Radiation Synthesis of Copolymers for Adsorption of Dyes from Their Industrial Wastes

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ABSTRACT: Copolymer hydrogels were prepared by γ-radiation copolymerization of *N*-vinyl-2-pyrrolidone (NVP) and methylmethacrylate (MMA) or acrylonitrile (AN). The effect of NVP/MMA and NVP/AN compositions and irradiation dose on the gel fraction yield in the prepared hydrogels was determined. It was found that as the content of NVP increased, the gel fraction yield decreased. The increase in irradiation dose resulted in increasing the crosslinked network structure and, consequently, the gel percentage increased. The thermal stability and swelling properties were also investigated as a function of comonomer composition. The nitrile groups (–CN) in the prepared copolymer were converted into their respective amidoxime groups by treating with NH_2OH-hydrochloride. Such a process resulted in improving both the swelling behavior and adsorption capacity. Characterization and some selected properties of the prepared hydrogels were studied and accordingly the possibility of its practicable use in the treatment of industrial waste dyes was determined. The thermodynamic parameters for the adsorption process were calculated. The effect of treatment time, pH of feed solution, effect of initial feed concentration, and temperature on the dye uptake was also investigated. The maximum uptake for investigated dyes was higher for treated NVP/AN hydrogel than that for untreated NVP/AN and NVP/MMA ones. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 753–763, 2005

Key words: radiation; copolymerization; dyes/pigments; adsorption; waste

INTRODUCTION

There has been increasing interest in the synthesis and various applications, such as high water sorption, of new hydrogels. Hydrogels are crosslinked hydrophilic polymers that are swollen in water, usually to equilibrium. If the water content is increased up to very high values, the decline in mechanical properties is unacceptable for most purposes. Many authors have emphasized the ways improved mechanical properties can be achieved by control of chemical (covalent) and physical (especially hydrophobic) crosslinking.[1] It was pointed out that small clusters of hydrophobic groups in a predominantly hydrophilic network may serve to increase load bearing yet with avoidance of the brittleness caused by carbon–carbon crosslinking.[2]

Hydrophobic groups have been introduced by copolymerization of various hydrophobic monomers with hydrophilic monomers, such as acrylamide. *N*-2-vinyl-pyrrolidone, and 2-hydroxyethymethacrylate.[3–5] 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 humankind. Although some treatment methods have been developed, economic removal of dyes still remains a significant problem.[6]

Dyeing and finishing wastewaters in the 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[7] 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 because of their economic advantages.[8]

The present study was designed to investigate the efficiency of prepared hydrogels, such as NVP/AN treated, NVP/AN untreated, and NVP/MMA copol-

ymers, in the removal of some dyes such as direct, reactive, and acid dyes from wastewater.

EXPERIMENTAL

Materials

Acrylonitrile (AN), methylmethacrylate (MMA), and N-vinyl-2-pyrrolidone (NVP Merck, Darmstadt, Germany) of purity 99%, were used without further purification.

The other chemicals and phosphate buffers were reagent grade and used as received.

The three types of dyes used, acid (Acid fast yellow), direct (Direct blue 3B), and reactive (Reactive red SH.B), were reagent grade.

Radiation copolymerization of hydrogel

Different comonomer compositions were prepared and subjected to γ-irradiation to different doses at a fixed dose rate of 1.43 Gy/s. Distilled water and a water/methanol mixture were used as diluents for the copolymerization processes. The prepared copolymer hydrogels were then dried at room temperature and weighed (W_d). The synthesized hydrogel with acrylonitrile was then treated with a hydroxylamine–hydrochloride solution (pH = 7) at 80°C for 3 h under reflux.[9] The prepared amidoxime was washed with distilled water to remove the hydroxylamine, and then dried at 70°C for 6 h.

Swelling measurements

The clean, dried, copolymerized hydrogels of known weights were immersed in distilled water at room temperature. Each hydrogel was removed from water after various time intervals and the excess water on the surface was removed, blotted by absorbent paper, and quickly weighed, then returned to the distilled water until equilibrium was reached (24 h in most cases). The water uptake (swelling %) was calculated as follows:

$$\text{Water uptake } \% = [(W_s - W_d)/W_d] \times 100$$

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

Gel determination

A known weight of the dry copolymer was extracted in distilled water for 48 h at 100°C to determine the insoluble parts of the hydrogel. The insoluble parts, taken out and washed with hot water to remove the soluble part, were then dried and weighed. This ex-

traction cycle was repeated until the weight became constant. The gel fraction yield in the hydrogel was determined from the following equation:

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

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

X-ray diffraction (XRD) measurements

X-ray diffraction patterns were obtained with a XD-DI Series apparatus (Shimadzu, Kyoto, Japan), using nickel-filtered and Cu–K_α target. This technique was performed to clarify the changes in morphological structure caused by the copolymerization process.

Thermal gravimetric analysis (TGA)

A Shimadzu TGA system (Type TGA-50), in nitrogen atmosphere at 20 mL/min, was used in this study in the temperature range from ambient to 600°C at a heating rate of 10°C/min.

Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained using a JSM-5400 scanning electron microscope (JEOL, Tokyo, Japan).

