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## RADIATION COPOLYMERIZATION OF (PVA/4-VP) HYDROGEL FOR TREATMENT OF INDUSTRIAL WASTE DYES

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*Poly (vinyl alcohol) / Poly (4 vinyl pyridine) copolymer hydrogel was prepared using gamma irradiation as initiator. The effect of PVA/4-VP composition and irradiation dose on the gel content in the prepared hydrogel was determined. It was found that as the content of 4-VP increased the gel percent increased. The increase in irradiation dose resulted in increasing the crosslinked network structure and consequently the gel percent increased. Swelling properties of the prepared hydrogel were also investigated as a function of immersion time, hydrogel composition and gel content. Thermal characterization was determined using TGA and DSC techniques to find that such hydrogel is thermally stable for heating up to 300°C. Thermal parameters are dependent on the hydrogel composition in which the glass transition temperature increased with 4-VP content. The possibility of practical use of the prepared hydrogel in the treatment of water from industrial waste dyes was studied. The effect of treatment time, temperature, pH of feed solution, type of dye and hydrogel composition on the dye uptake was also determined. The prepared hydrogel possessed good hydrophilic and thermal properties, high affinity towards acidic dyes, and good durability, which may make it promising for practical use in the separation processes.*

**Keywords:** Radiation copolymerization, poly (vinyl alcohol), 4-vinyl pyridine, thermal characterization, waste dyes removal

### INTRODUCTION

A hydrogel prepared by treating the aqueous solution of hydrophilic polymers and monomers with  $\gamma$ -rays is generally termed a “clean

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technique", not requiring any extra chemicals that leave some unwanted residue. It can be applied at any temperature and dose rate. Extensive work has been performed on methods for optimizing yields when monomers are radiation-co-polymerized with the backbone polymer, especially with a simultaneous technique [1,2].

Polymeric hydrogels have a series of particular characteristics; they are hydrophilic, insoluble in water, soft, elastic and swell with water, keeping their shapes but increasing in volume until reaching a physical/chemical equilibrium. Hydrogel properties depend strongly on the degree of cross-linking, chemical composition of polymer chains, and the interactions of network and surrounding liquid. The hydrophilicity of hydrogels is mainly dependent on the functional hydrophilic groups such as alcohols, carboxylic acids, amides, etc. Accordingly, the properties of the hydrogel can be changed with pH and temperature [3–6].

Poly (vinyl alcohol) PVA is a well known material of good stability, toughness, hydro-affinity and easy availability. However, because of its high solubility, it has to be turned into a completely insoluble stable material. Therefore, in this study a further modification has been done by copolymerization with 4-vinyl pyridine monomer using gamma rays as initiator to improve its swelling behavior and insolubility by crosslinking.

A trail was made for the use of such prepared hydrogels for the recovery of cationic and anionic dyes from wastewater. The effect of treatment conditions on the dye uptake was also determined. Characterization and swelling behavior were studied to elucidate the possibility of its practical use.

## EXPERIMENTAL

Poly (vinyl alcohol) (PVA), Laboratory Rasayan. S.d. Fine-Chem. Ltd., India, of M.W. app. 1,25,000 was used. 4-Vinyl pyridine (4VP) (Acros organics, USA) of purity 99% was used as received. The other chemicals, such as N,N-methylene diacrylamide (BAAm) as a crosslinker, and phosphate buffers were reagent grade and used as received.

### Preparation of Copolymer Hydrogel

A 5 g of PVA was dissolved in 100 ml distilled water and then mixed with N,N-methylene diacrylamide (BAAm) 0.5 g and different amounts of 4VP were then added to 20 ml of such prepared mixture. This mixture was then exposed to Co<sup>60</sup> gamma irradiation at a dose

rate ranging from 10.3–7.9 kGy/h. The hydrogel thus obtained was left to dry at room temperature.

### Gel Determination

The dried co-polymerized PVA were extracted with water for 48 h at 100°C in order to extract the insoluble parts of the hydrogel. The insoluble parts, i.e. the gelled parts, were taken out and washed with hot water to remove the soluble part, then dried and weighed. This extraction cycle was repeated till the weight became constant. The gel percent 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.

### Thermal Analysis

The weight loss and stability of the hydrogel at different temperatures were determined using Shimadzu TGA system of Type TGA-50 in nitrogen atmosphere at the rate of 20 ml/min. The temperature range was from ambient to 500°C at heating rate of 10°C/min.

The change in thermal parameters of the prepared hydrogel was measured using DSC technique. DSC measurements were carried out using a Perkin-Elmer DSC Calorimeter equipped with a DSC-7 data solution. The measurements were carried out in N<sub>2</sub> atmosphere at a heating rate of 20°C min<sup>-1</sup>.

