

# Radiation Crosslinking and Sorption Properties of Hydrogels Based on 1-Vinyl-2-Pyrrolidone, Hydroxyethyl Methacrylate, and Their Copolymers

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**ABSTRACT:** This work has been concerned with the synthesis of the hydrogels of poly (vinyl pyrrolidone) (NVP), poly (hydroxy ethylmethacrylate) (HEMA), and their copolymer under the effect of gamma radiation in the presence of *N,N*-methylenebisacryl-amide (MBAm) as a crosslinking agent. The effect of the different factors that may affect the gelation and yield product, such as solvent composition and irradiation dose, was investigated. The formed hydrogels were characterized in terms of swelling in water and different organic solvents, X-ray diffraction (XRD), and IR spectroscopic analysis. The sorption capability of these hydrogels towards some commercial basic and acid dyes was also studied. The results showed that a solvent mixture composed of equal contents of water and methanol is the

most suitable to afford the minimum sol fraction and the highest yield product at a minimal irradiation dose of 10 kGy. It was observed that NVP hydrogel displayed the highest swelling in water, alcohols, and dimethylformamide of ~1300% and a lower tendency to swell in nonpolar solvents. The results showed that HEMA hydrogel has a high affinity to absorb basic dyes while NVP has a tendency for acid dyes. Also, the sorption of either the basic or acid dyes by the different hydrogels was found to greatly depend on the concentration of dye in solution and the mass of the used hydrogel. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3274–3280, 2004

**Key words:** radiation; crosslinking; hydrogels; dye sorption

## INTRODUCTION

Radiation synthesis and application of hydrogels have been of increasing interest in recent years, particularly in the field of biomaterials to replace tissue, organ, or function of the body.<sup>1–3</sup> More promising hydrogels are used as wound dressings to inhibit the loss of body fluids, deliver oxygen to the wound, and thus accelerate the healing process.<sup>4,5</sup> Also, a very important application of hydrogels is in the field of a drug delivery system, in which they enable sustained and controlled release of embedded medicines to body fluids after their implantation, injection, or otherwise introduced into the organs.<sup>6,7</sup>

Contrary to the physical form of hydrogels through weak interaction between chains, radiation-formed hydrogel macromolecules are connected to each other through covalent bonds, which makes them non-soluble even at high temperatures. Therefore, it is one of our interests to prepare hydrogels under the effect of gamma radiation and to investigate their applica-

tion in the removal of toxic pollutants. In this regard, hydrogels based essentially on polyacrylic (PAAc) acid with trithioglycolic acid or 2-mercaptobenzimidazole were recently synthesized by gamma radiation crosslinking and applied in the recovery of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  ions.<sup>8,9</sup>

In the textile industry, different dyestuffs, belonging to different classes, are being used in dyeing natural and synthetics.<sup>10</sup> The residual of these aromatic compounds from the dyeing process causes a great pollution problem due to the nonbiodegradability of these materials by ordinary methods. Therefore, the sorption of some dyestuffs from wastewater by hydrogels based on PAAc/glycerol or ethylene glycol synthesized by gamma radiation was investigated.<sup>11,12</sup> Also, the sorption of acid and basic dyes from wastewater by insoluble poly(vinyl alcohol)/carboxymethyl cellulose blend was studied.<sup>13</sup>

Even though there is extensive work on the preparation of hydrogels based on NVP<sup>14–17</sup> or HEMA,<sup>18–20</sup> there are no available reports on the preparation of hydrogels based on their copolymers. In the present work, the factors that may affect the radiation crosslinking of different hydrogels based on *N*-vinyl pyrrolidone and hydroxyethyl methacrylate was investigated. Also, the sorption of some acid and basic dyes by these hydrogels was studied.

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## EXPERIMENTAL

### Materials

A laboratory grade of the monomers N-vinyl pyrrolidone (NVP) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Merck (Germany) and used as received. *N,N*-methylenebisacrylamide (MBAm) as a crosslinking agent was of laboratory grade and was obtained from BDH, England. All the organic solvents used in the swelling study were of pure grade and used as received without further purification.

