



Adsorption of methyl violet in aqueous solutions by poly(acrylamide-co-acrylic acid) hydrogels

D. Şolpan^{a,*}, S. Duran^a, D. Saraydin^b, O. Güven^a

^aDepartment of Chemistry, Hacettepe University, 06532 Beytepe, Ankara, Turkey

^bDepartment of Chemistry, Cumhuriyet University, 58140 Sivas, Turkey

Received 2 August 2001; accepted 22 July 2002

Abstract

In this study, Acrylamide(AAm)/Acrylic Acid(AAc) monomer mixtures which contain different quantities of acrylic acid have been irradiated to form hydrogels with γ -radiation. Acrylamide/Acrylic Acid (AAm/AAc) monomer mixtures which contain 15%, 20%, 30% AAm and irradiated with 8.0 kGy were used for swelling and diffusion studies in water and solutions of methyl violet. Diffusions of water and methyl violet within the hydrogels were found to be non-Fickian in character. In experiments on the adsorption of methyl violet, Type-S adsorption was found. Poly(AAm-co-AAc) hydrogel adsorbed methyl violet, while poly(AAm) hydrogel did not adsorb any dye. (ΔH) Heat of adsorption, (ΔG) Free energy of adsorption, (ΔS) Entropy of adsorption were calculated. These results show that poly(AAm-co-AAc) hydrogels can be used as a sorbent for water pollutants such as dyes and treatment of these organic contaminants from wastewater.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Dye; γ -irradiation; Hydrogel; Acrylamide; Acrylic acid

1. Introduction

With the growing use of a variety of dyes, pollution from dye wastewater is one of the major environmental problems of the world. There are about 3000 types of dyes in the world market. Dyes that have low biodegradability greatly influence natural ecosystems and thus humans. Although some treatment methods have been developed, economic removal of dyes still remains a significant problem (Sarkar and Poddar, 1994).

Dyeing and finishing wastewaters in textile industry are generally high in both color and organic content. A combination of several processes is generally necessary to achieve adequate removal of all contaminants. Therefore, adsorption has evolved into one of the most effective physical processes for decolorization of textile

wastewaters. The most commonly used adsorbent for color removal is activated carbon (McKay, 1982) but it is relatively expensive. The application of other adsorbents such as peat, wood, fired clay and some other low-cost materials has been studied and recently received further attention owing to their economic advantages (McKay, 1983). The objective of this work was to determine the efficiency of color removal of methyl violet (MV) dye wastewaters using poly(Acrylamide-co-Acrylic Acid) poly(AAm-co-AAc) hydrogels.

2. Experimental

2.1. Materials

All chemicals were used as received. Acrylamide (AAm) and Acrylic Acid (AAc) monomers used in this study were obtained from BDH. Sodium phosphate, disodium hydrogen phosphate-2-hydrate used to prepare phosphate buffer solutions were obtained BDH.

*Corresponding author. Tel.: +90-312-2992163; fax: +90-312-2992163.

E-mail address: solpan@hacettepe.edu.tr (D. Şolpan).

Deionized water was used in the preparation of buffer solutions. Methyl violet (MV) was supplied from Allied Chemical and was used without any further purification. Chemical formula of monomers and some properties of methyl violet (MV) are listed in Table 1.

2.2. Preparation of hydrogels

The solutions of monomers of AAm and AAc were prepared in three different compositions (AAm/AAc mole ratios, 30/70, 20/80, 15/85). These solutions were placed in polyvinylchloride tubes of 3 mm diameter and irradiated in air at ambient temperature in a Gamma-cell-220 type γ -irradiator. Doses between 2.6 and 27.0 kGy were applied at a fixed dose rate of 0.16 kGyh⁻¹. Hydrogels obtained in long cylindrical shapes were cut, washed with distilled water for removal of unreacted monomers and dried in air and in vacuum and stored for later evaluations. The percent conversion

was determined gravimetrically. The percent gelation of poly(AAm-co-AAc) hydrogels is presented in Table 2. As can be seen from this table, the percent gelation of these hydrogels increases with increasing irradiation doses. Poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3 were prepared using three different compositions of poly(AAm-co-AAc) hydrogels which were obtained by using AAm/AAc monomer mixtures at three different mole percents, which are 30/70, 20/80 and 15/85, respectively.

2.3. Spectroscopic analysis of poly(AAm-co-AAc)-dye system

To examine the nature of the interaction between dye and poly(AAm-co-AAc) hydrogel, FTIR spectra of MV, poly(AAm-co-AAc)-MV and poly(AAm-co-AAc)3 are given in Fig. 1. The bands observed at 3416 cm⁻¹ is N-H stretching band of secondary amine group in dye, the

Table 1
Chemical formulas and some properties of dye and monomers

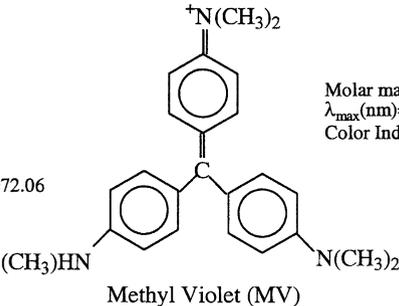
$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{C} & = & \text{C} \\ & & \\ \text{H} & & \text{CONH}_2 \end{array}$ <p>Acrylamide Molar mass (gmol⁻¹)=71.08</p>	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{C} & = & \text{C} \\ & & \\ \text{H} & & \text{COOH} \end{array}$ <p>Acrylic Acid Molar mass (gmol⁻¹)=72.06</p>	 <p>Methyl Violet (MV)</p> <p>Molar mass (gmol⁻¹)=393 λ_{max}(nm)=598 Color Index(CI)=42555</p>
--	--	---

Table 2
The percent gelation of AAm/AAc monomer mixtures irradiated at various doses

Dose (kGy)	% Gelation		
	Poly(AAm-co-AAc)1	Poly(AAm-co-AAc)2	Poly(AAm-co-AAc)3
2.6	40	36	32
3.0	75	72	66
4.0	86	83	73
8.0	99	99	99
12.0	91	89	84
16.0	89	88	84
20.0	88	82	90
23.4	90	88	89
27.0	85	86	86

Initial mole ratios of AAm/AAc monomer mixtures are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3. Dose rate: 0.16 kGyh⁻¹.