### Swelling Measurements

The clean, dried, co-polymerized hydrogel of known weights was immersed in distilled water at room temperature. The hydrogel was removed from water after various times and the excess water on the surface was removed, blotted by absorbent paper and quickly weighed, then returned back 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.

## Dye Uptake

A known weight of dry hydrogel was soaked in aqueous solution containing dye of known concentration ( $C_0$ ) and left for different time intervals. The concentration of remaining dye ( $C_1$ ) was then determined. The  $C_0$  and  $C_1$  were determined using UV-Visible spectrophotometer Milton Roy Spectronic 1201 in the range between 190-900 nm. The dye uptake percent was calculated from the following equation:

$$\text{Dye Uptake \%} = (C_0 - C_1) \times 100$$

## Infrared Spectroscopy

Infrared spectroscopy was carried out using Mattson 1000, Unicam, England in the range from 400–4000  $\text{cm}^{-1}$ .

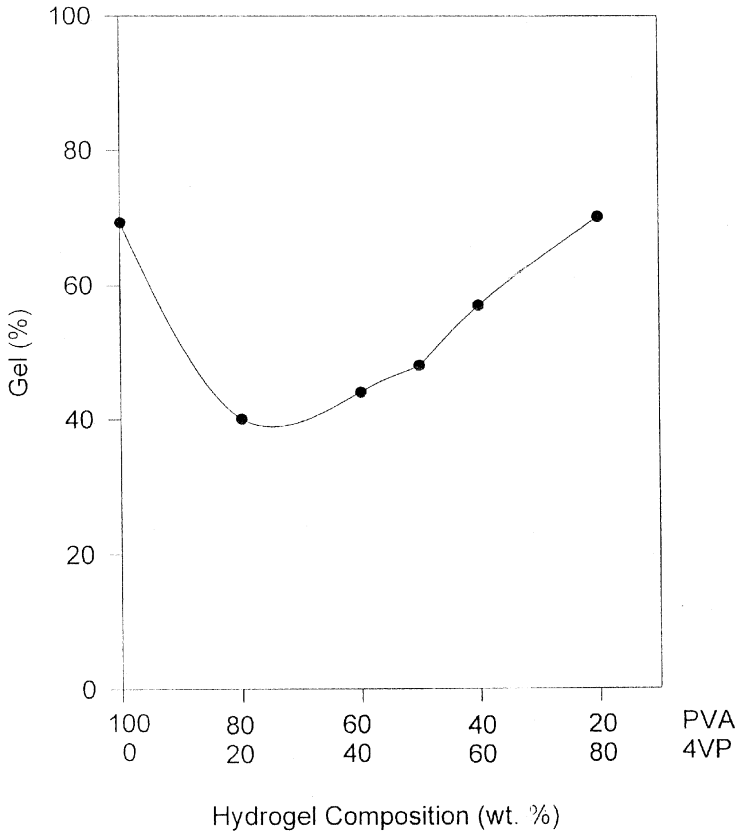
## X-Ray Diffraction (XRD)

X-ray diffraction patterns were obtained with a XD-DI Series, Shimadzu, Japan, using nickel-filtered and Cu-K $\alpha$  target. This technique was performed to clarify the changes in morphological structure caused by the copolymerization and crosslinking.

## RESULTS AND DISCUSSION

### Hydrogel Preparation

Preparation of hydrogel was carried out by copolymerization of PVA and 4-VP in the presence of BAAM as a crosslinker using gamma irradiation as initiator. The conversion yield was measured as a function of dose and monomer content in the copolymerized system by gel determination. The effect of PVA/4-VP composition and irradiation dose on the gel percent in the prepared hydrogel is shown in Figures 1 and 2, respectively. It can be seen that the gel percent (insoluble gelled part) increases as the 4-VP content increases in the PVA/4-VP mixture (Fig. 1). This clearly indicates that 4-VP enhanced the crosslinking formation by its copolymerization with PVA and resulted in an insoluble hydrogel. From Figure 2, it is also seen that the gel percent increases with irradiation dose, at a given PVA/4-VP composition. Such increase in gel content with dose is due to crosslinking network structure, which is formed by free radical copolymerization process. As it is well known that the higher the dose the higher the concentration of free radicals, accordingly the crosslinking content increased.

