelling is one half the equilibrium value and  $r$  is the radius of cylindrical polymer sample. For the (NaAlg/AAm)IPN hydrogels,  $F$  versus  $t^{1/2}$  plots were plotted, and are shown

**TABLE I**  
Swelling and Diffusion Parameters of the (NaAlg/AAm)IPN Hydrogels in Water and in 10 ppm Dye Solutions at pH 7.0 and 25°C

	$D$ ( $\text{cm}^2 \text{min}^{-1}$ )	$k$	$n$
Water	0.0149	0.047	0.2264
Magenta	0.0173	0.062	0.2233
Methylene Blue	0.0191	0.068	0.2246
Safranin-O	0.0214	0.078	0.2214
Methyl Violet	0.0254	0.097	0.2146

$I = 0.1$ , dose: 5.0 kGy.



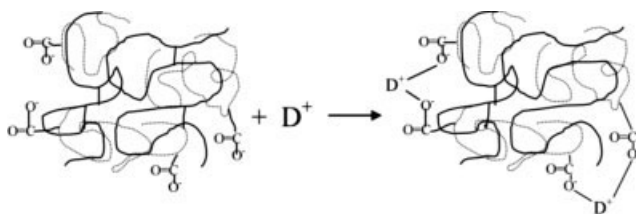
**Figure 7** Plots of  $F$  versus  $t^{1/2}$  of (NaAlg/AAm)IPN hydrogel in water and in 10 ppm dye solutions at pH 7.0 and 25°C.  $I = 0.1$ , dose: 5.0 kGy.

in Figure 7 with the assessment of  $F$  versus  $t^{1/2}$  graphs, the obtained diffusion coefficients were presented in Table I. As shown from the table, the diffusion coefficients were varied from  $1.49 \times 10^{-2}$  to  $2.54 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . We can say that the diffusion coefficient is highly affected by the structure of dye molecules. Penetration of the solvent and dyes into the (NaAlg/AAm)IPN hydrogel was in the following order at pH 7.0.

water > Magenta > Methylene Blue  
> Safranin-O > Methyl Violet

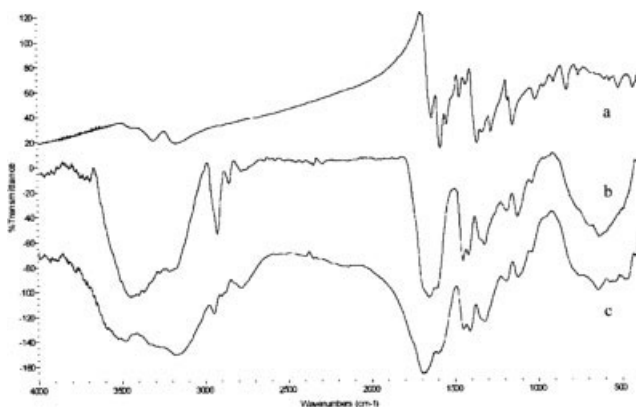
#### Spectroscopic analysis of (NaAlg/AAm)IPN-dye systems

In this study, we tried to develop mechanical and thermal stability and other physical properties of alginates by preparing IPN hydrogels with sodium alginate and acrylamide. The adsorption of aqueous solutions of dyes such as Magenta, Safranin-O, Methylene Blue, and Methyl Violet into (NaAlg/AAm)IPN hydrogels was investigated. A possible interaction between negative charges of NaAlg and positive charges of dyes are shown in Figure 8. To examine the nature of the interaction between the dyes and (NaAlg/AAm)IPN hydrogel, FTIR spectra of (NaAlg/AAm)IPN, (NaAlg/AAm)IPN-Magenta, (NaAlg/AAm)IPN-Safranin-O, (NaAlg/AAm)IPN-MethyleneBlue, (NaAlg/AAm)IPN-Methyl Violet systems and Magenta, Safranin-O, Methylene Blue, and Methyl Violet were given in Figures 9–12. In the FTIR spectrum of the (NaAlg/AAm)IPN the absorption peaks at  $1633 \text{ cm}^{-1}$ ,  $1440 \text{ cm}^{-1}$  shifted to lower frequencies ( $1590$  and  $1416 \text{ cm}^{-1}$ ). Upon coordination the  $-\text{COO}^-$  stretching frequency is lowered to  $1590$  and  $1416 \text{ cm}^{-1}$ , indicating complexation with