### Preparation of hydrogels

The hydrogels were prepared by dissolving the ratio (w/v %) of the individual monomers (NVP or HEMA) or their comonomers with a constant ratio of the crosslinking agent MBAm of 0.5 w/v % in the solvent mixture (v %) in test tubes such that the total volume of solution was 15 mL. The comonomer mixture is composed of equal ratios of NVP and HEMA throughout this work. The tubes were then subjected to gamma radiation for different durations to obtain different doses (5–15 kGy) depending on a dose rate of 7.2 kGy h<sup>-1</sup>. Gamma irradiation was carried out in the cobalt-60 cell facility of the National Center for Radiation Research and Technology, Cairo, Egypt. The contents of the tubes were washed thoroughly with bidistilled water to remove unreacted monomers, while homopolymer formed was removed by extraction with bidistilled water and drying in a vacuum oven until constant weight.

### Determination of sol fraction

Samples of the prepared hydrogels were accurately weighed ( $W_0$ ) and then extracted with bidistilled water using soxhlet system for 24 h. After extraction, the samples were dried in a vacuum oven at 50°C to a constant weight ( $W_1$ ). The sol fraction was calculated according to the following equation.

$$\text{Sol fraction (S.F)} = (W_0 - W_1)/W_0$$

### Swelling behavior in water and different organic solvents

A known weight of the insoluble hydrogel ( $W_1$ ) was soaked in bidistilled water and different solvents for 24 h at room temperature. The sample was then removed and blotted on a filter paper to remove the excess water or solvent on the surface and weighed ( $W_2$ ). The percentage swelling was calculated according to the following equation:

$$\text{Swelling (\%)} = [(W_2 - W_1)/W_1] \times 100$$

### IR spectroscopic analysis

The infrared spectra of the different hydrogels were performed on a Mattson 5000 FTIR spectrometer over the range of 200–4000 cm<sup>-1</sup>. The samples for IR analysis were prepared by grinding 5 mg of the hydrogel to a very fine powder and mixed with a highly dried powder (30 mg) of KBr and then pressing to a transparent disk.

### X-ray diffraction analysis

The X-ray diffraction patterns of prepared hydrogels were performed on Shimadzu Diffractometer XD-DI series, which is operated fully automatically. The X-ray copper target tube was operated at 40 kV and 30 mA. All the diffraction patterns were examined at room temperature with scanning speed of 20 mm/min.

### Dye sorption measurements

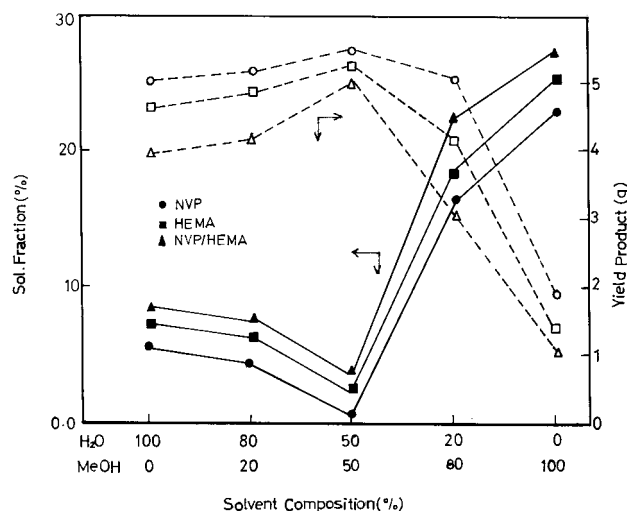
The percentage sorption of Remacryl Blue (basic dye) and Sandolan E-3GL (acid dye) by the different hydrogels was determined by a procedure based on spectrophotometric analysis as described in a previous report.<sup>13</sup> The basic dye was generously supplied by Hoechst, Germany, while the acid one was a product of Sandoz, Switzerland.