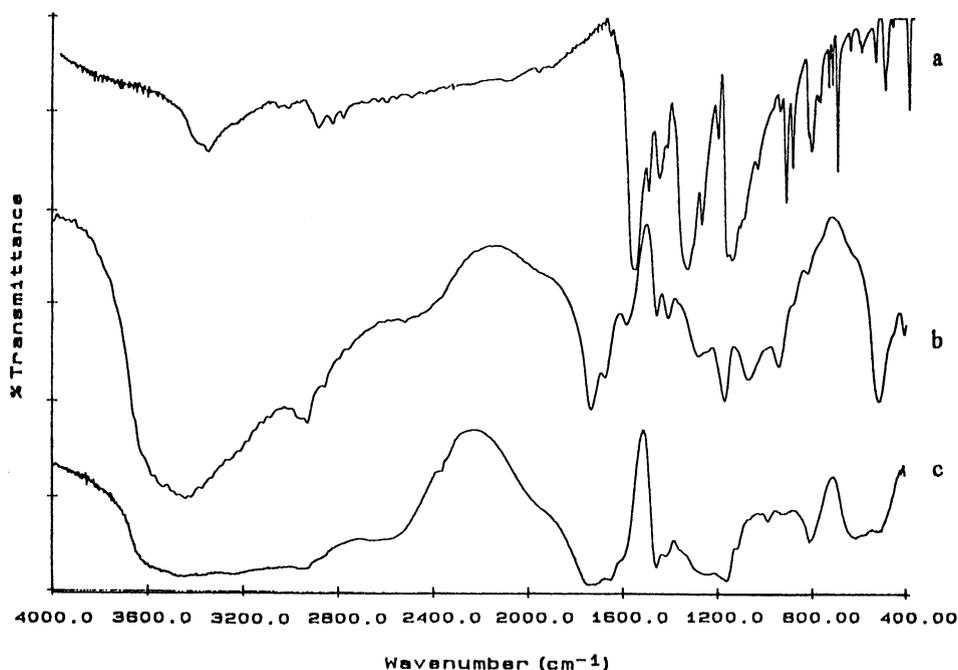


Fig. 1. FTIR spectra of methyl violet (MV) (a), poly(AAm-co-AAc)-MV (b), poly(AAm-co-AAc)3.

absorbances in the range of 3100–3500 cm^{-1} are O–H and N–H bands in poly(AAm-co-AAc)-MV and poly(AAm-co-AAc)3 hydrogel. The absorbance observed at 3437 cm^{-1} in poly(AAm-co-AAc)-MV is N–H stretching band of secondary amine group in MV. The weak peaks at 2900 cm^{-1} are C–H stretching bands. The sharper peak at 1581 cm^{-1} in MV structure is olefinic C=C stretching band this peak is observed weakly at 1588 cm^{-1} in poly(AAm-co-AAc)-MV. C=O group connected to the carboxyl group gives absorption peak at 1736 cm^{-1} , this peak is sharper than in the hydrogel. C=O group connected to the amide group gives absorption peak at 1679 cm^{-1} in poly(AAm-co-AAc)-MV. Aliphatic C–N stretching band is observed 1159–1173 cm^{-1} in all structure, and aromatic C–N band is observed 1356 cm^{-1} in MV structure. A possible interaction between negative charges of poly(AAm-co-AAc) hydrogel and positive charges of cationic dyes is shown in Fig. 2. The interaction between the cationic groups of cationic dye and carbonyl groups of hydrogel is ion–ion interaction (Hwang and Chen, 1993). These may occur between the negative charge of carboxyl group on the hydrogel and the positive charge on the tertiary nitrogen of the dye. It can be seen that there is an interaction between MV and poly(AAm-co-AAc) hydrogel by comparing Figs. 1 and 2.

2.4. Swelling and diffusion

Dried poly(AAm-co-AAc) hydrogels irradiated to 8.0 kGy were swollen in distilled water and aqueous

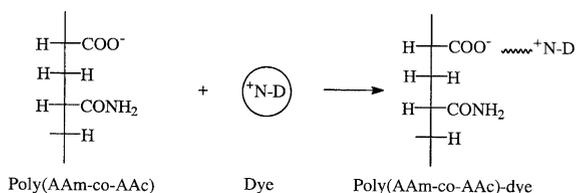


Fig. 2. A possible interaction between negative charges of poly(AAm-co-AAc) hydrogel and positive charges of dye.

dye solutions at pH (3.0–8.0), ionic strength $I=0.05$ –0.3, at 25°C to measure the parameters of diffusion and swelling. Swollen hydrogels removed from the water at regular intervals were dried superficially with filter paper, weighed and placed in the same bath again. The measurements were continued until a constant weight was reached for each sample.

2.5. Equilibrium dye adsorption measurements

Stock solutions of the dye containing approximately 5–50 mg l^{-1} MV in distilled water were prepared. AAm/AAc monomer mixtures containing 70%, 80%, 85% mole of AAc and irradiated to 8.0 kGy was refluxed in a known volume of dye solution until equilibrium was reached. The amounts of dye adsorbed were determined from the initial and final concentrations of the solutions, calculated from the measured absorbances.