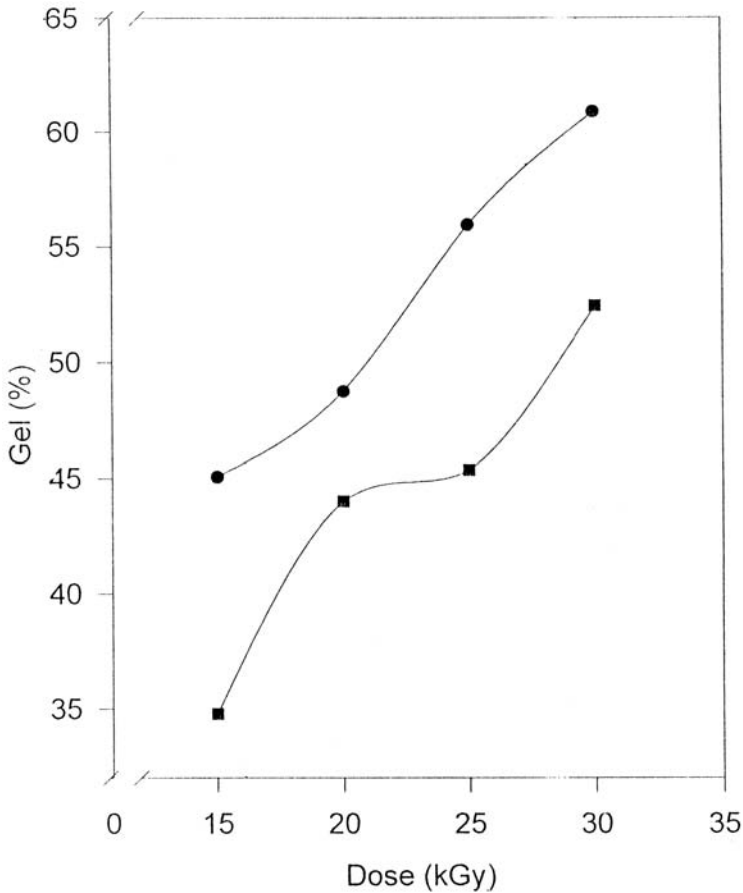


**FIGURE 1** Effect of Polymer/monomer composition on Gel %. Preparation conditions; Radiation dose; 20 kGy and BAAM concentration; 0.5 wt%.

## Characterization and Properties of Prepared Hydrogel

### **Swelling behavior**

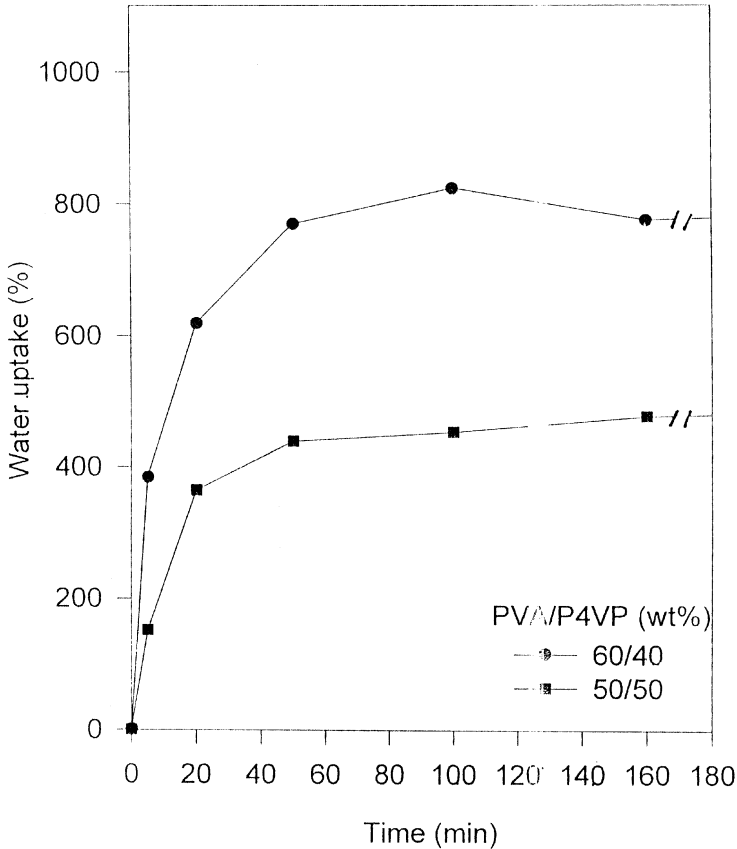
From the practical point of view, it is very important to know the swelling behavior and capacity of crosslinked polymers for serving in liquid media. Figure 3 shows the effect of soaking time on the water uptake % for PVA/4-VP hydrogel that was prepared at two different compositions. It can be seen that water uptake increases with time to reach a certain limiting value, at which it levels off. This behavior is observed for both hydrogels prepared at 60/40 and 50/50 wt% of PVA/4-VP compositions. Meanwhile, the hydrogel prepared from 60/40 wt% of PVA/4-VP possesses much hydrophilicity and water uptake than that prepared from 50/50 wt%.