## RESULTS AND DISCUSSION

### Effect of solvent composition on sol fraction and yield product

The first process in radiation formed hydrogels is the polymerization of monomer(s) followed by crosslinking reactions, in which the macromolecules are connected to each other through covalent bonds to form a network structure. Polymers can be radiation crosslinked both in the solid state and in solution. However, crosslinking in the solid state requires higher doses before the first insoluble fraction of gel (gelation dose) appears in the system. Moreover, the mobility of chains in the solid state is limited, especially in the case of crystalline areas. It has been reported that the gelation dose of poly(vinyl pyrrolidone) in the solid state is 130 kGy, while its gelation dose in aqueous solution is 3.5 kGy.<sup>20</sup>

Radiation crosslinked hydrogels based on individual N-vinyl pyrrolidone (NVP) and Hydroxyethylmethacrylate (HEMA) as well as their mixture were prepared in the presence of *N,N*-methylenebisacrylamide as a crosslinking enhancer. A solvent mixture composed of various ratios of water and methanol was used as a medium for the preparation of hydrogels under the effect of a constant dose of 10 kGy as shown in Figure 1. The sol fraction of the different hydrogels was found to decrease with increasing the content of methanol component to reach its minimum value at a

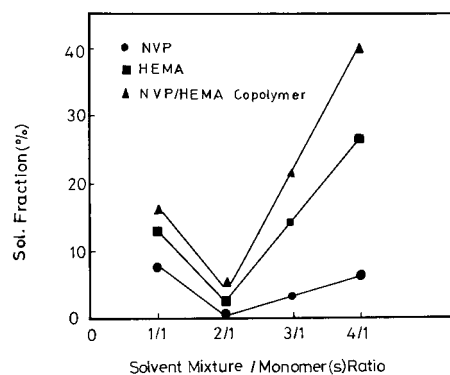


**Figure 1** Effect of H<sub>2</sub>O/MeOH solvent composition on the sol fraction and yield product of different gamma radiation crosslinked hydrogels. Preparation conditions: solvent mixture/monomer(s) ratio, 2/1; irradiation dose, 10 kGy; MBAm ratio, 0.5 w/v %; comonomer composition, NVP/HEMA (50/50 w/v %).

solvent mixture composed of equal ratios of water and methanol. A sudden increase in sol fraction can be observed by increasing methanol content to reach its maximum value at pure methanol. However, the sol fraction of hydrogels prepared in pure methanol is much higher than in pure water. At any solvent composition, the sol fraction of NVP hydrogel is the lowest, NVP/HEMA mixture is the highest, while HEMA hydrogel comes in an intermediate position. On the other hand, the yield product of hydrogels is in accordance with the corresponding sol fraction values at any solvent composition.

#### Effect of solvent mixture/monomers ratio and irradiation dose on the sol fraction

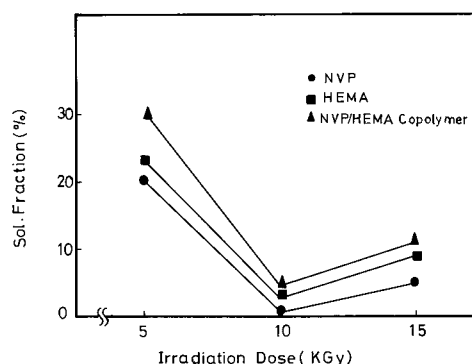
In the above experiment, the solvent mixture/monomers ratio was kept constant throughout at 2/1. It seems that this ratio has a significant effect on the gel formation as shown in Figure 2. Thus, to obtain high gel fraction of the different hydrogels, it is not proper to use equal ratios of monomer(s)/solvent or higher ratios than 1/2. It is evident that an irradiation dose of 5 kGy is not enough to achieve the gel formation of the different polymers, while at high doses of 15 kGy, the sol fraction tends to slightly increase as shown in Figure 3. Meanwhile, at any event of solvent mixture/monomer (s) ratio or irradiation dose, NVP monomer gives the highest gel fraction. This behavior can be attributed to the factor of solubility parameter as well as the  $G(x)$  values of the different systems.