Measurements of adsorption capacity

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

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

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

where m is the weight of dry hydrogel (g); V is the volume of solution (L); K and n are constants; and C_1 and C_2 are the concentrations of dye solution before and after adsorption (mg/L), respectively, which are determined by UV–visible spectrophotometry at identical wavelengths, using the standard calibration curve previously determined.
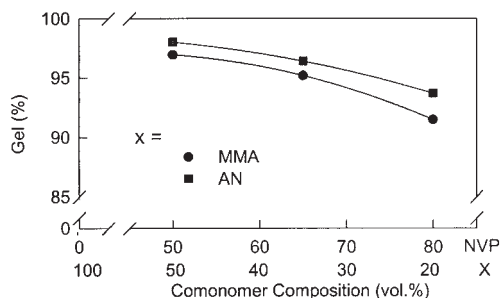
Figure 1 Effect of NVP content on gel (%) for NVP/AN copolymer hydrogel in H_2O/MeOH and NVP/MMA copolymer hydrogel in H_2O. Dose: 15 kGy.

Figure 3 Effect of dose on the gel (%) for NVP/AN copolymer hydrogel at different NVP/AN compositions. Comonomer concentration, 80 vol %, in H_2O/MeOH (80/20 vol %).

RESULTS AND DISCUSSION

Effect of copolymer composition

The influence of NVP/AN and NVP/MMA composition on the gel fraction yield formed in the respective copolymer was determined and is shown in Figure 1. It is observed that as the NVP content increases, the gel fraction yield decreases. This behavior is observed for both NVP/MMA and NVP/AN binary monomer systems in which the content of gel is slightly higher for NVP/AN at a given composition. These results indicate that enhancement of the crosslinking process arising from the monomer-rich solution and also the enhancement of such monomers for the crosslinking process[10] are attributed to the high electric potential of AN, carrying alone pair of electrons (charge) on the nitrogen atom and the probable electron delocalization, which increase the electric potential over that of the NVP/MMA hydrogel.

Effect of irradiation dose

The effect of radiation dose on the gel fraction yield in NVP/AN and NVP/MMA systems is shown in Figures 2 and 3, respectively. It is observed that the higher the dose, the higher the gel fraction yield is obtained, at a given comononer composition. Results
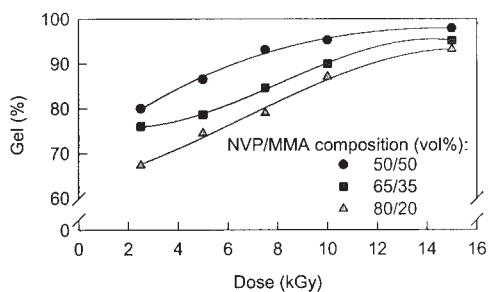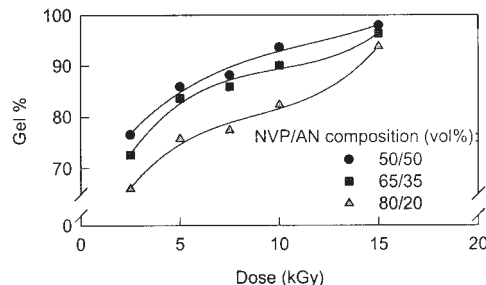
also indicated that the crosslinking process in the prepared hydrogel is enhanced at higher doses. Meanwhile, the lower the NVP content in the comonomer composition, the higher the gel fraction yield obtained. This behavior is observed for both NVP/AN and NVP/MMA systems.

The results suggested that the concentration of free radicals formed in the NVP/monomer system increases with irradiation dose, which increases the gel fraction yield or, in other words, the crosslinked network structure.

Characterization and some selected properties of the hydrogel

Swelling behavior

Determination of the degree of swelling is used in practice for testing finished polymer articles intended for service in liquid media. The influence of swelling time on the water uptake percentage for different hydrogels, prepared at various comonomer compositions, is shown in Figures 4 and 5, respectively. It can be seen that the water uptake percentage increases as the swelling time increases, to reach a certain limiting value after almost 8 to 10 h, which is called here the equilibrium swelling degree (S_{max}), for NVP/MMA and NVP/AN copolymers. The NVP-rich content in
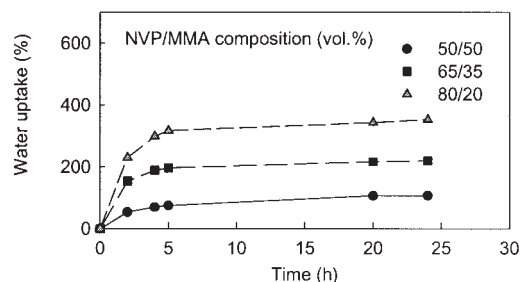

Figure 2 Effect of dose on the gel (%) for NVP/MMA copolymer hydrogel at different NVP/MMA compositions. Comonomer concentration: 80 vol %.

Figure 4 Effect of swelling time on the water uptake (%) for different NVP/MMA compositions, at 15 kGy.
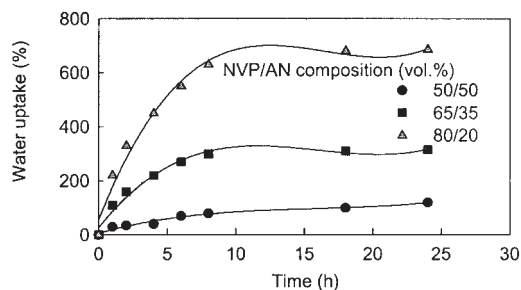
Figure 5 Effect of swelling time on the water uptake (%) for different NVP/AN compositions, at 15 kGy.
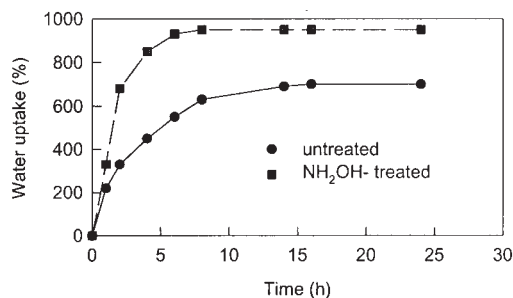

Figure 6 Effect of swelling time on the water uptake (%) for NH$_2$OH-treated and untreated NVP/An (80/20 vol %) copolymer hydrogel, at 10 kGy.

the initial comonomer feed solution resulted in the hydrogel having higher swelling behavior. It also shows a value of S_{max} at a certain swelling time, which varies depending on the comonomer composition and swelling time.