3. Results and discussion

The swelling behaviors of poly(AAm-co-AAc) hydrogels prepared from AAm/AAc monomer mixtures containing 70%, 80%, 85% mole of AAc and irradiated to 8.0 kGy in water and in 50 mg l⁻¹ MV solution at pH 3.0, 5.0, 7.0, 8.0 were followed gravimetrically. The percentage swelling of each hydrogel was calculated from the following relation (Güven and Şen, 1990;

Buckley and Berger, 1962):

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

where m_t is the mass of swollen gel at time t , and m_0 is the initial mass of the dry gel. The swelling curves of poly(AAm-co-AAc)3 hydrogels in distilled water and dye solutions are shown at different pH values in Figs. 3 and 4. These figures show that the swelling behaviors of poly(AAm-co-AAc) hydrogels in water and aqueous

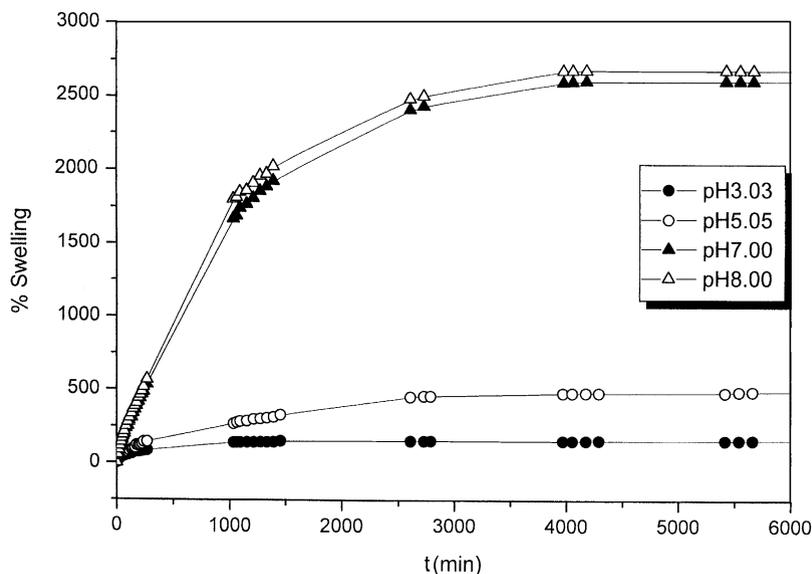


Fig. 3. Effect of pH on swelling behaviour of poly(AAm-co-AAc)3 hydrogels in water at 25°C. Initial mole ratio of AAm/AAc is 15/85 for poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

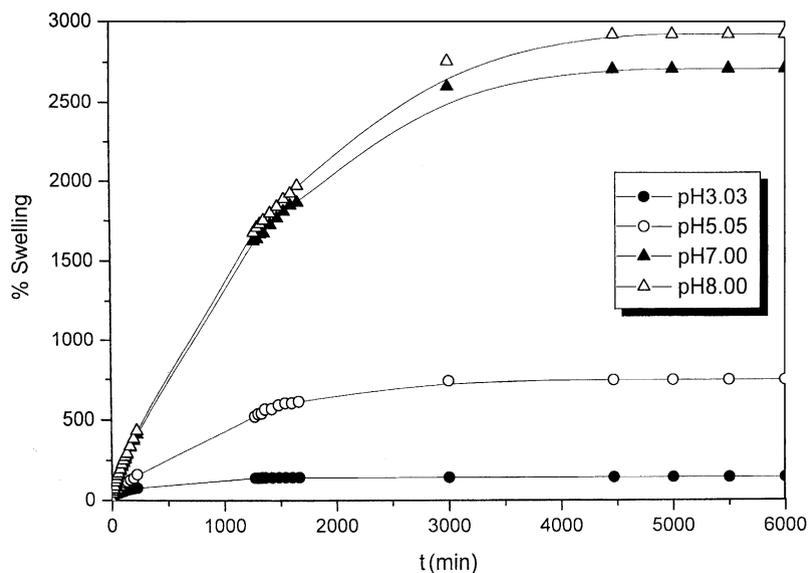


Fig. 4. Effect of pH on swelling behaviour of poly(AAm-co-AAc)3 hydrogel in 50 mg l⁻¹ methyl violet solution at 25°C. Initial mole ratio of AAm/AAc is 15/85 for poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

solution of dye are similar to each other, and the percentage swelling of hydrogels in dye solutions are somewhat higher than those in water. The equilibrium swelling of poly(AAm-co-AAc)3 hydrogels in dye solutions as a function of pH at 25°C and 0.1 M ionic strength is given in Fig. 5. The equilibrium swelling for poly(AAm-co-AAc) hydrogels at three different compositions is maximum at pH 8.00. The swelling of poly(AAm-co-AAc)3 hydrogels increases as the dye molecules adsorb water into the gels. The cationic dye molecules (MV) interact with the negative charges of poly(AAm-co-AAc) hydrogel, so in basic medium the hydrophilic groups of the poly(AAm-co-AAc) do not contain bonded water in the polymer initially, but adsorb water subsequently.

The nature of diffusion of dye solutions into poly (AAm-co-AAc) hydrogels characterized by the following equation:

$$F = kt^n. \quad (2)$$

In this equation, F denotes the amount of solvent fraction at time t . The constant k is related to the structure of the network, and the exponential n is a number to determine the type of diffusion. This equation is applied to the initial stages of swelling, and plots of $\ln(F)$ versus $\ln(t)$ are presented in Fig. 6. The exponents (n) and k were calculated from the slope and intercept of the lines and the results are given in Table 3.

For hydrogel characterization, the diffusion coefficient can be calculated by various methods. The short-time approximation method is used for calculation of diffusion coefficients of poly(AAm-co-AAc) hydrogels.