**Figure 2** Effect of solvent mixture/monomer(s) ratio on the sol fraction of radiation crosslinked hydrogels. Preparation conditions: solvent composition, equal ratio of H<sub>2</sub>O and MeOH; irradiation dose, 10 kGy.

#### Swelling behavior of hydrogels in water and organic solvents

Covalent bonds joining the chains of hydrogels are the same bonds as in the main chains, so they are resistant to any solvent. When a hydrogel begins to absorb water or generally speaking, the molecules of solvent, the water molecules hydrate the polar hydrophilic groups in a subsequent steps to form bound water at equilibrium, resulting in hydrogel expanding. The swelling behavior of the different hydrogels, prepared at different conditions of solvent mixture/monomer(s) ratio and irradiation dose, in water and different organic solvents is shown in Tables I and II. It is clear that the percentage uptake of water or the organic solvents by NVP and the copolymer is higher than the HEMA hydrogel. This can also be explained on the basis of the solubility parameters for HEMA and NVP monomer(s). However, it can be seen that NVP has a higher affinity to swell in both polar and nonpolar solvents than HEMA or their copolymer. Thus, it may be concluded that the different kinds of hydrogels



**Figure 3** Effect of irradiation dose on the sol fraction of crosslinked hydrogels. Preparation conditions: solvent mixture/monomer(s) ratio, 2/1; solvent composition, equal ratios of H<sub>2</sub>O and MeOH.

**TABLE I**  
**Water Uptake of Different Radiation Crosslinked Hydrogels Prepared at Different Solvent\*/Monomer(s) Ratios and Different Irradiation Doses**

Solvent mixture/ monomer (s) ratio	Irradiation dose (KGy)	Water uptake (%)		
		NVP	HEMA	NVP/HEMA
1/1	10	1000	53	213
2/1	5	244	223	112
	10	1207	522	977
3/1	15	485	112	100
	10	1070	315	532
4/1	10	796	213	377

<sup>a</sup> In all cases the solvent is composed of equal ratios of H<sub>2</sub>O and MeOH.

have a great affinity for polar solvents rather than nonpolar solvents.

### IR spectroscopic analysis

Figure 4 shows the IR spectra of radiation crosslinked hydrogels prepared at the optimum conditions. For the HEMA hydrogel, as with almost all organic compounds, an absorption band can be seen at 2954 cm<sup>-1</sup>, which is due to the C=O of the ester group. The strong absorption band can be seen at about 3000–3500 cm<sup>-1</sup>, which is possibly due to O—H stretching. The less extensive and less intense of these bands is due to the presence of hydrogen bonding. It is obvious that the IR spectra of the crosslinked hydrogel showed the same spectra of the original monomer, except that the IR spectra does not show the presence of C=C absorption, which is utilized during radiation crosslinking.

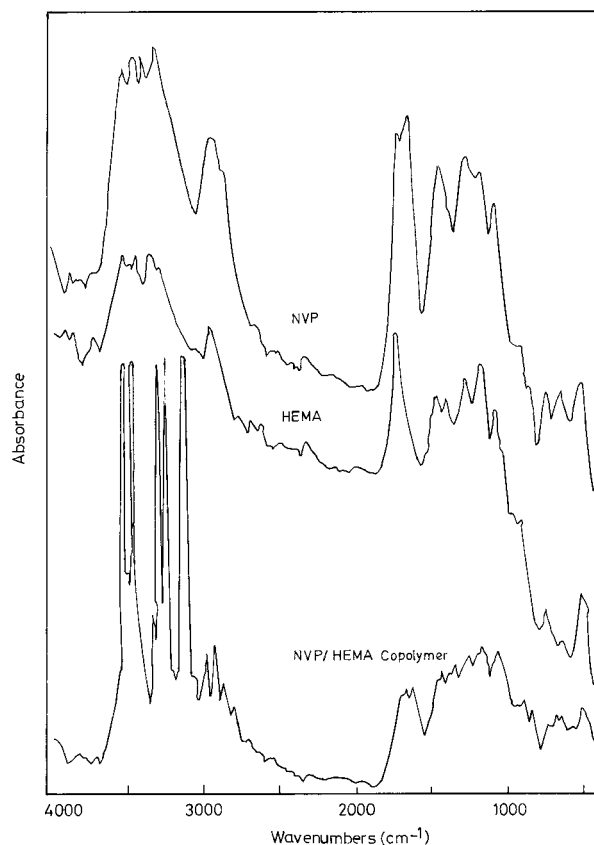
### Sorption of basic and acid dyestuffs by hydrogels