**FIGURE 2** Effect of Dose on the Gel % for the PVA/P4VP hydrogel at different PVA/4VP compositions (wt%); (●) 60/40 and (■) 50/50.

These results confirmed that the crosslinking content is enhanced by increasing the 4-VP content in the hydrogel. Such crosslinked network structure restricts the diffusivity of water through the copolymer matrix, resulting in lowering the water uptake.

The influence of irradiation dose and gel percent on the water uptake percent for the hydrogels prepared at two different compositions of PVA/4-VP is shown in Table 1. Results shown in this table confirm the aforementioned assumption and show clearly that the swelling behavior is mainly dependent on the crosslinking content.



**FIGURE 3** Effect of soaking time on the water uptake % for different PVA/P4VP compositions at room temperature and copolymerized at 20 kGy.

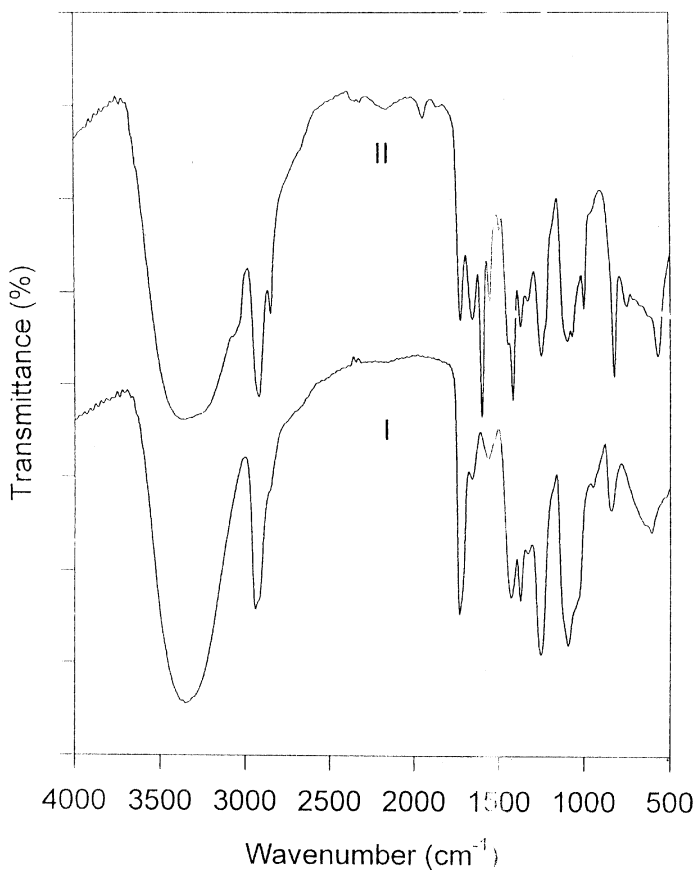
### ***IR-spectroscopy***

IR-analysis was made for the co-polymerized and original PVA to confirm the formation of the hydrogel copolymer and to get some knowledge about its structure ( Fig. 4). The characteristic bands<sup>(7)</sup> of hydroxyl groups of PVA appeared at  $3040\text{--}3500\text{ cm}^{-1}$  and  $1300\text{--}1400\text{ cm}^{-1}$ . The appearance of  $\text{C}=\text{O}$  groups at  $1740\text{ cm}^{-1}$  in the IR Spectrum of PVA indicates the presence of poly (vinyl acetate) in its structure. The spectrum of (PVA/P4VP) copolymer hydrogel shows the characteristic bands for both PVA and 4-VP. This confirms the copolymerization of PVA with 4-VP and form a chemically bonded copolymer in which the broad hydroxyl group appeared at  $3200\text{--}3480\text{ cm}^{-1}$  due to the incorporation of hydrogen bonding from pyridine structure.