The short-time approximation is valid for the first 60% of the swelling. The diffusion coefficients of the cylindrical poly(AAm-co-AAc) hydrogels are calculated from the following relations (Buckley and Berger, 1962):

$$F = 4(Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2) - \pi/3(Dt/\pi r^2)^{3/2}, \quad (3)$$

where D is in $\text{cm}^2 \text{min}^{-1}$, t is the time at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and r is the radius of the swollen cylindrical sample. A graphical comparison of Eqs. (2) and (3) shows the semi-empirical Eq. (2) and $k = 4(D/\pi r^2)^{1/2}$ and $D = 0.049/(t/4r^2)^{1/2}$. For the hydrogels, F versus $t^{1/2}$ curves are given in Fig. 7. The slopes of the lines of F versus $t^{1/2}$ give the diffusion coefficients that are listed for three different hydrogels in Table 3. The n values ranged between 0.40 and 0.70. The diffusion of aqueous solutions of dye into poly(AAm-co-AAc) hydrogels was taken as a non-Fickian character. The percent swelling of hydrogels is high (146–3088%) in dye solutions but low in water. Penetration of solvent and dye into poly(AAm-co-AAc) hydrogels increased with increasing pH of the solvent and aqueous dye solutions. In ionic polymeric networks, ionization may control the water diffusion process, thus affecting the relative magnitude of diffusion and relaxation times. Non-Fickian transport is observed as the pH of the surrounding fluid increases above pK_a . For cylindrical hydrogels, in Non-Fickian type diffusion, n is between 0.45 and 1.00. Hence, the diffusion into poly(AAm-co-AAc) hydrogels was taken to be as a non-Fickian. It can be said that for higher swelling values of the hydrogels and higher pH values (above pK_a), the transport of

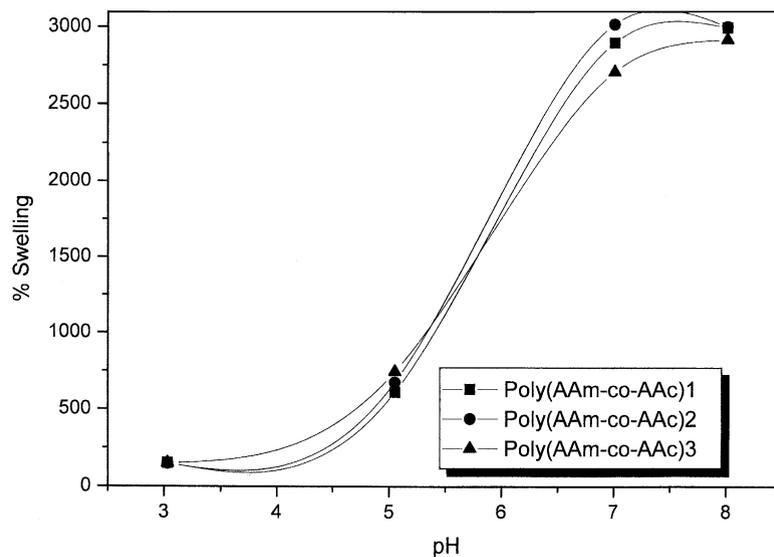


Fig. 5. Swelling curves of poly(AAm-co-AAc) hydrogels in 50 mg l^{-1} methyl violet solution as a function of pH at 25°C. Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3: I: 0.1, total dose given: 8.0 kGy.

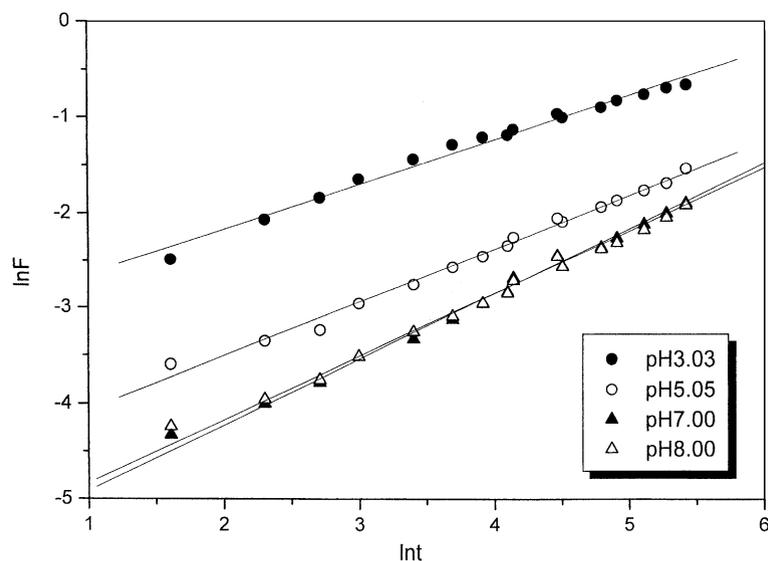


Fig. 6. Plots of $\ln F$ versus $\ln t$ of poly(AAm-co-AAc)3 hydrogel at different pH values in 50 mg l^{-1} methyl violet solution at 25°C . Initial mole ratio of AAm/AAc is 15/85 for poly(AAm-co-AAc)3 hydrogel: I: 0.1, total dose given: 8.0 kGy.

Table 3

Swelling and diffusion parameters of poly(AAm-co-AAc) hydrogels in water and methyl violet solutions at various pH and 25°C

PH	Water			Poly(AAm-co-AAc)1			Poly(AAm-co-AAc)2			Poly(AAm-co-AAc)3		
	$k \times 10^2$	n	$D \times 10^5$	$k \times 10^2$	n	$D \times 10^5$	$k \times 10^2$	n	$D \times 10^5$	$k \times 10^2$	n	$D \times 10^5$
3.00	3.81	0.46	1.42	4.27	0.43	1.31	4.71	0.46	1.87	5.96	0.40	1.89
5.05	0.60	0.65	1.04	0.84	0.58	2.31	0.88	0.59	2.29	0.98	0.56	2.69
7.00	0.35	0.76	2.48	0.37	0.70	4.85	0.55	0.64	2.88	0.37	0.69	4.72
8.00	0.50	0.69	2.78	0.62	0.67	4.46	0.54	0.64	2.89	0.36	0.69	5.06

D : $\text{cm}^2 \text{min}^{-1}$.

Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3. I: 0.1, total dose given: 8.0 kGy.

water into the hydrogels becomes more non-Fickian. This is generally explained as a consequence of the slow relaxation rate of the polymer matrix. The equilibrium swelling for poly(AAm-co-AAc) hydrogels at three different compositions is maximum at pH 8.0. The equilibrium swelling of poly(AAm-co-AAc)3 hydrogels is higher than those of the other hydrogels. The cationic dye molecules interact with the carboxyl groups of acrylic acid in poly(AAm-co-AAc) hydrogel, so the hydrophilic groups of the poly(AAm-co-AAc) are not bonded with water. Thus, swelling of the hydrogel increased in the aqueous solutions of cationic dyes.

3.1. Adsorption for removing dye pollutants

To observe the adsorption of MV, poly(AAm-co-AAc) hydrogels were placed in aqueous solutions of (MV) and allowed to equilibrate for 2 days. At the end

of this time, poly(AAm-co-AAc) hydrogels in the MV solutions showed the dark coloration. The amount of adsorption per unit mass of the poly(AAm/AAc) hydrogels were evaluated by using the following equation:

$$q_e = [(C_0 - C_e)V]/W, \quad (4)$$

where q_e is the amount of dyes adsorbed onto unit dry mass of the poly(AAm/AAc) hydrogels (mg g^{-1}), C_0 and C_e are the concentrations of the dyes in the initial solution and the aqueous phase after treatment for a certain period of time, respectively (mg l^{-1}), V is the volume of the aqueous phase (l) and W is the amount of dry poly(AAm/AAc) hydrogels (g).

In an adsorption system at equilibrium, the total solute concentration (C_t , mol l^{-1}) is

$$C_t = C_b + C_e, \quad (5)$$

where C_b is the equilibrium mol number of the solute on the adsorbent per litre solution (bound solute

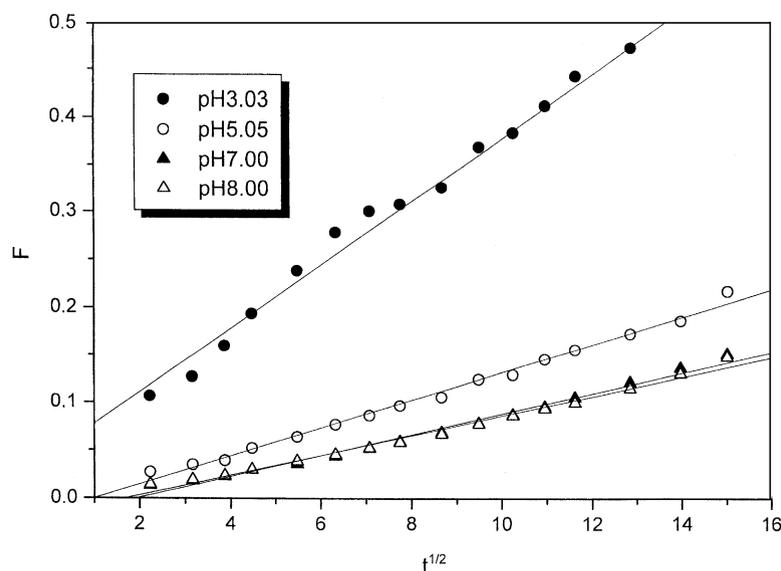


Fig. 7. Plots of F versus $t^{1/2}$ of poly(AAm-co-AAc)3 hydrogel at different pH values in 50 mg l^{-1} methyl violet solution at 25°C . Initial mole ratio of AAm/AAc is 15/85 for poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy .

concentration) and C_c is the equilibrium concentration of the solute in the solution in mol l^{-1} (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

$$r = C_b/P. \quad (6)$$

Thus, with C_b in mol l^{-1} and P in base mol (moles of monomer units) per litre solution, r then represents the average number of molecules of solute bound each monomer unit at that free solute concentration (Karadağ and Saraydin, 1996).

To determine the adsorption kinetics of methyl violet (MV) into poly(AAm-co-AAc) hydrogels, a plot of the binding ratio (r) against time is shown in Fig. 8. Adsorption increased with increasing time and reached equilibrium in 2 days. The binding ratio of cationic dye (MV) into hydrogel systems gradually increases with the increasing of content of AAc in AAm/AAc monomer mixtures used to prepare poly(AAm-co-AAc) hydrogel. To find the order of adsorption kinetic of MV, the first-order kinetic equation was tested but the straight lines could not be obtained. Then, t/r versus t graphs were plotted. These graphs are shown in Fig. 9. The binding ratio of MV into poly(AAm-co-AAc) hydrogels is second order. Rate constant; k , initial rate; r_i , and maximum binding ratio; r_{max} , were calculated from the slope and intersection of these lines by using Eq. (7) and

were presented in Table 4.

$$t/r = 1/kr_{\text{max}} + t(1/r_{\text{max}}). \quad (7)$$

The calculations showed that the values of r_{max} increased with increasing content of AAc in poly(AAm-co-AAc) hydrogels.

3.2. Effect of pH of dye solution on adsorption

To investigate the influence of the pH on the adsorption of MV into poly(AAm-co-AAc) hydrogels, adsorption studies were performed in MV solutions at various pH. The binding ratio (r) (mol dye/mol monomeric unit of hydrogel) quantities were calculated and these results are given in Table 5. According to the protonation of the carboxylic acid groups of hydrogels and amine groups of the dye, MV can be adsorbed more or less into poly(AAm-co-AAc) hydrogel in basic and acidic medium, respectively. At pH 5.05, adsorption decreases since there is less protonation of amine groups of the dye and the diffusion of dye solution decreases. Table 5 gives data for r , % Ads. and q_e at different pH-values. At the highest pH of the solution, for the three different compositions, r , % Ads., q_e are the highest values depending on the carboxyl groups in these hydrogels. For the amine groups, there is a reverse situation, at the lowest pH of the solution, for the hydrogels at three different compositions, r , % Ads. and q_e values are high since the amine groups become protonated when the pH of the solution was changed from pH 7 to 5.