The environment is getting more and more charged with organic pollutants, particularly dye wastes nor-

**TABLE II**  
**Percentage Swelling of Different Gamma Radiation Crosslinked Hydrogels in Different Organic Solvents**

Organic solvent	NVP	HEMA	NVP/HEMA
Methanol	1301	300	520
Ethanol	1290	280	425
Dimethylformamide	1230	112	365
Acetone	98	96	40
Benzene	90	20	50
Toulene	64	20	30

Preparation conditions: solvent mixture/monomer, 2/1; solvent mixture, H<sub>2</sub>O (50%) /MeOH (50%); comonomer, NVP (50%)/HEMA (50%), irradiation dose, 10 kGy; and MBAm ratio, 0.5 w/v %. All these ratios were taken on the basis of a total volume of 15 mL.

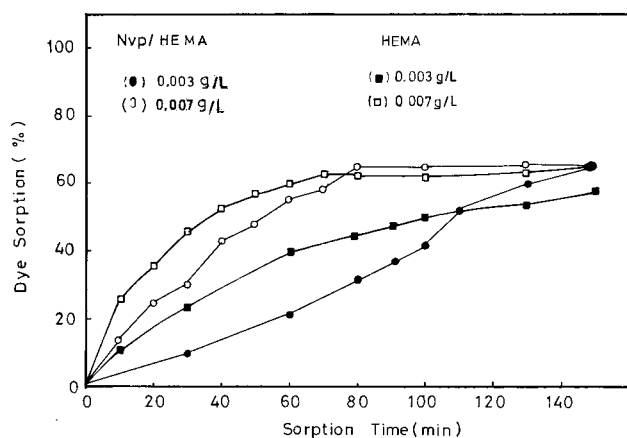


**Figure 4** IR spectra of radiation crosslinked hydrogels.

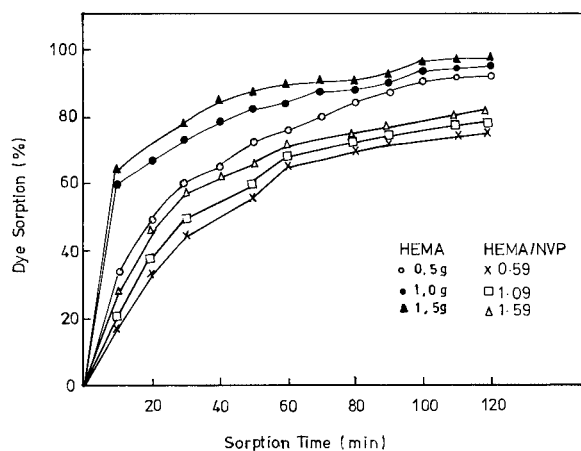
mally released from textile factors. The decomposition of these dyestuffs by extremely severe treatments even with high energy radiation or biodegradation so far is difficult under normal conditions. Synthetic polymeric absorbents used in the sorption of dyestuff have many advantages over other methods such as high mechanical properties even in the swollen state, high thermal stability, chemical resistance, and can be used several times.

In the present work, two dyestuffs usually used in dyeing protein and polyacrylic fibers have been chosen. From the different factors that may affect the sorption of dyestuffs by hydrogels, dye concentration, sorption time, and weight of hydrogels in addition to pH strength and temperature. The preliminary experiments showed that NVP hydrogel has nearly no affinity to absorb the basic dye Remacryl Blue even from concentrated dye solutions or by large masses of the hydrogel even at high temperature.