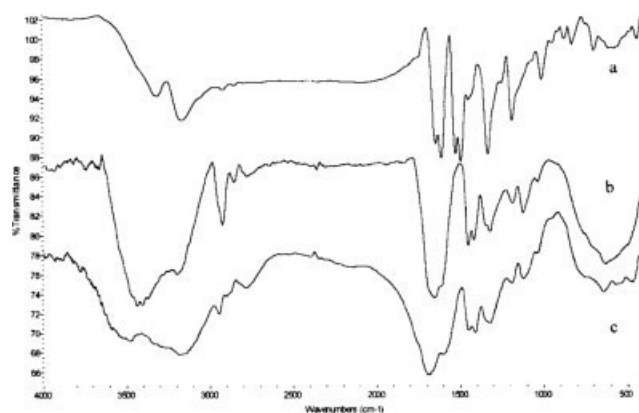


**Figure 8** Possible IPN hydrogel-dye interaction mechanism.

dyes as well as an increase in intensity. To investigate the interaction of (NaAlg/AAm)IPN-dye systems, the FTIR spectra of (NaAlg/AAm)IPN systems were recorded. In Figure 9, for (NaAlg/AAm)IPN-Magenta system, the observed peaks at  $1335\text{ cm}^{-1}$  and at  $1595\text{ cm}^{-1}$  are due to aromatic C–N stretching and C=C stretching in aromatic structure, respectively. In Figure 10, the characteristic peak for primer amine at  $3400\text{ cm}^{-1}$  is observed for Safranin-O. In (NaAlg/AAm)IPN-Safranin-O system, at  $1637$ ,  $1454$ , and  $1342\text{ cm}^{-1}$  C=C stretching vibrations and aromatic C–N stretching vibrations are observed, which are the constituents of Safranin-O. The broad peaks in Figure 10 at  $3500\text{--}3600\text{ cm}^{-1}$  are due to  $\text{—NH}_2$  and  $\text{—OH}$  groups. In Figure 11, for (NaAlg/AAm)IPN-Methylene Blue system, peaks at  $1450\text{ cm}^{-1}$  and  $1326\text{ cm}^{-1}$  are for  $\text{CH}_3\text{—N}$  bonding, broad peaks at  $3600\text{--}3400\text{ cm}^{-1}$  are due to  $\text{—N—H}$  and  $\text{—OH}$  groups. In Figure 12, concerning (NaAlg/AAm)IPN-Methyl Violet system, the peak at  $3416\text{ cm}^{-1}$  is stands seconder amine  $\text{—N—H}$  stretching in dyes, whereas broad peaks at  $3500\text{--}3100\text{ cm}^{-1}$  are due to  $\text{—NH}$  and  $\text{—OH}$  groups. The olefinic C=C group in methyl violet is observed as a sharp peak at  $1581\text{ cm}^{-1}$  and the intensity of this peak in IPN is relatively low. The peak for aromatic CN group is observed at  $1356\text{ cm}^{-1}$  for Methyl Violet.



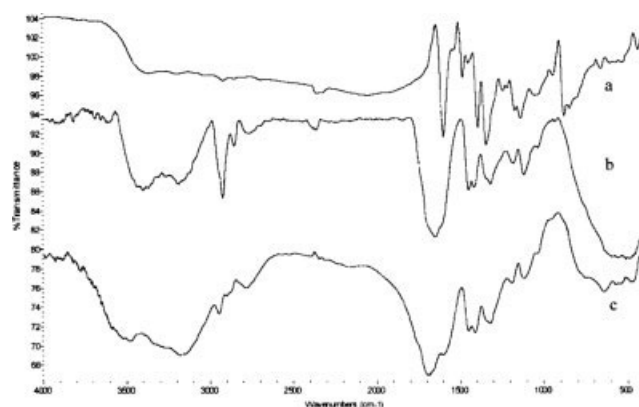
**Figure 9** FTIR spectra of (a) Magenta, (b) (NaAlg/AAm)IPN-Magenta system, (c) (NaAlg/AAm)IPN hydrogel.