The influence of irradiation dose on the water uptake percentage for the hydrogels prepared at different compositions, for NVP/MMA and NVP/AN hydrogels, is shown in Table I. Meanwhile, the S_{max} in NVP/MMA increases with irradiation dose up to 15 kGy and thereafter it decreases. This phenomenon is attributed to the enhancement of the crosslinking process at higher doses and, as a consequence, the diffusion and swelling properties are hindered by network structure formation, although in the NVP/AN hydrogel it decreases with increasing irradiation dose.[1]

Amidoxization of the nitrile (CN) groups, by reacting the hydrogel with hydroxylamine, causes further modification for the hydrogel with respect to hydrophilicity and chelation properties.[9] Figure 6 shows that the water uptake percentage for treated NVP/AN hydrogel is higher than that for untreated NVP/AN hydrogel because of the increase in hydrophilic properties.

Thermal gravimetric analysis (TGA)

Investigating the change in thermal properties of NVP/MMA and NVP/AN hydrogels is important for

their application as well as characterization and determination of the chemical and physical changes occurring by copolymerization.

From a practical perspective, the prepared hydrogel should possess good thermal stability in the range of applicable temperature. Figures 7 and 8 show TGA curves and weight loss of the prepared hydrogels as a function of temperature. TGA curves of different hydrogels reveal that there are three distinct steps of weight loss. It is suggested that in the initial stage of the thermal diagram, in the range from ambient temperature to 250°C, the weight loss is a result of the dehydration process of the water contained in such a hydrophilic hydrogel. At the second stage, from 250 to 450°C, there is decomposition in the side groups and branches of the hydrogel. However, at the third stage, above 450°C, the weight loss is attributed to the main chain scission in the polymer chain and matrices. Heating the hydrogel at a temperature higher than 450°C results in rapid decomposition to carbon dioxide and volatile hydrocarbons. When compared between different compositions of NVP/AN hydrogels, the degradation temperatures shift toward the pure PAN degradation with the increase of AN content in the hydrogels.

It was reported that TGA of pure PAN shows that only 35% of PAN degraded by heating up to 600°C. The reason for this is the ring formation between CN groups, which leads to very high thermal stability. For the pure PNVP it shows characteristic single-step degradation, with a maximum at 458°C and 98% of weight loss.[9]

Application of prepared hydrogels in treatment of waste dyes

The removal of dyes from textile wastewater is a major environmental problem because of the difficulty of treating such water by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and
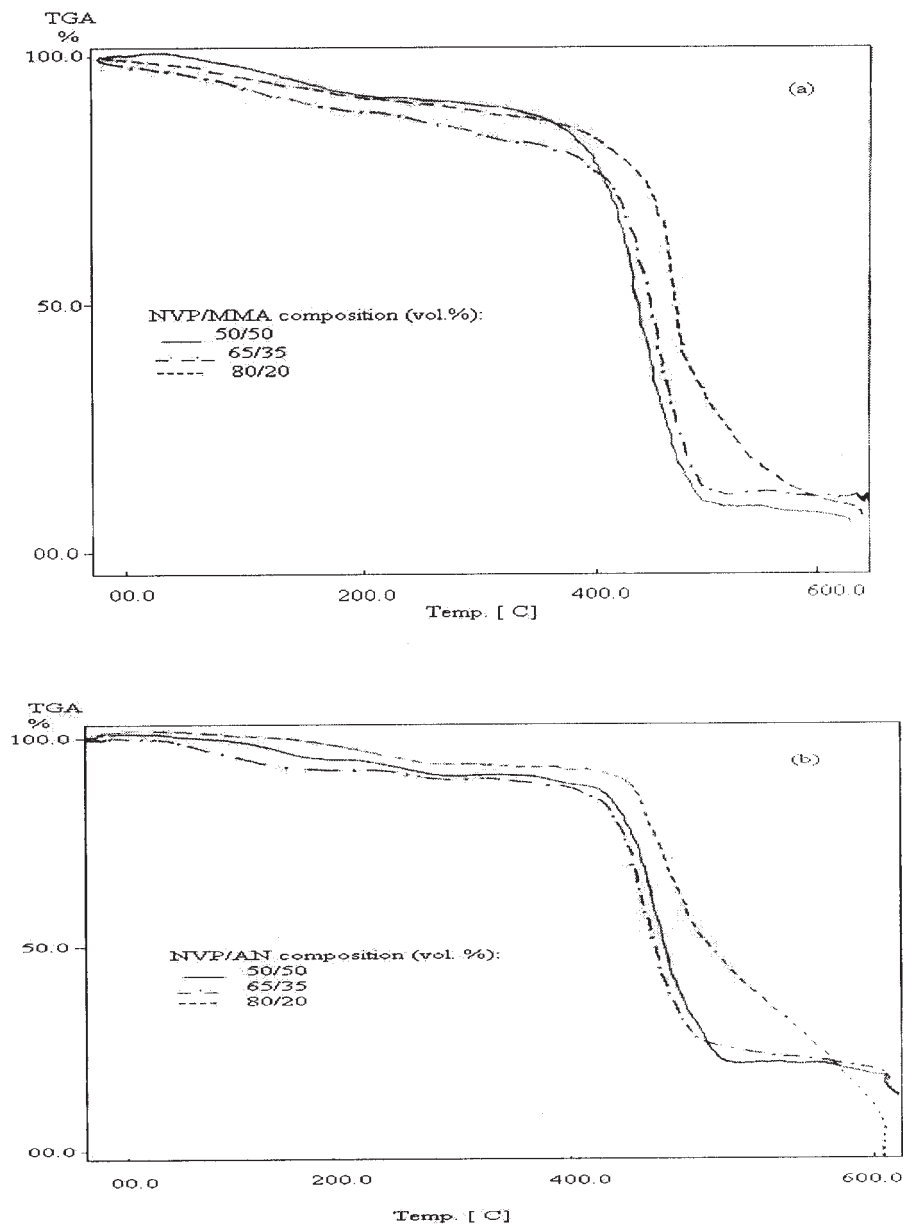
TABLE I
Effect of Comonomer Composition and Dose (kGy) on the Water Uptake %, at Swelling Time of 6 h