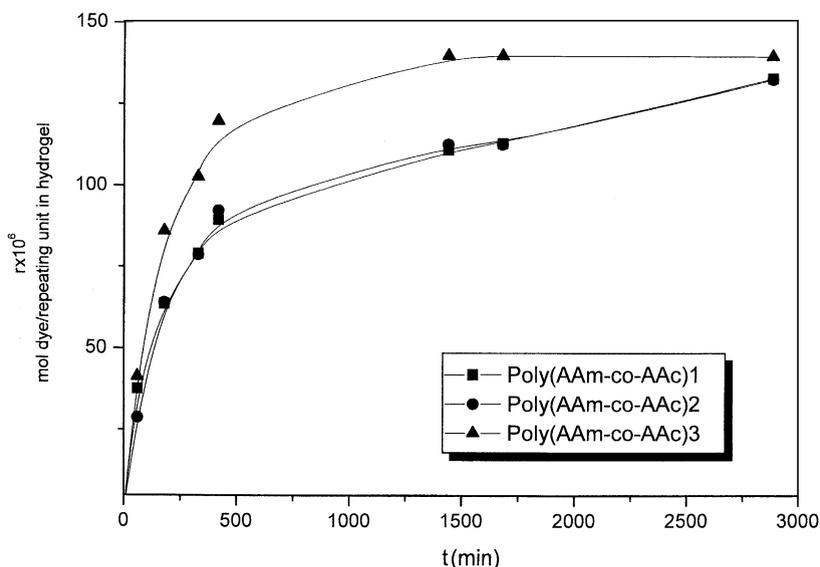


Fig. 8. The variations of binding ratio (r) of poly(AAm-co-AAc) hydrogels–dye systems with time in 5 mg l^{-1} methyl violet solution at 25°C . Initial mole ratio of AAm/AAc is 15/85 for poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

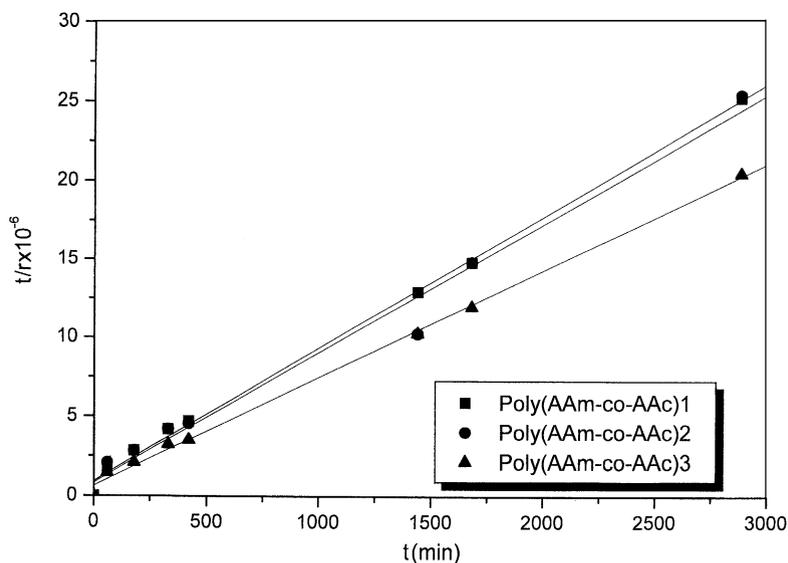


Fig. 9. Swelling kinetics of poly(AAm-co-AAc) hydrogels–dye systems in 5 mg l^{-1} methyl violet solution at pH 7.0 and 25°C . Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3: I: 0.1, total dose given: 8.0 kGy.

3.3. Effect of temperature of dye solution on adsorption

One of the important parameters which affect adsorption capacity is temperature. The effect of temperature on the adsorption of MV on poly(AAm-co-AAc) hydrogels is shown in Fig. 10. The adsorption capacity of poly(AAm-co-AAc) hydrogels decreases with the increase in the temperature of the aqueous dye solution. To determine the heats of adsorption of

poly(AAm-co-AAc) hydrogel–dye systems, adsorption experiments were carried out at various temperatures. The heat of adsorption of these systems were calculated by the following equation:

$$\ln(C_{e2}/C_{e1}) = (\Delta H/R)[(1/T_1) - (1/T_2)], \quad (8)$$

where C_{e1} and C_{e2} are the free dye concentrations at absolute temperature T_1 and T_2 , respectively. R is the universal gas constant, ΔH is the heat of adsorption.

Table 4
Adsorption kinetic parameters of poly(AAm-co-AAc) hydrogels in 50 mg l⁻¹ methyl violet solutions at pH 7.0 and 25°C

Hydrogel	Methyl violet (MV)		
	$r_m \times 10^4$	$r_i \times 10^7$	k
Poly(AAm-co-AAc)1	1.11	8.46	52.61
Poly(AAm-co-AAc)2	1.22	8.92	53.22
Poly(AAm-co-AAc)3	1.50	12.08	53.91

r_m : mol dye/repeating unit in hydrogel.

r_i : (mol dye/repeating unit in hydrogel)/min.

k : (repeating unit in hydrogel/mol dye)/min.

Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3. I: 0.1, total dose given: 8.0 kGy.