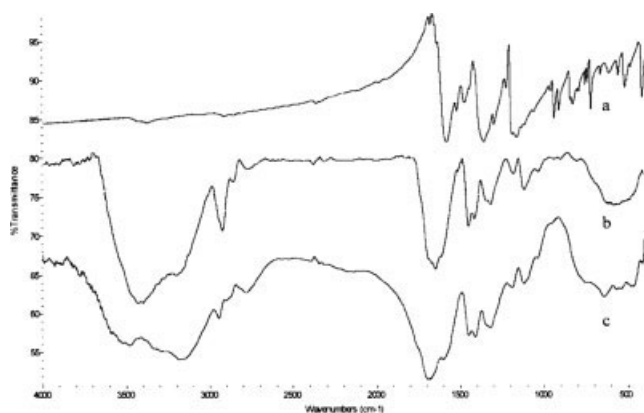
**Figure 10** FTIR spectra of (a) Safranin-O, (b) (NaAlg/AAm)IPN-Safranin-O system, (c) (NaAlg/AAm)IPN hydrogel.

### Thermal analysis of (NaAlg/AAm)IPN-dye systems

To determine the thermal properties of (NaAlg/AAm)IPN-dye systems, it was investigated whether the temperature for maximum weight loss ( $T_{\text{max}}$ ) and the temperature for half-life ( $T_{1/2}$ ) and the decomposition temperatures, the thermal stabilities of (NaAlg/AAm)IPN-dye systems change. For this purpose, the thermograms of (NaAlg/AAm)IPN, (NaAlg/AAm)IPN-Magenta, (NaAlg/AAm)IPN-Safranin-O, (NaAlg/AAm)IPN-Methylene Blue, and (NaAlg/AAm)IPN-Methyl Violet were examined and are shown in Figure 13. Thermogravimetry of (NaAlg/AAm)IPN-dye systems reveals the variation of thermal stability by complexation with metal dyes. The thermal decomposition behavior of a (NaAlg/AAm)IPN-dye systems depends on the macromolecular characteristics of the polymer support and the type of coordination geometry.<sup>10</sup> The decomposition of (NaAlg/AAm)IPN hydrogel occurred in a five-stage process (Fig. 13). The thermograms of (NaAlg/AAm)IPN-dye systems are similar to each other. Consequently, it may be explained



**Figure 11** FTIR spectra of (a) Methylene Blue, (b) (NaAlg/AAm)IPN-Methylene Blue system, (c) (NaAlg/AAm)IPN hydrogel.

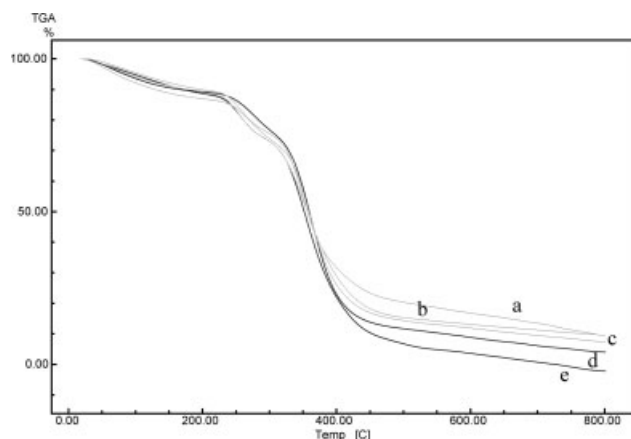


**Figure 12** FTIR spectra of (a) Methyl Violet, (b) (NaAlg/AAm)IPN-Methyl Violet system, (c) (NaAlg/AAm)IPN hydrogel.

that the thermal stabilities of (NaAlg/AAm)IPN-dye systems are somewhat more stable than (NaAlg/AAm)IPN hydrogel. The thermal stabilities of (NaAlg/AAm)IPN-dye systems increased in the order: (NaAlg/AAm)IPN-Safranine-O > (NaAlg/AAm)IPN (NaAlg/AAm)IPN-Methylene Blue > (NaAlg/AAm)IPN-Methyl Violet > (NaAlg/AAm)IPN-Magenta.