Dose (kGy)	Water uptake (%)					
	NVP/AN vol %			NVP/MMA vol %		
	50/50	65/35	80/20	50/50	65/35	80/20
5	200	420	700	30	85	200
7.5	185	400	650	87	180	332
10	170	355	599	96	219	353
15	160	375	500	107	230	364
20	149	350	470	93	211	353

Figure 7 TGA thermograms for different hydrogel compositions: (a) NVP/MMA; (b) NVP/AN.

agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions.[11] Hydrogels are crosslinked hydrophilic polymers that swell in water, usually to equilibrium. The adsorption of these pollutants was studied for the three groups of dyes (acid, direct, and reactive). The adsorption of the pollutants on prepared hydrogels such as NVP/MMA, NVP/AN, and treated NVP/AN hydrogels was investigated at various pH values using equilibrium studies. The concentration of the dyes ranged from 25 to 100 mg/L.

PVP can be cationic in character on the polar lactam ring because of the resulting ketoenol tautomerism.[12] Furthermore, electrostatic interactions together with hydrophobic interactions and hydrogen bonding can occur between cationic groups of NVP and anionic groups of the dyes. Hydrophobic effects are specifically aqueous solution interactions, which in the present case will involve the aromatic rings and the methyl and methine groups on the dye molecules and methine groups on the gel. Hydrogen bonding will be expected to occur between amine groups of the oxygen atom on the dye molecules and the carbonyl groups on the monomer units of the crosslinked copolymer.

Although poly(vinyl pyrrolidone) in aqueous solution is shown by electrophoresis to carry a net nega-
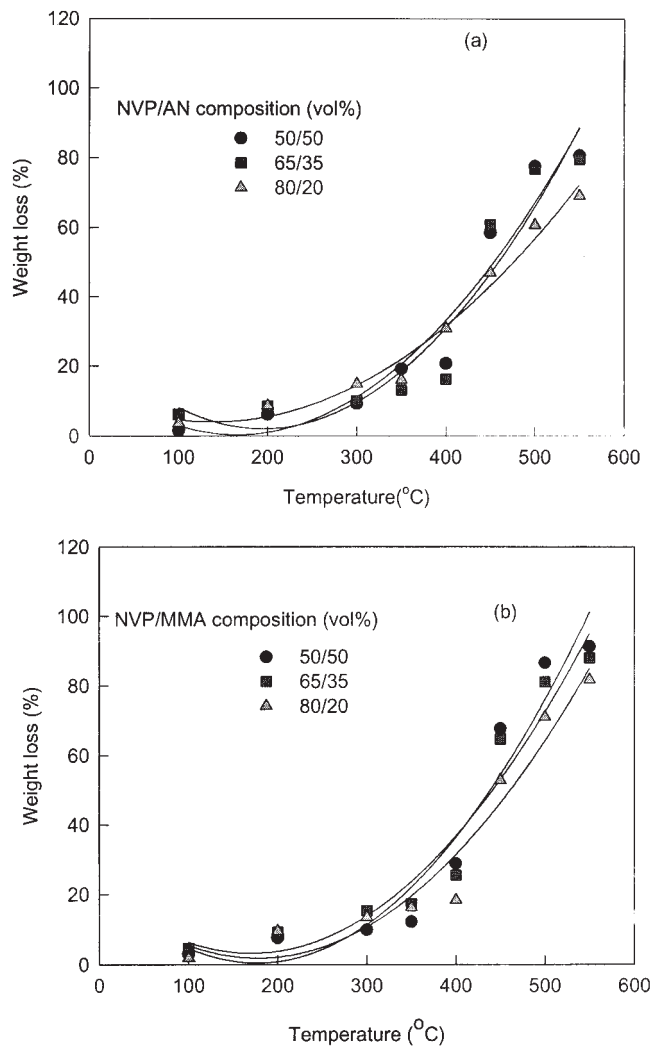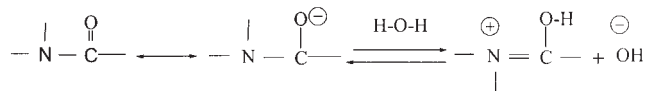
Figure 8 Effect of comonomer composition on the weight loss (%) at various elevated temperatures prepared at 20 kGy for (a) NVP/AN hydrogels and (b) NVP/MMA hydrogels.

tive charge, a partially positive charge on a nitrogen atom can be considered by the following scheme:

Effect of treatment time

The time needed for treatment of wastewater dye is an important factor from an economical perspective. In this respect, the effect of treatment time on dye uptake and its maximum was investigated. Figure 9(a)–(c) shows the dye uptake as a function of time for different dyes using NVP/MMA, and both untreated and treated NVP/AN hydrogels. Results show that the dye uptake increases with time, to reach its maximum

after 6 days. This behavior is observed for all hydrogels investigated here (direct, acid, and reactive dyes).