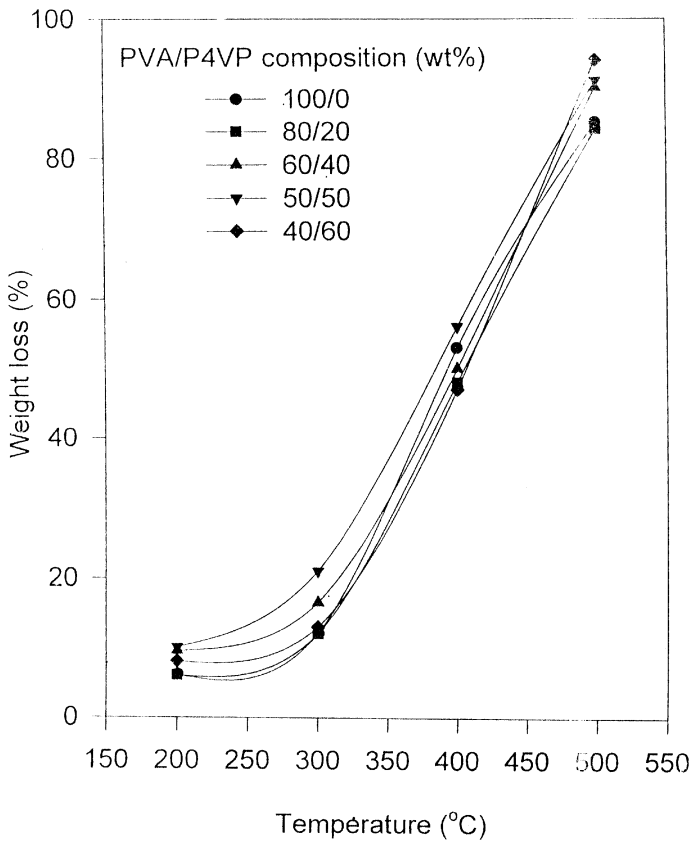
**TABLE 1** Effect of irradiation dose on water uptake % for different PVA/P4VP compositions. Soaking time: 3 hours

Dose (kGy)	Gel (%)		Water Uptake (%)	
	(PVA/4-VP) wt %			
	60/40	50/50	60/40	50/50
10	39	31	845	650
15	45	35	1565	670
20	49	43	1590	1060
25	56	46	1565	790
30	61	53	826	770

**FIGURE 4** IR spectra for original PVA (I) and PVA/P4VP (II) hydrogel.

### Thermal stability of prepared hydrogel

From the practical point of view, the prepared hydrogel should possess good thermal stability in the range of applicable temperature. Figure 5 and Table 2 show the thermal properties for hydrogels having different compositions at various elevated temperatures. The initial stage of weight loss in the range up to 200°C may be due to the dehydration process in such hydrophilic hydrogels. The second stage of weight loss, in the range of 200 to 300°C, is due to the decomposition of side groups and branches of the hydrogel. Finally, above 300°C, the weight loss is due to the main chain scission of the copolymer. Results showed that such a hydrogel is thermally stable to heating up to 300°C, which is suitable for its practical uses.



**FIGURE 5** Effect of temperature on weight loss for various compositions of PVA/P4VP hydrogels.

**TABLE 2** Effect of PVA/4VP composition on the thermal stability of the PVA/P4VP hydrogel at various elevated temperatures. Preparation conditions; Irradiation dose; 20 kGy at dose rate of 7.9 kGy/h

PVA/4-VP (wt.%)	Weight loss (%)			
	200°C	300°C	400°C	500°C
100/0	7	12	53	85
80/20	6	12	48	84
60/40	9.5	16.5	50	90
50/50	10	21	56	91
40/60	8	13	47	94

### Thermal Parameters of (PVA/P4VP) Hydrogel

Change in melting temperature ( $T_m$ ) at the first and second heating runs for (PVA/P4VP) hydrogel is shown in Table 3. It can be seen that at the first heating run,  $T_m$  of PVA sharply decreases due to the incorporation of 4VP structure in the copolymer. Meanwhile, by increasing (P4VP) content in PVA, the  $T_m$  slightly increases; however, it still lower than that of original PVA. However, at the 2nd heating run,  $T_m$  increases due to further modification and ordering in the structure of the copolymer hydrogel. This may be a resulted from the re-crystallization process of the hydrogel by cooling from the molten state after the first heating run.

Table 3 also shows that the heat of melting ( $\Delta H$ ) of PVA sharply increases with 4VP content to reach a maximum at PVA/4-VP composition of 80/20 wt%. Thereafter, it gradually decreases as the 4VP

**TABLE 3** Effect of Hydrogel Composition on the Thermal Properties of (PVA/4VP)

(PVA/4-VP) (wt. %)	$T_m$ (°C)		$\Delta H_m$ (J/g)	$T_g$ (°C)	$T_{re}$ (°C)
	First Heating Run	Second Heating Run			
100/0	178	174.5	71	71	127
80/20	128	174	128	73	118
60/40	140	176.5	116.5	76	116
50/50	145	176	112	79	111
40/60	146	183	94	83	108

content increases; however, it is still higher than that for pure PVA polymer. This may indicate the decrease in crystallinity of PVA with increasing 4-VP content. This may confirm the results obtained for  $T_m$ .