#### Swelling and diffusion studies of (NaAlg/AAm)IPN hydrogels in aqueous solutions of dyes

The effect of dyes on swelling capacity of (NaAlg/AAm)IPN hydrogels was investigated. The swelling curves of (NaAlg/AAm)IPN hydrogels in aqueous solutions of dyes are given at pH 7.0 for Magenta, Safranine-O, Methylene Blue, and Methyl Violet in Figure 5. As shown this figure, the swelling capacities of (NaAlg/AAm)IPN hydrogel-dye systems are in the range 800–2200% in the aqueous solution of dyes at pH 7.0. This figure shows that the swelling



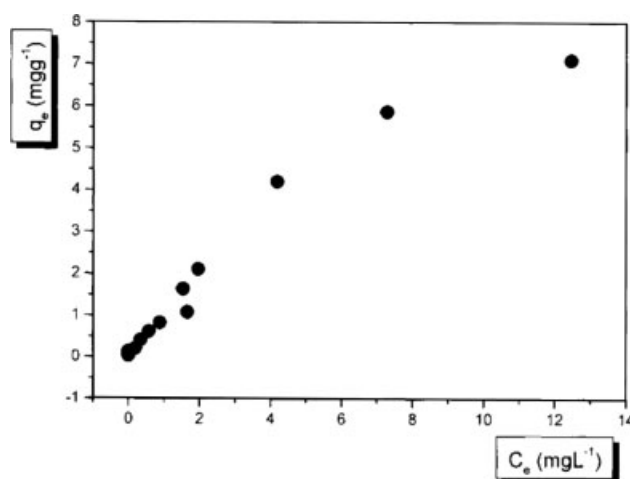
**Figure 13** The thermogram of (a) (NaAlg/AAm)IPN-Safranine-O, (b) (NaAlg/AAm)IPN-hydrogel, (c) (NaAlg/AAm)IPN-Methylene Blue, (d) (NaAlg/AAm)IPN-Methyl Violet, (e) (NaAlg/AAm)IPN-Magenta.

behaviors of (NaAlg/AAm)IPN hydrogel in water and aqueous solution of dyes are similar to each other. The equilibrium swelling values for (NaAlg/AAm)IPN hydrogel in dye solutions reached a steady state within a pH of  $\sim 5.5$ –7.0. The dye molecules interact with the carboxyl groups of NaAlg in (NaAlg/AAm)IPN hydrogel, so that the hydrophilic groups of the (NaAlg/AAm)IPN hydrogels are not bonded with water. Thus, swelling of the hydrogel increased in the aqueous solutions of dyes at pH 7.0. At the end of these evaluations, (NaAlg/AAm)IPN hydrogel in the aqueous solution of dyes were swollen in the following order at pH 7.0.

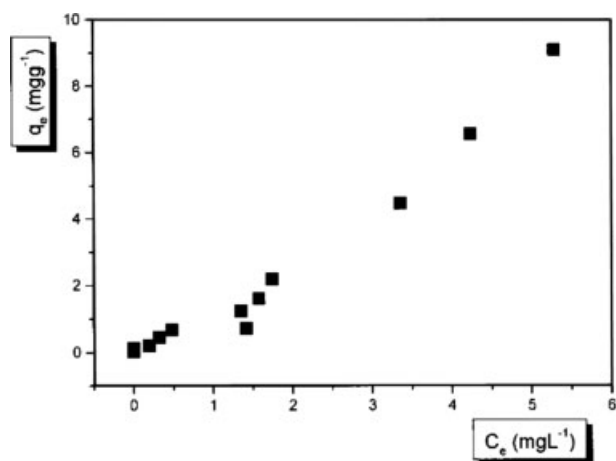
water > Magenta > Methylene Blue  
> Safranine-O > Methyl Violet