To ensure attainment of equilibrium dye uptake, the dyeing was carried out for 8 days. The NH_2OH-treated ones were imparted a characteristic dyeability as a result of the introduction of amidoxime groups in the polymer structure. This functional group has an affinity for the anions of the reactive, acid, and direct dye molecules. It must be noted that the treated NVP/AN hydrogel has a higher affinity toward these dyes and this also a result of its high affinity toward swelling in water, a behavior that facilitates the diffusion of dye through its matrices.

To investigate the nature of the interaction between the dye and poly(NVP/AN) hydrogel, FTIR spectroscopy for hydrogel–dye interaction was performed and results are shown in Figure 10. The band observed at 3416 cm^{-1} is the N—H stretching band of the secondary amine group in dye; the absorbance in the range of $3100–3500 \text{ cm}^{-1}$ is attributed to O—H and N—H
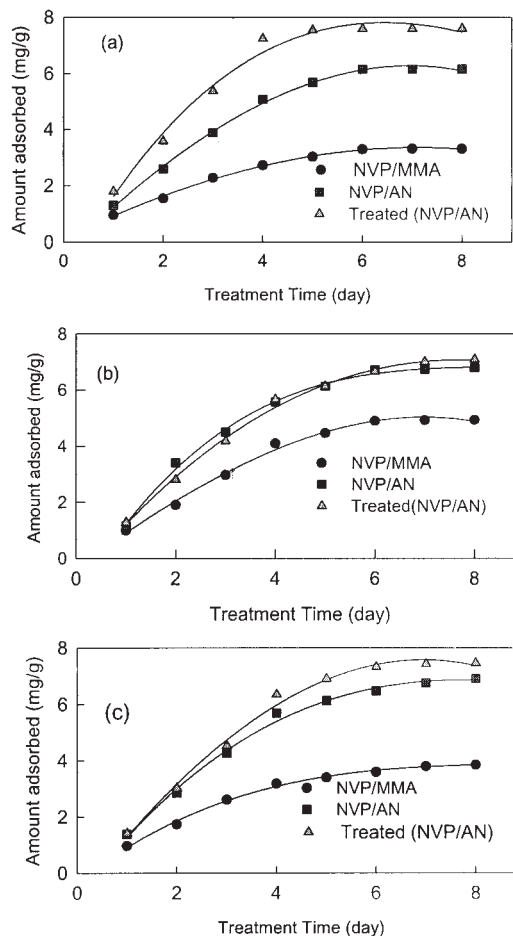

Figure 9 Effect of treatment time on the dye uptake for different hydrogels, at initial feed concentration of 100 mg/L and pH 7: (a) Acid fast yellow G; (b) Direct blue 3B; (c) Reactive red SH.B.
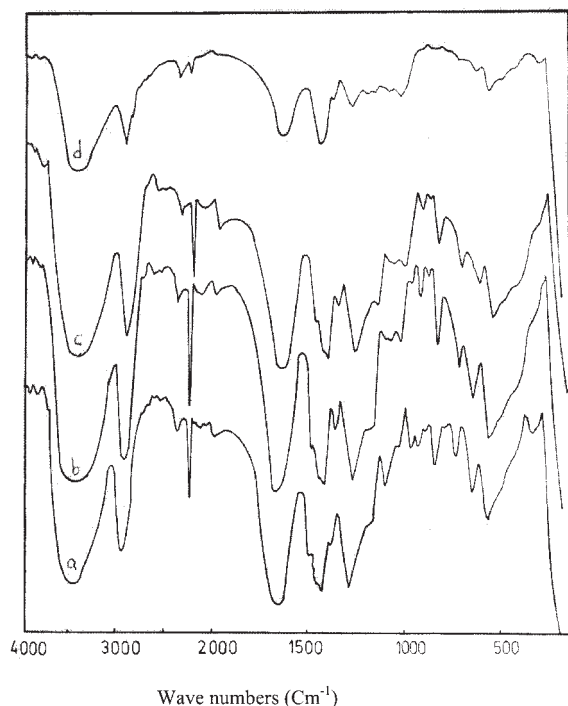
Figure 10 IR spectrum of NVP/AN copolymer hydrogel before and after uptake of some dyes: (a) NVP/AN hydrogel; (b) Reactive red SH.B; (c) Acid fast yellow G; (d) Direct blue 3B.

bands in poly(NVP/AN)–dye and poly(NVP/AN) hydrogel. The absorbance observed at 3424 cm^{-1} in poly(NVP/AN)–Direct blue 3B is the N—H stretching band of the secondary amine group in Direct blue 3B. The weak peaks at 2900 cm^{-1} are attributed to C—H stretching bands. The C=O group gives an absorption peak at 1660 cm^{-1}. An aliphatic C—N stretching band is observed at 1175 cm^{-1} in Acid fast yellow G, and an aromatic C—N band is observed at 1371–1381 cm^{-1} in structure. The band observed at 1452 cm^{-1} is attributed to N=N group in dyes.