The change in the glass transition temperature ( $T_g$ ) for (PVA/4-VP) hydrogel is also shown in Table 3. It is observed that the  $T_g$  increases with 4-VP content in the hydrogel. This can be reasonably understood by considering the restriction of chain mobility during transformation to the glassy state and melting, caused by the high degree of crosslinking network structure formed during radiation copolymerization process. Such increase in  $T_g$  value is good evidence for the formation of crosslinking, which is the predominant process during radiation copolymerization.

Recrystallization process of the copolymer was performed after the first heating run above the melting temperature; the sample was held at that melt temperature at which the polymer turned into the complete amorphous state. By cooling the sample from such molten state at a rate of 20°C/min, it re-crystallizes again. Table 3 also shows the change in the recrystallization temperature  $T_{rc}$  of PVA/4VP copolymer hydrogel. It can be seen that a decrease in  $T_{rc}$  took place with the increase of 4VP content. This is due to the restriction of chain mobility, which is necessary for the re-crystallization process. Such decrease in  $T_{rc}$  also indicates the formation of crosslinking in the prepared hydrogel.

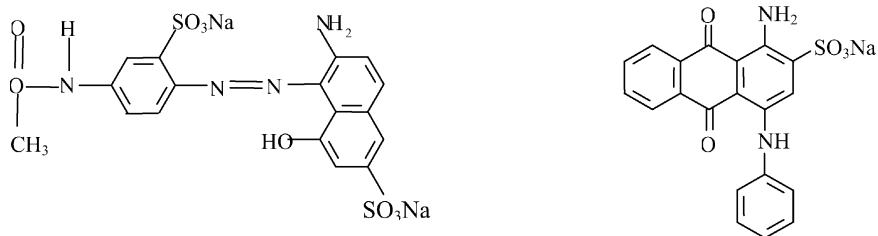
### Change in Crystallinity of PVA Hydrogel

XRD patterns show the change in PVA crystallinity by the incorporation of P4-VP chains in the copolymer (Fig. 6). The diffraction curves of the copolymers recorded in the same region do not show any new diffraction peak, implying the amorphous structure of this component, PVA/P4VP. It appears that P4VP present in an amorphous phase and the crystalline regions is contributed by PVA sequence.

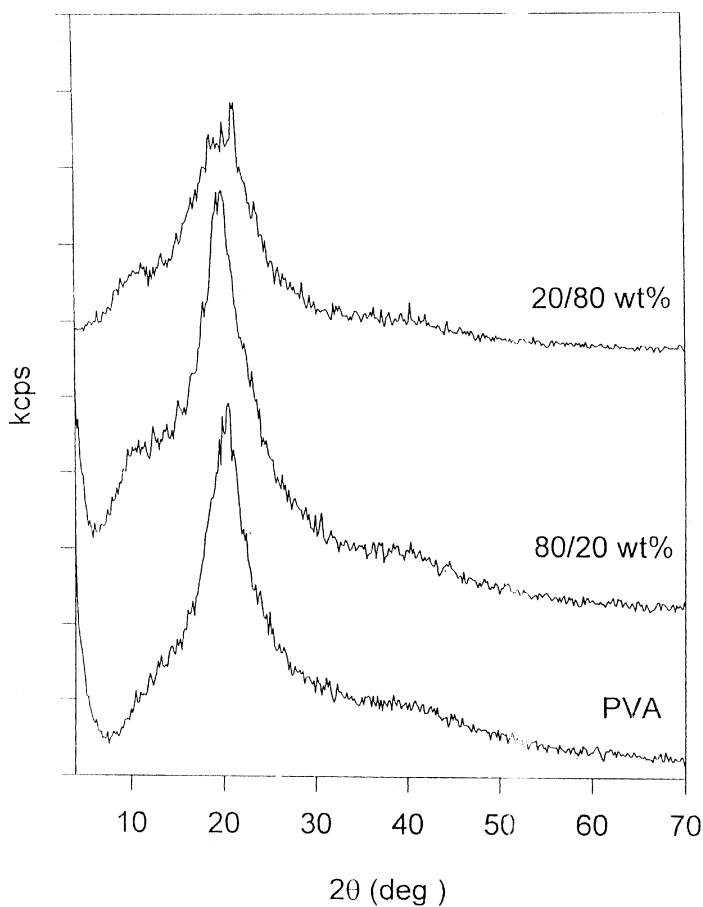
### Waste Dye Treatment by Prepared Hydrogel

The applicability of the prepared polymer hydrogel was investigated for the treatment of wastewater from different dyes. In this connection, the effect of different parameters such as treatment time, hydrogel structure and composition, pH of dye feed solution, temperature, etc., on the dye uptake was investigated.