The dye sorption at room temperature of different concentrations of the basic dye Remacryl Blue by HEMA and its copolymer with NVP hydrogels, as a function of sorption time is shown in Figure 5. It can be seen that the higher the concentration of the basic dye in solution, the higher the dye sorption by both hydrogels. However, the percentage sorption of high concentration by both hydrogels tends to reach



**Figure 5** Dye sorption (%) of different concentrations of the basic dye Remacryl blue at room temperature by gamma radiation crosslinked HEMA and its copolymer with NVP as a function of time.



**Figure 6** Dye sorption (%) of a constant concentration (0.003 g/L) of the basic dye Remcyl Blue at room temperature by different weightes of gamma radiation crosslinked HEMA and copolymer with NVP as a function of time.

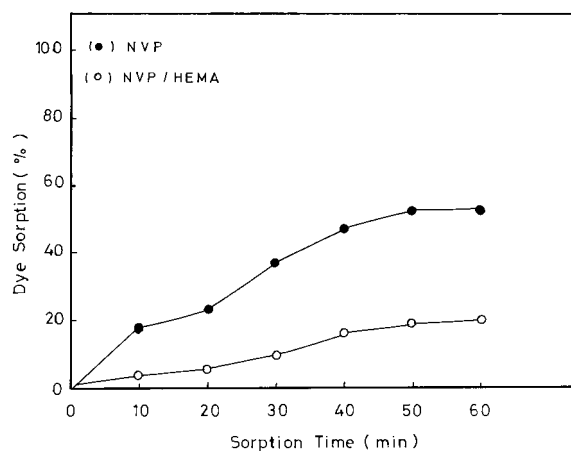
a saturation state after a period of 80 min, while the percentage sorption of low concentrations was found to gradually increase with increasing sorption time. In general, the percentage sorption by HEMA hydrogel is relatively higher than that by NVP/HEMA hydrogel regardless of dye concentration. Meanwhile, the percentage sorption of high concentration of the basic dye by NVP/HEMA hydrogel after a period of 80 min tends to be slightly higher than that by HEMA hydrogel. A similar trend can be observed after a sorption time of 110 min, in which the percentage sorption of low concentration of the basic dye by NVP/HEMA hydrogel is higher than that by the HEMA hydrogel.

In the previous experiment the dye sorption process was performed by a constant mass of hydrogels of 0.5 g immersed in an aqueous solution of constant volume of 15 mL. The sorption of the same basic dye was investigated by different masses of the hydrogels from a constant volume of dye solution as a function of sorption time as shown in Figure 6. Once again, the HEMA hydrogel showed a higher affinity for the basic dye than that by NVP/HEMA hydrogel. Meanwhile, the percentage dye sorption was found to increase with increasing the mass of hydrogels. However, at any event of hydrogel mass, the percentage sorption of the basic dye was found to greatly increase after a very short time and then tends to substantially increase with increasing the sorption time. It seems the mass of hydrogel is an effective factor regarding dye sorption than the concentration of dye present in solution. Also, the rate of sorption by increased mass is much higher than if the sorption process was performed from different dye concentration as shown in Figure 6.

The mechanism of dyeing with the basic dyes implies the presence of an anionic part in the me-

diu to react with the cationic part of the dye through an anionic bond.<sup>10</sup> The sorption of the basic dye will take place through the reaction with the negatively charged O—H groups on the hydrogels and the cationic groups of the dye. Therefore, in the sorption process by hydrogels, the aqueous dye solution is completely absorbed in the first stage followed by the chemical reaction between the O—H groups and the cationic groups of the basic dye. These finding may be explain by the dependency of the sorption of the basic dye on the mass of hydrogel and the concentration of dye solution.

Figure 7 shows the percentage sorption of the acid dye Sandolan by NVP and NVP/HEMA hydrogels as a function of sorption time at the room temperature. It should be noted that the sorption process



**Figure 7** Dye sorption (%) of a constant concentration (0.003 g/L) of the acid dye Sandolan E-3 GSL at room temperature by gamma radiation crosslinked NVP and its copolymer with HEMA as a function of time.