Effect of pH of the feed solution

Each dyestuff is applied in a bath of specific pH at which the efficiency of the colored component is maximum. The effect of pH of the bath (i.e., hydrogen ion concentration) on the dye uptake for the hydrogels was investigated and results are shown in Figure 11(a)–(c). From the results it may be seen that the uptake of direct and reactive dyes decreases with increasing pH, until it reaches its minimum value at pH 10. Meanwhile, the dye uptake for the NH$_2$OH-treated hydrogel is higher than that for the untreated hydrogel. By increasing the pH, the efficiency of the color component of the dye decreases and consequently the dye uptake decreases. For acid dye, the dye uptake

decreases with increasing pH, up to pH 7, then starts to increase at a faster rate beyond pH 7.

It has been well established that the change in pH of the dye solution affects the structure of the dye as well as the structure of the polymeric material itself. Considering that the mechanism of dye uptake is attributed to the electrostatic attraction force between the dye and the polymeric material, any change in either charge would affect the uptake percentage.

The relationship between log equilibrium concentration (residual concentration) and log amount adsorbed (log adsorption capacity mg/g) at different pH values was calculated and results are presented in Table II for the different hydrogels. The numerical values for k show high adsorption affinity of the adsorbents at different pH values. Variation in the slopes ($1/n$) and intercepts of the line (k) reflect the effect of physicochemical characteristics of the dyes on the adsorption process and their affinity for adsorption. In general, as the k-value increases the adsorption capacity of adsorbent for a given compound increases. The
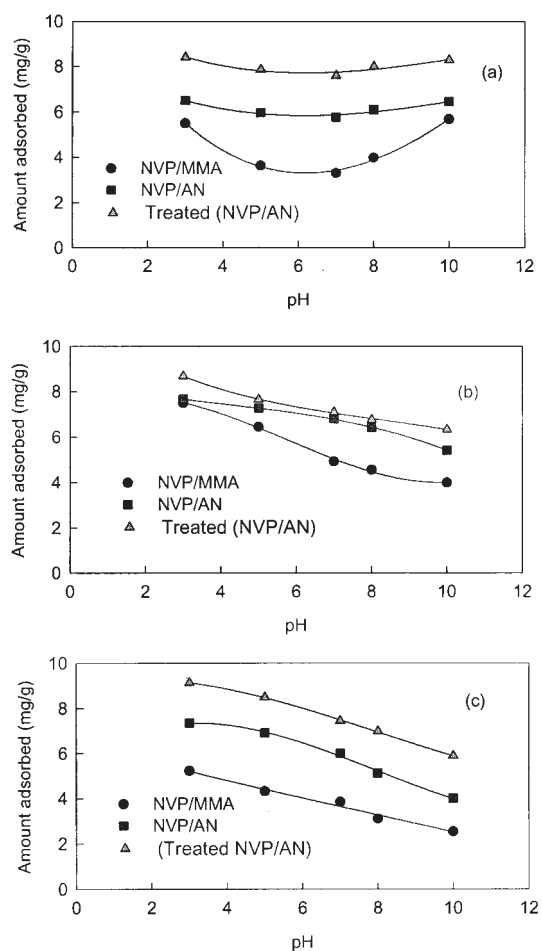

Figure 11 Effect of pH on the dye uptake for different hydrogels, at initial feed concentration of 100 mg/L: (a) Acid fast yellow G; (b) Direct blue 3B; (c) Reactive red SH.B.

TABLE II
Adsorption Isotherm Parameter (Freundlich Constants k and $1/n$) for Different Hydrogels and Different Dyes at pH 3

Dye	Type of hydrogel					
	NVP/AN treated		NVP/AN untreated		NVP/MMAc	
	$1/n$	k	$1/n$	k	$1/n$	k
Acid fast yellow G	1.13	0.531	1.12	0.126	1.031	0.1
Direct blue 3B	1.44	1.37	1.36	3.39	1	0.19
Reactive red SH.B	0.935	1.66	0.757	1.096	0.92	0.37

slope of the isotherm line may also characterize the adsorption process. Steeper slopes indicate relatively good adsorption of the compound when present in high concentration. Slight slopes indicate comparable adsorption over the entire range of concentrations. Consequently, the adsorption parameters (k and $1/n$) describe, on a quantitative basis, the adsorption pro-
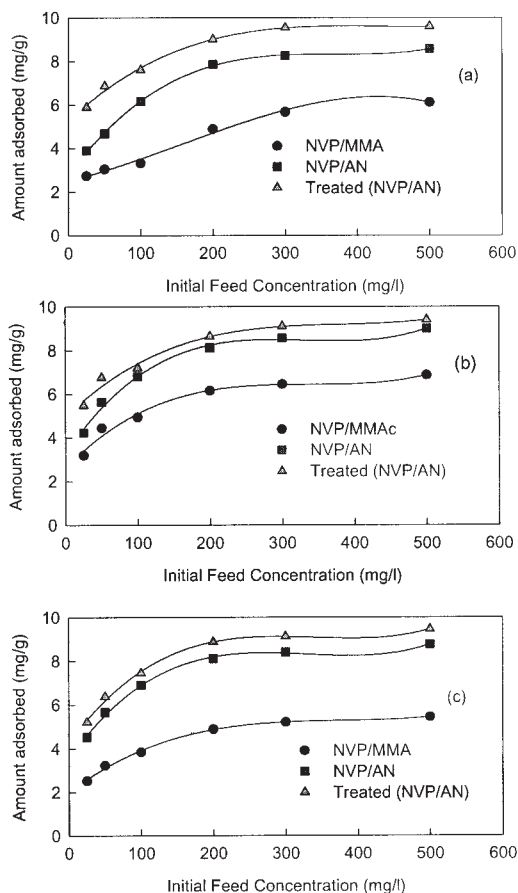