Two types of dyes were investigated in this study; their chemical structures are presented in the following:



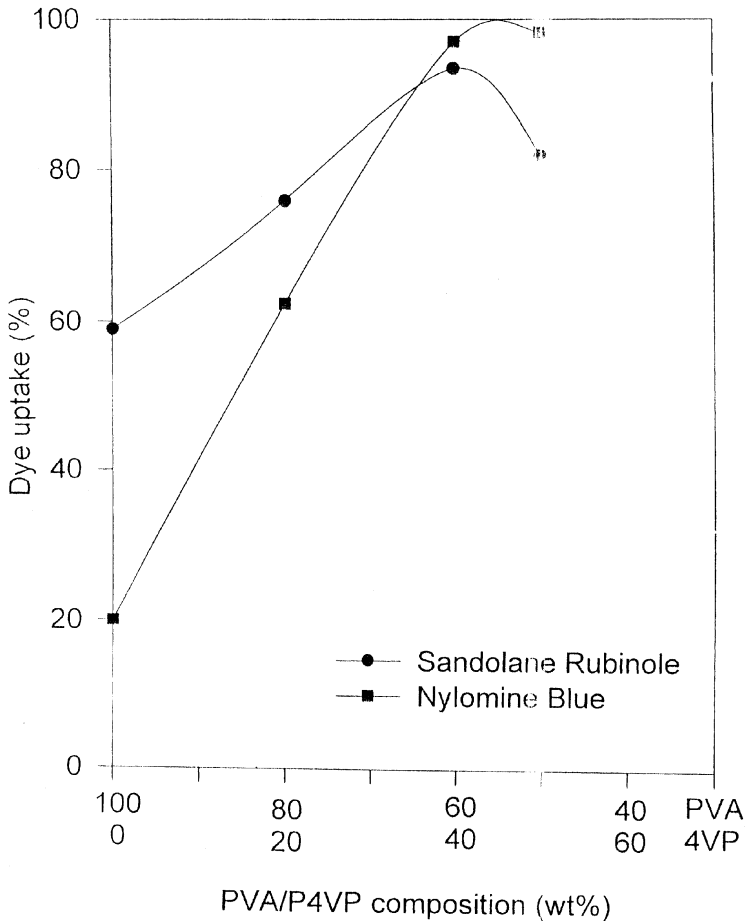
**SCHEME 1** a. Acid Red 37 (Sandolane Rubinole E-3GSL); b. Acid Blue (Nylomine Blue AG)IA



**FIGURE 6** XRD-patterns for the original PVA and different PVA/P4VP hydrogel compositions.

## Effect of Treatment Time and Temperature on Dye Uptake

Figure 7 shows the effect of treatment time on the dye uptake at different temperatures. It can be seen that the dye uptake increases sharply with time to reach the equilibrium state within 60 min at elevated temperature (60–80°C). But it takes about 120 min at ambient temperature (30°C) to reach the equilibrium state. Meanwhile, the higher the temperature, the higher the dye uptake at a given treatment time. This can be reasonably explained by considering



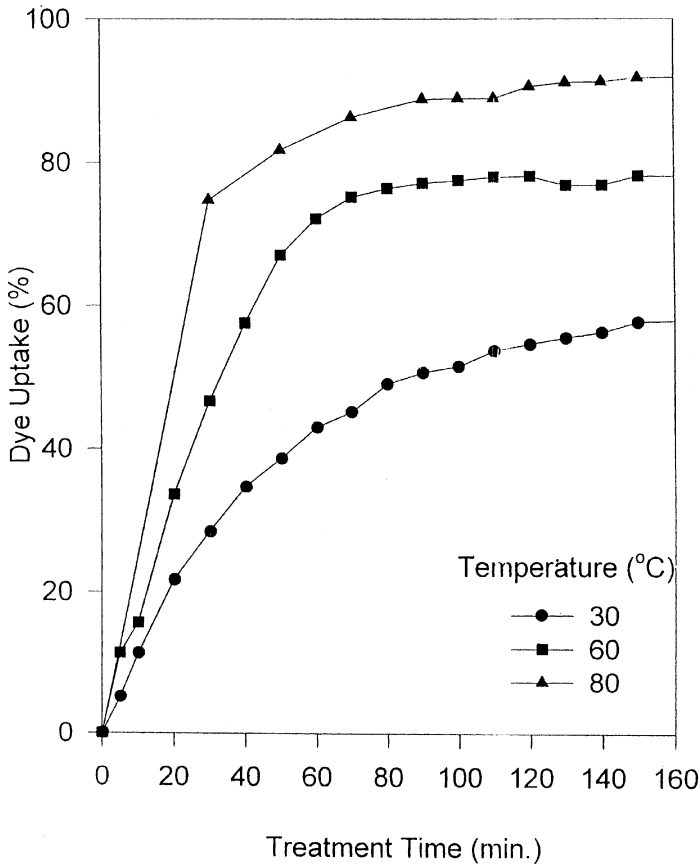
**FIGURE 7** Effect of treatment time on the Sandolane Rubinoles dye uptake % at different temperatures using PVA/P4VP hydrogel prepared from (80/20 wt%) composition.

the higher diffusivity of dyes through the hydrogel matrix at such elevated temperature.