Table 5

Values of binding ratio (r), % adsorption and q_e for poly(AAm-co-AAc) hydrogels in 50 mg l⁻¹ methyl violet solution at various pH values and 25°C

pH	Poly(AAm-co-AAc)1			Poly(AAm-co-AAc)2			Poly(AAm-co-AAc)3		
	$r \times 10^6$	% Ads.	q_e	$r \times 10^6$	% Ads.	q_e	$r \times 10^6$	% Ads.	q_e
3.00	1133	76.82	6.23	1177	76.92	6.42	1162	78.59	6.37
5.05	936	66.96	5.14	987	70.46	5.41	1005	68.08	5.51
7.00	1162	91.80	6.38	1364	92.76	7.48	1375	93.40	7.53
8.00	1337	91.94	7.34	1487	99.46	8.15	1537	94.80	8.42

r : mol dye/repeating unit in hydrogel.

q_e : mg dye/g hydrogel.

Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3. I: 0.1, total dose given: 8.0 kGy.

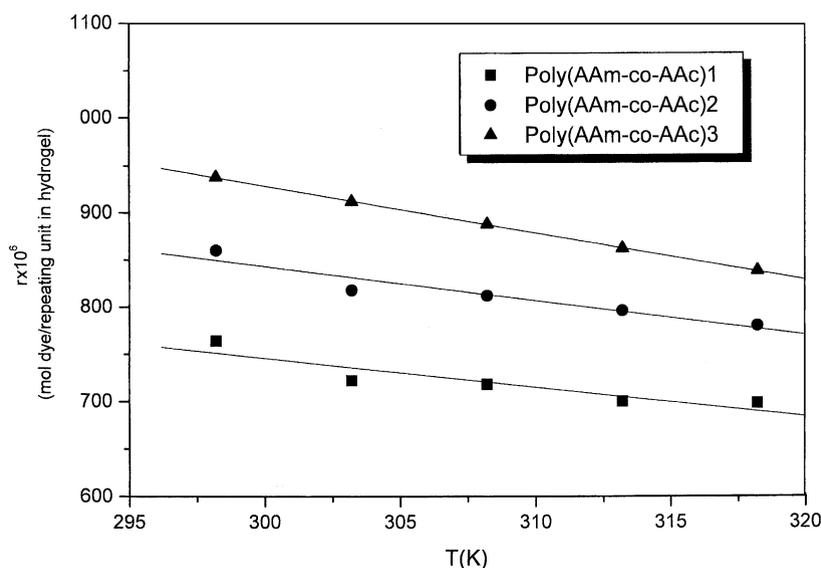


Fig. 10. The variations of binding ratio (r) of poly(AAm-co-AAc) hydrogels–dye systems with temperature in 25 mg l⁻¹ methyl violet solution at pH 7.0 and 25°C. Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

Fig. 11 shows $\ln C_e$ versus $1/T$. The slopes of these graphs give $\Delta H/R$ values.

3.4. Effect of concentration of dye solution on adsorption

To determine the effect of concentration of dye solution on adsorption, plots of the binding ratio (r) against the free concentrations of the dyes in solutions (C , $\mu\text{mol dye l}^{-1}$) are shown in Fig. 12. This figure shows that adsorption of dye within different compositions of poly(AAm-co-AAc) hydrogels correspond to type-S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (Giles and MacEwan, 1960).

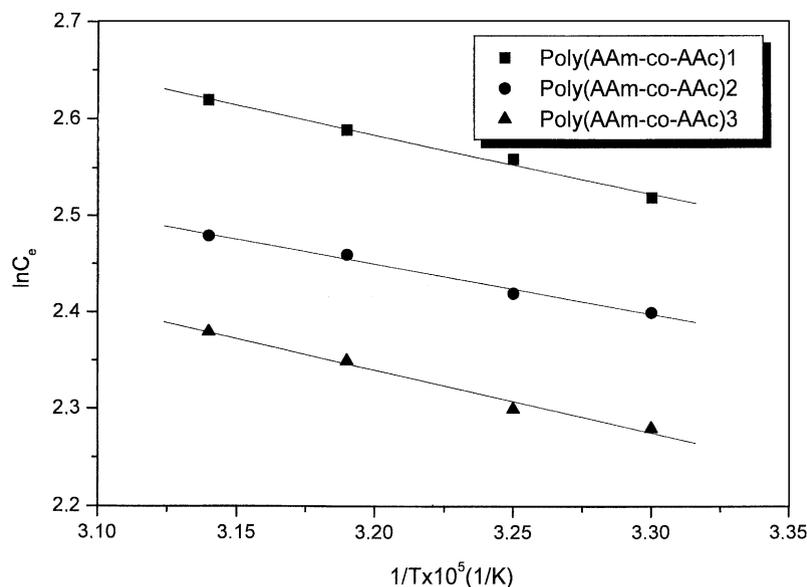


Fig. 11. The variations of $\ln C_e$ of poly(AAm-co-AAc) hydrogels–dye systems with $1/T$ in 25 mg l^{-1} methyl violet solution at pH 7.0 and 25°C . Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