#### Adsorption studies

In the adsorption studies, it was purposed that the uptake investigation of dye molecules onto (NaAlg/AAm)IPN hydrogels and usability as a sorbent for dyes. To observe the adsorption of dyes (Magenta, Safranine-O, Methylene Blue, and Methyl Violet), (NaAlg/AAm)IPN hydrogels were placed in solutions of Magenta, Safranine-O, Methylene Blue, Methyl Violet and allowed to equilibrate for 2 days. Effects of the initial concentration of dye solutions on the adsorption rate and capacity were studied. The dye solutions were prepared in the concentration ranges 4–40.0 mg L<sup>-1</sup> for Magenta, Safranine-O, Methylene Blue, and Methyl Violet. Approximately, 0.05 g (NaAlg/AAm)IPN hydrogels containing 3% NaAlg were transferred into 20 mL of dye solutions at pH 7.0 and after reaching saturation of adsorption (2 days), the amount of adsorbent per unit mass of



**Figure 14** Effect of Magenta concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C.  $I = 0.1$ , dose: 5.0 kGy.

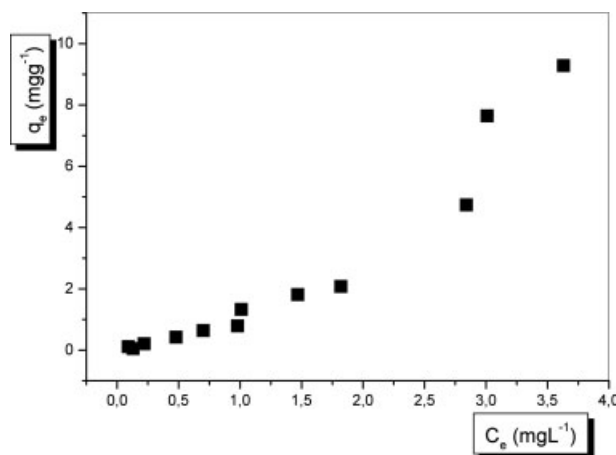


**Figure 15** Effect of Safranin-O concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C.  $I = 0.1$ , dose: 5.0 kGy.

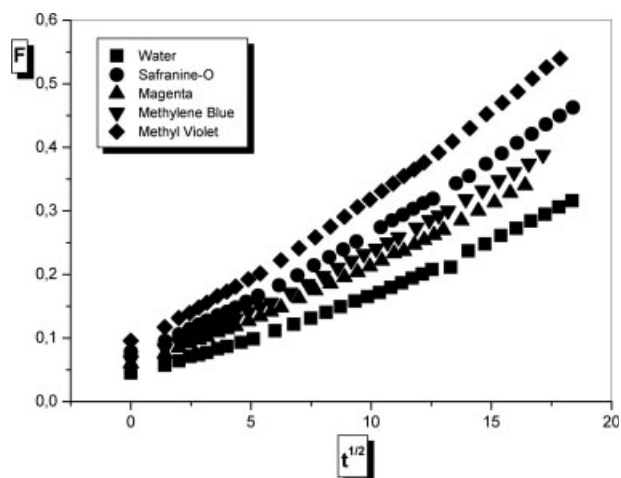
the (NaAlg/AAm)IPN hydrogels were evaluated by using eq. (2).

To determine the effect of concentration of dye solutions on adsorption, the graphs were plotted for the amount of heavy metal ion adsorbed per unit dry mass of (NaAlg/AAm)IPN hydrogels,  $q_e$ , against initial concentration of the dye. As can be seen from Figures 14–17, the adsorption of dyes onto the hydrogels increase with an increase of functional groups in the dye molecules and dye concentrations. The carboxyl groups in the hydrogel have electrostatic interactions between the cationic dye molecules and the anionic groups of alginic acid in the IPN hydrogels.

The capacity of (NaAlg/AAm)IPN hydrogels for Magenta, Safranin-O, Methylene Blue, and Methyl Violet can be determined by constructing adsorption isotherms.<sup>11–13</sup> The curves shown in Figures 14–17



**Figure 16** Effect of Methylene Blue concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C.  $I = 0.1$ , dose: 5.0 kGy.