**TABLE III**  
**Interlayer Spacing at the Strongest Peak of Different Crosslinked Polymer before and after Absorbing the Basic and Acid Dyes**

Crosslinked polymer	Interlayer spacing (Å)
NVP before acid dye sorption	6.426 at $2\theta = 13.77$
NVP after acid dye sorption	6.000 at $2\theta = 14.79$
HEMA before basic dye sorption	5.372 at $2\theta = 16.49$
HEMA after basic dye sorption	5.852 at $2\theta = 15.13$
NVP/HEMA before basic dye sorption	6.588 at $2\theta = 13.43$
NVP/HEMA after basic dye sorption	6.847 at $2\theta = 12.92$

was carried out at similar conditions to the sorption of the basic dye. It is clear that NVP hydrogel has a high affinity to absorb the acid dye than by NVP/HEMA hydrogel. However, the affinity of NVP hydrogel for the acid dye is lower than that by HEMA hydrogel for the basic dye. The affinity of NVP hydrogel for the acid dye can be explained on the basis of dyeing protein fibers. It has been reported that the basic mechanism in dyeing protein fibers with acid dyes is salt formation with amino groups as follows:<sup>10</sup>



In a similar manner, the unshared electrons on the pyridine nucleus of NVP will create a positive charge, due to the hybridization of the nitrogen atom, capable of forming the salt linkage with the anionic groups of the acid dye molecules. The lower affinity of NVP for acid dye may be attributed to its high affinity of water (1207%, as shown in Table I). Thus, if we start with a hydrogel mass of 0.5 g and a total volume of dye solution of 50 mL containing  $7 \times 10^{-3}$  g/L, the hydrogel mass will increase to 6.5 g at maximum swelling. In turn, the absorbed quantity of aqueous dye solution will represent  $\sim 1/5$  of the total solution containing a limited dye concentration. Therefore, the sorption of acid dye should be carried out from a very concentrated solution. The effect of the dye sorption on the interlayer spacing of the different hydrogels was investigated by X-ray diffraction, as shown in Table III. It can be seen that there is a decrease in the value of the interlayer spacing (Å) for the NVP hydrogel after absorbing the acid dye. This may be attributed to the occurrence of chemical chains between the dye and the hydrogel intermolecules. The increase of crosslinking causes a decrease in the interlayer spacing (Å) between the chains of the polymer. In the case of the copolymer NVP/HEMA, the interlayer spacing tends to increase after absorbing the basic dye due to the occurrence of physical interaction between the dye and the polymer chains.

## CONCLUSIONS

The results presented in this work have dealt with the radiation synthesis of a new hydrogel based on the NVP/HEMA copolymer and its application in the removal of some dyestuffs from wastewater. For comparison, the hydrogels of the individual components were also prepared under the same conditions. The results showed that the composition of the feed comonomer or monomer(s)/solvent ratio and irradiation dose are determining factors specifying the properties of the obtained hydrogels. In this regard, the change of the solvent/monomer(s) ratio from 1/1 to 4/1 at a constant dose of 10 kGy results in a change of the percentage water uptake by the individual HEMA and NVP/HEMA hydrogels from 53 and 213% to 213 and 377%, respectively. On the other hand, in a similar manner, the percentage water uptake by individual NVP was decreased from 1000 to 796%. In the removal of pollutants from wastewater a compromise between the capability of the absorbents for water and for the substance to be removed should be considered. Also, the mechanism by which the removal takes place in terms of the formation of some sort of chemical bonding or physical adsorption determines to a great extent the efficiency of the absorbent. On this basis, NVP hydrogel showed an affinity for acid dyes, while HEMA or NVP/HEMA hydrogels showed affinity for basic dyes. On the other hand, NVP showed no affinity for basic dyes, while HEMA and NVP/HEMA hydrogels showed no affinity for acid dyes. The results clearly indicate that the capability of the hydrogels to absorb the acid or basic dyes was greatly affected by the capability of hydrogels to absorb water. In this regard, the quantity of absorbed acid dye by NVP hydrogels (water uptake 1207%) was lower than the absorbed basic dye by HEMA hydrogel (water uptake 522%) at the same conditions of preparation and dye sorption.

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