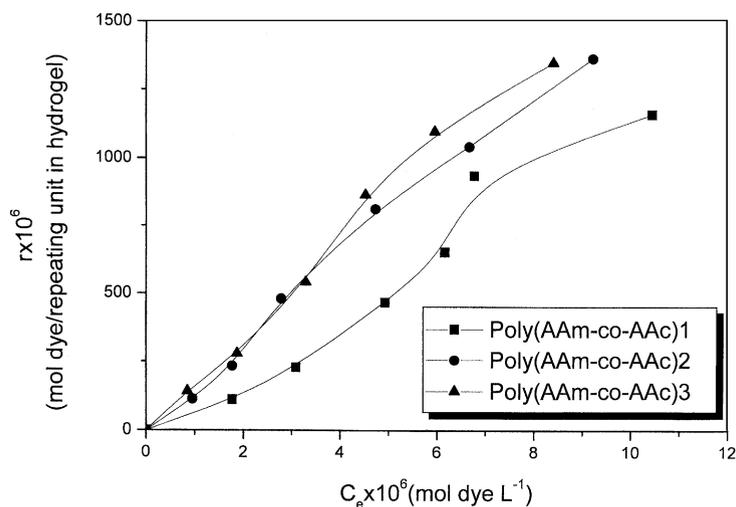


Fig. 12. The variations of binding ratio (r) of poly(AAm-co-AAc) hydrogels–dye systems with the equilibrium concentration in methyl violet solutions at pH 7.0 and 25°C . Initial mole ratios of AAm/AAc are 30/70, 20/80, 15/85 for poly(AAm-co-AAc)1, poly(AAm-co-AAc)2, poly(AAm-co-AAc)3 hydrogel. I: 0.1, total dose given: 8.0 kGy.

In the S curves, the initial direction of curvature shows that adsorption becomes stronger as concentration rises. In practice, the S curve usually appears when three conditions are fulfilled; the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition for substrate sites, from molecules of the solvent or of another adsorbed species. The weakness of the adsor-

bent–adsorbate forces will cause the uptake at low concentrations to be small but once a molecule has become adsorbed, the adsorbate–adsorbate forces will promote the adsorption of further molecules—a cooperative process—so that the isotherm will become convex to the concentration axis. Type S isotherms may originate through the adsorption of either non-polar molecules or polar molecules, always provided that the adsorbent–adsorbate force is relatively weak.

Table 6
Thermodynamic parameters of poly(AAm-co-AAc)-dye system

Hydrogel	Methyl violet (MV)		
	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/Kmol)
Poly(AAm-co-AAc)1	-13.72	-4.53	30.84
Poly(AAm-co-AAc)2	-14.96	-4.36	35.57
Poly(AAm-co-AAc)3	-15.30	-4.06	37.72

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. Not surprisingly, water provided many examples of type S isotherms. The hydrogel 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 dyes, so that a type S isotherm should result. In a system that gives rise to a type S isotherm, however, multiple layers are built up on some parts of the surface while a monolayer is still incomplete on other parts.

Some adsorption thermodynamic parameters can be derived for poly(AAm-co-AAc) hydrogel–dye systems by using the adsorption isotherms. The slope of linear part of plots of the binding ratio (r) against free concentrations of the cationic dye gives the equilibrium constant of adsorption, K . Free energy and entropy of adsorption (ΔG and ΔS) of poly(AAm-co-AAc) hydrogel–dye systems were calculated and are tabulated in Table 6.

All of ΔG values for poly(AAm-co-AAc)–dye systems are negative and between -13 and -15 kJ mol^{-1} ; therefore binding process of methyl violet (MV) onto poly(AAm-co-AAc) hydrogels is spontaneously negative enthalpy values suggest that these adsorption processes are exothermic. If ΔH values are $< 20 \text{ kJ mol}^{-1}$, then adsorption process is physical adsorption. On the other hand, poly(AAm-co-AAc)–MV systems show positive entropy of adsorption. Hence, the electrostatic repulsion weakens the adsorption force and increases the degree of freedom of the molecules.

4. Conclusions

- Poly(AAm-co-AAc) hydrogel prepared from AAm/AAc monomer mixtures containing the more AAc,

showed maximum percent swelling in distilled water and dye solution at basic medium due to electrostatic repulsions between the carboxylic acid in hydrogel and in ions in buffer solutions.

- Diffusion of water and the dye solutions within hydrogels was found to be of a non-Fickian character.
- Diffusion coefficients were calculated for poly(AAm-co-AAc) hydrogel in water and MV solution.
- Swelling and adsorption kinetic of poly(AAm-co-AAc) hydrogel in distilled water and dye solution were found to be second order.
- Initial swelling rate increased with increased pH and AAc content in hydrogel.
- Adsorption capacity of poly(AAm-co-AAc) hydrogels was changed with pH of the aqueous solution of dye and adsorption isotherms of poly(AAm-co-AAc) hydrogels were S type.
- Thermodynamic parameters such as ΔG , ΔH and ΔS for poly(AAm-co-AAc)–dye systems were calculated and ΔH values were $< 20 \text{ kJ mol}^{-1}$ so adsorption process is a physical adsorption.

References

- Buckley, J.D., Berger, M., 1962. The swelling of polymer system in solvents. II. Mathematics of diffusion. *J. Polym.Sci.* 56, 175–188.
- Giles, C.H., MacEwan, T.H., 1960. Studies in adsorption part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* 3973–3993.
- Güven, O., Şen, M., 1990. Preparation and characterization of poly(N-vinyl-2-pyrrolidone) hydrogels. *Polymer* 32 (13), 2491–2496.
- Hwang, M.C., Chen, K.M., 1993. The removal of color from effluents using polyamide-epichlorohydrin-cellulose polymer. I. Preparation and use in direct dye removal. *J. Appl. Polym. Sci.* 48, 299–311.
- Karadağ, E., Saraydin, D., 1996. Interaction of some cationic dyes with acrylamide/Itaconic acid hydrogels. *J. Appl. Polym. Sci.* 61, 2372–2376.
- McKay, G., 1982. Adsorption of dyestuffs from aqueous solutions with activated carbon. I. Equilibrium and batch contact-time studies. *J.Chem.Tech.Biotechnol.* 32, 759–772.
- McKay, G., 1983. Adsorption of dyestuffs from aqueous solutions with activated carbon. III. Intraparticle diffusion processes. *J.Chem.Tech.Biotechnol.* 33A, 196–204.
- Sarkar, M., Poddar, S., 1994. Study of the adsorption of methyl violet onto fly ash. *Analytical Proceedings Including Analytical Communications* 31, 213–215.