**Figure 17** Effect of Methyl Violet concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C.  $I = 0.1$ , dose: 5.0 kGy.

show adsorptions of dye molecules within (NaAlg/AAm)IPN hydrogels correspond to S type adsorption isotherms in the Giles classification system for adsorption of a solute from its solution.<sup>14</sup>

When the adsorption capacities of (NaAlg/AAm)IPN hydrogels for Magenta, Safranin-O, Methylene Blue, and Methyl Violet are compared, it was determined that the adsorption of Magenta, Safranin-O, Methylene Blue, and Methyl Violet onto (NaAlg/AAm)IPN hydrogels is in the following order at pH 7.0 due to having functional groups and molecular size adsorbent-adsorbate interaction would be reduced to the weak dispersion energy of water with the other dye molecules.

Methyl Violet > Methylene Blue >, Safranin-O

> Magenta

## CONCLUSIONS

(NaAlg/AAm)IPN hydrogels have been prepared at definite composition and irradiated in  $^{60}\text{Co}$ - $\gamma$  source at 5.0 kGy dose. Hundred percent conversion of NaAlg/AAm mixtures into IPN were achieved at 5.0 kGy. Spectroscopic analyses, i.e., FTIR were done to investigate the interaction of (NaAlg/AAm)IPN with dyes. The maximum weight loss temperature of (NaAlg/AAm)IPN was found between those of PAAm and NaAlg. For (NaAlg/AAm)IPN-dye systems, the thermal stabilities were higher than (NaAlg/AAm)IPN and their homopolymers. At initial stages of swelling in water and dye solutions diffusion of water and dye molecules into (NaAlg/AAm)IPN hydrogels was found to be of a Fickian character. Diffusion coefficients were calculated for (NaAlg/AAm)IPN in aqueous solution of Magenta, Safranin-O, Methylene Blue, and Methyl Violet. Adsorption capacity of (NaAlg/AAm)IPN hydrogel



was determined and adsorption isotherm of (NaAlg/AAm)IPN-dye systems was S-type. For removing of Magenta, Safranin-O, Methylene Blue, and Methyl Violet from water, the optimum conditions are 0.05 g (NaAlg/AAm)IPN hydrogel, 0.1 ionic strength, 25°C, and pH 7.0.

### References

1. Nagasawa, N.; Mitimo, H.; Yoshii, F.; Kume, T. *Polym Degrad Stab* 2000, 69, 279.
2. Min, J. H.; Hering, J. G. *Water Res* 1988, 32, 1544.
3. Tripathy, T.; Pandey, S. R.; Karmakar, N. C.; Bhagat, R. P.; Singh, R. P. *Eur Polym J* 1999, 35, 2057.
4. Li, Y.; Tanaka, T. *J Chem Phys* 1990, 92, 1365.
5. Gupte, A.; D'Souza, S. *J Biochem Biophys Methods* 1999, 40, 39.
6. Xiao, C.; Lu, Y.; Liu, H.; Zhang, L. *J Macromol Sci Pure Appl Chem* 2000, 37, 1663.
7. Shiaw-Guang Hu, D.; Jium-Nan Chou, K. *Polymer* 1996, 37, 1019.
8. Buckley, J. D.; Berger, M.; Poller, D. *J Polym Sci* 1962, 56, 163.
9. Polishchuk, A. Y.; Zaikov, G. E.; Petropoulos, J. H. *Int J Polym Mater* 1993, 19, 1.
10. Sebastian, N.; George, B.; Mathew, B. *Polym Degrad Stab* 1998, 60, 371.
11. Hwang, M. C.; Chen, K. M. *J Appl Polym Sci* 1993, 49, 975.
12. Juang, R.; Tseng, R.; Wu, F.; Lee, S. *J Chem Tech Biotechnol* 1997, 70, 391.
13. Hsu, Y.; Chiang, C.; Yu, M. *Sep Sci Technol* 1997, 32, 2513.
14. Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. *J Chem Soc* 1969, 74, 3973.