### Effect of PVA/4-VP Composition on the Dye Uptake

The effect of 4VP content in the copolymer hydrogel on dye uptake is shown in Figure 8. It is obvious that the dye uptake percent increases with 4VP content to reach its maximum value at 60/40 wt% composition of PVA/4VP. Thereafter, it levels off for Nylomine Blue uptake, but it decreases for Sandolane Rubinoles uptake.

Results suggested that, at 4VP contents higher than 40%, the maximum dye uptake decreases due to the restriction of its diffusion

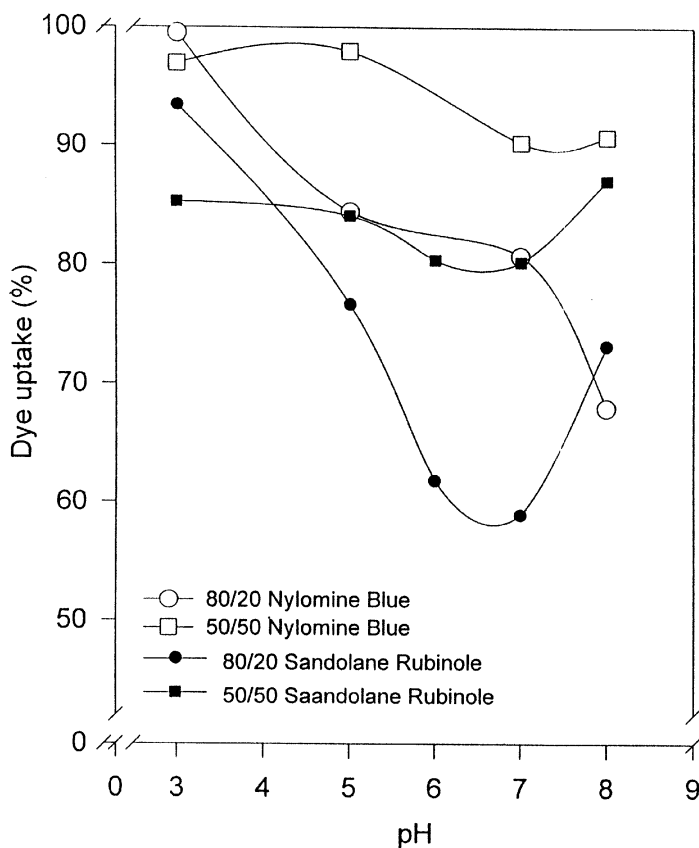


**FIGURE 8** Effect of PVA/4VP composition on the acid dye uptake % prepared with 0.5 wt% BAAM at 20 kGy.

through the highly crosslinked network structure, which is enhanced at such high 4VP contents.

### Effect of pH on Dye Uptake

The effect of pH on the dye uptake percent by PVA/P4VP hydrogel is shown in Figure 9, for acid Nylomine Blue and acid Sandolane Rubinole dyes, respectively. It can be seen that for the former dye, the uptake percent remarkably decreases with increasing pH of dye solution. Such decrease slowly occurs in the pH range of 5–7. This behavior is observed for both hydrogels of different PVA/4-VP compositions. However, for acid Sandolane Rubinole dye uptake, no



**FIGURE 9** Effect of pH on the uptake % of acid dye for different PVA/4VP (wt%) compositions.



significant change is observed by changing the pH when (50/50 wt%) hydrogel composition is used. But, a recognized decrease is observed with increasing pH, when (80/20 wt%) hydrogel composition is used.

This can be explained by the fact that the pyridine groups, which are considered as a weak base [8], and also the -OH functional groups, are responsible for the uptake of dye. The change in pH of the dye solution would affect the structure of dyes as well as the structure of the polymeric material itself. However, such prepared hydrogel possessed good affinity towards both dyes and a reasonable high uptake occurred.

## CONCLUSION

It can be concluded that the prepared hydrogel possessed good removal properties towards acid dyes, even at very low concentrations of feed dye solutions. Another good advantage is the reasonable uptake of the investigated dyes as a whole from their wastewater. The prepared hydrogels have good thermal stability and durability, which may make them acceptable for practical use in the treatment of water from industrial waste dyes.

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