Figure 12 Effect of initial concentration on the dye uptake for different hydrogels; time 6 days: (a) Acid fast yellow G; (b) Direct blue 3B; (c) Reactive red SH.B.
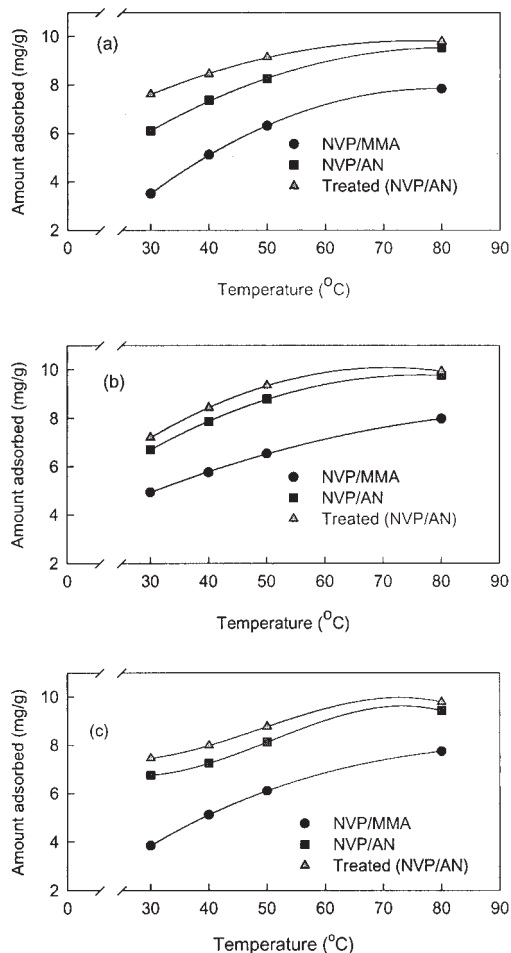

Figure 13 Effect of temperature on the dye uptake for different hydrogels, at initial concentration of 100 ppm and pH 7: (a) Acid fast yellow G; (b) Direct blue 3B; (c) Reactive red SH.B.

cess and account for the variation in adsorbent doses required for the removal of dyes.[13,14]

Effect of initial feed concentration

The effect of initial feed concentration of different dyes was investigated and results are shown in Figure 12(a)–(c). It can be seen that the dye uptake initially increases with the feed concentration up to 200 mg/L; thereafter, it tends to level off. This behavior is observed for all types of dyes investigated and also for different hydrogels. Meanwhile, the treated NVP/AN hydrogel possesses a higher affinity toward dye uptake, and the NVP/MMA hydrogel, a lower affinity.

Effect of temperature

The temperature of the medium is an important factor in determining the dye uptake by hydrogels. Figure 13(a)–(c) shows the relation between the amount of

dye uptake and temperature. It can be seen that the dye uptake increases with temperature. This means that, as the temperature increases, the diffusion of the dye takes place directly into the hydrogel, which is in the mobile phase because of thermal effect that enhances the diffusion of dyes. The kinetic energy of the dye molecule increases concomitantly with the increases temperature, leading to higher diffusion of the dye molecules to the dyeing sites. Diffusion is a function of the ease of penetration of the dye molecules through the polymer matrix. It was observed that the maximum dye uptake was obtained at 60°C of the solution after 6 h in the case of direct dye and 8 h in the case of acid and reactive dyes.

To determine the thermodynamic parameters, adsorption experiments were repeated at constant concentration (100 mg/L) at 25 and 35°C. Adsorption heats (ΔH), adsorption free energy (ΔG), and adsorption entropy (ΔS) of hydrogel–dye systems were calculated by the following equations:

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

$$\Delta G = -RT \ln k$$

$$\Delta G = \Delta H - T\Delta S$$

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. Figure 14(a)–(c) shows In C_e versus $1/T$; the slopes of these graphs give $\Delta H/R$ values. The thermodynamic parameters of the hydrogel–dye systems were calculated at 25°C and results are tabulated in Table III.

Some of ΔG values for the hydrogel–dye systems are negative; therefore the binding process of Direct blue 3B and Reactive red SH.B onto treated and untreated NVP/AN hydrogels results in spontaneously negative enthalpy values, suggesting that these adsorption processes are exothermic.

If ΔH values are <20 kJ mol^{-1}, then the adsorption process is that of physical adsorption. This occurs in the case of NVP/MMA hydrogel with any kind of dyes but in the case of treated and untreated NVP/AN the ΔH values are >20 kJ mol^{-1} and thus the adsorp-
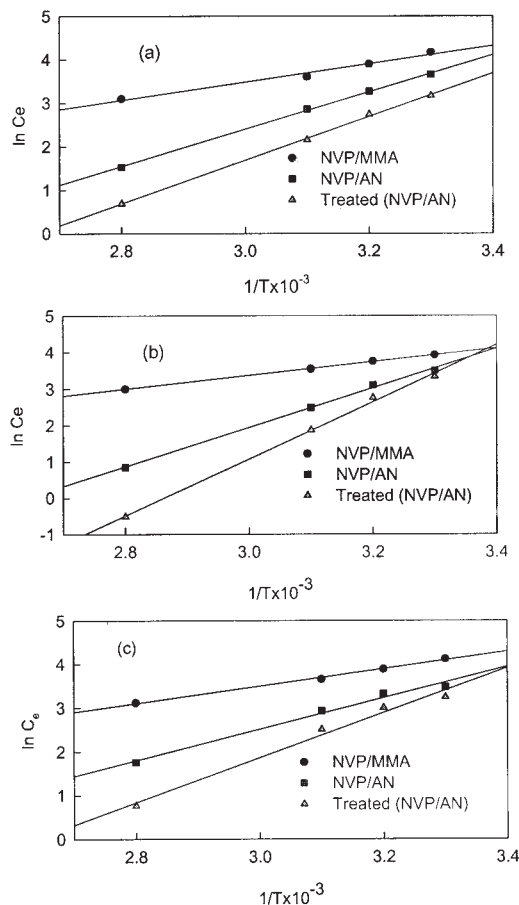

Figure 14 Variation of ln C_e of hydrogel–dye system with $1/T$, at initial feed concentration of 100 mg/L and pH 7: (a) Acid fast yellow G; (b) Direct blue 3B; (c) Reactive red SH.B.

tion process is that of chemical adsorption. On the other hand, hydrogel–dye systems show positive entropy of adsorption; thus the electrostatic repulsion weakens the adsorption force and increases the degree of freedom of the molecules.

The resultant phenomena in the binding mentioned show that the hydrophobic portions of the dyes play an important role in enhancement of the binding in aqueous surroundings.[15] Thus hydrophobic interaction must be appreciated to interpret this situation. The increase in the binding arises from the attachment

TABLE III
Thermodynamic Parameters of Hydrogels: Interaction of Dyes at pH 3 and 25°C

Dye	NVP/MMA			NVP/AN (untreated)			NVP/AN (treated)		
	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (eu)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (eu)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (eu)
Acid fast yellow G	17.1	5.7	38.3	35.4	5.13	102	41.2	1.57	133
Direct blue 3B	15.3	4.11	37.5	44	−3.03	158	63.8	−0.83	217
Reactive red SH.B	16.6	2.46	47.5	28.58	−0.26	96.8	41.14	−0.38	139

of the nonpolar portions of the dyes to the hydrophobic loci on the polymer, and this binding arises from a hydrophobic interaction between the two hydrophobic parts.

X-ray diffraction

Results of X-ray diffraction of the NVP/AN hydrogel before and after adsorption by different pollutant (dyes) are shown in Table IV. This technique is used to represent the morphological structure and the change in its crystal form resulting from the effect of swelling and interaction of pollutant compounds onto the hydrogel polymer structure. The diffraction curves of the dye uptake in the hydrogel record the change between 2θ for NVP/AN before and after the dye's uptake is observed. However, a difference in the particle size d (Å) is found and determined by Schrer equation[16] as follows:

$$d(\text{Å}) = \frac{K\lambda}{\beta_{1/2}\cos\theta}$$

TABLE IV
X-ray Diffraction Patterns for NVP/MMAc and NVP/AN Hydrogels Before and After Dye Adsorption

Lattice parameter	NVP/ MMA hydrogel	NVP/AN hydrogel			
		Without dye	Acid fast yellow G	Direct blue 3B	Reactive red SH.B
2θ	16.318	23.671	13.308	29.786	28.597
FWHM°	1.016	0.680	5.351	0.00	0.00
$\beta_{1/2}$ (radian)	0.018	0.012	0.0933	0	0
d (Å)	76.936	116.73	14.794	—	—
Integrated intensity (counts)	670	135	1480	0	0

where K is the Schrer constant (0.89), λ is the wavelength of the X-ray beam (1.5405), $\beta_{1/2}$ is the full width half maximum (FWHM) in radians, and θ is the diffraction angle of the main diffraction line.
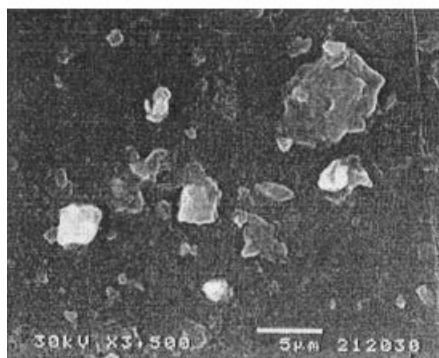
The integrated intensity (counts) is taken as an indication of the amorphous and crystallinity percent-
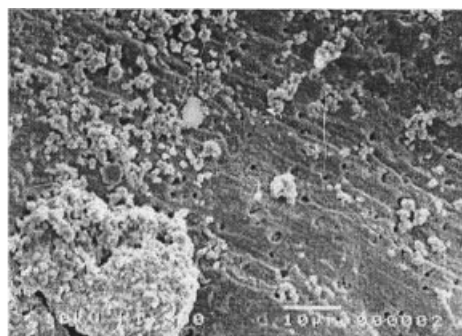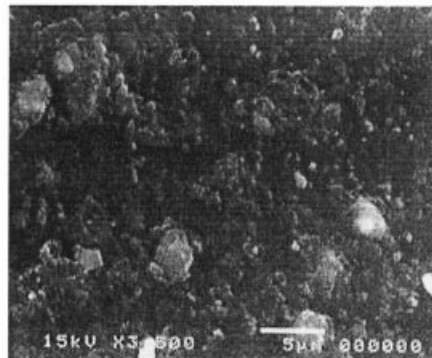

NVP/AN (hydrogel free)

Reactive red SH.B

Acid fast yellow G

Direct blue 3B

Figure 15 SEM micrographs of NVP/AN hydrogel (free and containing different dyes).

age of the polymer according to the area under the peak obtained from the charts of X-ray diffraction patterns. It was found that when the integrated intensity increases, the crystallinity also increases. It is also shown in Table IV that the hydrogel–dye free and hydrogel–dye complexes are in the amorphous state and almost no change is observed.

Scanning electron microscopy

Scanning electron micrographs of NVP/AN hydrogel before and after dyes uptake are shown in Figure 15. It is shown that the surface of NVP/AN hydrogel before uptake of dyes is smooth, but the surface of the hydrogel after uptake of dyes became

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