

# Sorption of Dye Wastes by Poly(vinyl alcohol)/Poly(carboxymethyl cellulose) Blend Grafted Through a Radiation Method

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Received 3 June 2000; accepted 10 November 2000

**ABSTRACT:** The instability in water of poly(vinyl alcohol) (PVA)/poly(carboxymethyl cellulose) (CMC) was improved through radiation-induced grafting with a styrene monomer. The PVA/CMC blend graft copolymer was used as a sorbent for dye wastes normally released from textile factories. The factors that may affect the sorption process such as time, temperature, weight of the blend graft copolymer, and volume of the dye waste were investigated. The sorption of dyestuffs by the blend graft copolymer was determined by a method based on spectroscopic analysis. The results showed that the blend graft copolymer has a high affinity for basic, acid, and reactive dyes. Meanwhile, it was observed that the sorption of dyes is more effective at the high temperature of 70°C. Moreover, it was found that the sorption of dyes depends on the weight of the blend graft copolymer and does not depend on the volume of the waste solution. The sorption of the dyestuffs by a PVA/CMC graft copolymer may be considered to be a practical method to remove organic pollutants. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 136–142, 2001

**Key words:** PVA/CMC blend; grafting; sorption; dye waste

## INTRODUCTION

Poly(vinyl alcohol)<sup>1</sup> (PVA) has wide commercial application due to its unique chemical and physical properties. It is a nontoxic, highly crystalline, and water-soluble polymer and has good film-forming and high hydrophilic properties. However, PVA as a soluble polymer cannot be used in the treatment of waste waters. Thus, it has to be converted to a completely insoluble material with high mechanical properties.

The structure–property behavior and compatibility of PVA with other polymers have been investigated by only a few authors. In this regard,

the compatibility of PVA/silk fibron (SF) blends was investigated by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), X-ray diffractometry, scanning electron microscopy (SEM), and thermal electron microscopy (TEM).<sup>1</sup> On the basis of all these analyses, it was reported that PVA and SF are incompatible. To improve the hydrophilicity and transport flux of a nylon-4/PVA membrane for dialysis, PVA was esterified with formic acid.<sup>2</sup> By this method, the instability of PVA in water was improved. The salt permeability, water content, partition coefficient, diffusivity, and mechanical strength of the esterified nylon/PVA membranes were also investigated.

Although extensive research work has been carried out on the synthesis and application of polymeric materials in the field of treatment of

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*Journal of Applied Polymer Science*, Vol. 82, 136–142 (2001)  
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waste waters, few authors were concerned with PVA/poly(carboxymethyl cellulose) (CMC) polymer blends. It has been reported that the introduction of 6–16% of CMC Na salt to the PVA matrix leads to an increased sorption capacity with respect to water vapor.<sup>3</sup>

In the present work, the instability of a PVA/CMC polymer blend in water was improved through radiation-induced grafting of a styrene monomer. The sorption capacity of the PVA/CMC graft copolymer for different dyestuffs was investigated.

## EXPERIMENTAL

### Materials

The PVA, laboratory grade, used in this study was in the form of a powder, had an average molecular weight ( $\bar{M}_w$ ) of 125,000, and was obtained from the Laboratory Rasayan. CMC sodium salt (pure grade reagent) was a low-viscosity polymer in the form of granules and was supplied by El-Nasr Pharmaceutical Chemical-Prolabo (Cairo, Egypt). Four dyestuffs, belonging to different classes, were used throughout this work. These dyes were Remacryl Blue (basic dye), supplied by Hoechst (Germany); Sandolan E-3GSL (acid dye) and Drimarene Blue K-3GL (reactive dye), supplied by Sandoz (Switzerland); and Solophenyl Olive EGL (direct dye), supplied by Ciba-Geigy (Switzerland). The industrial dye waste was taken from the draining released from Hossni Dyers & Finishers Co. (Cairo, Egypt). It contained different colors of the reactive dye Remazole (product of Hoechst), sodium sulfate (Glauber salt), sodium hydroxide, and detergents.

### Preparation of PVA/CMC Polymer Blend

Films of a CMC/PVA blend (20/80 wt %) were prepared by the casting-solution technique. The PVA powder was dissolved in distilled water at 95°C, while the sodium salt of CMC was dissolved in distilled water at room temperature. The polymer solutions were then mixed, with continuous stirring, to complete miscibility and subsequently cast onto glass dishes to form transparent films. The cast films were dried in a vacuum oven at 80°C for 24 h.

### Preparation of Blend Graft Copolymer

The PVA/CMC blend was grafted with the styrene monomer in the presence of methyl alcohol and 4% carbon tetrachloride using the direct method of radiation grafting in an air atmo-

sphere. Films of the PVA/CMC polymer blends were weighed and immersed in the grafting solution in glass tubes. The tubes containing the blend films, monomer, and solvents were exposed to gamma-irradiation. The grafted films were then removed and extracted in methanol to get rid of the unreacted styrene monomer. Finally, the grafted films were extracted in benzene to remove the polystyrene homopolymer and dried in a vacuum oven at 60°C to a constant weight. The degree of grafting was determined by the percent increase in weight as follows:

$$\text{Graft yield (\%)} = [(W_1 - W_0)/W_0] \times 100$$

where  $W_0$  and  $W_1$  are the weights of the initial and grafted films, respectively.

The grafting conditions, such as the styrene concentration and radiation dose, were selected so that the true graft yield of polystyrene onto the PVA/CMC blend was ~30%. At this graft yield, the blend graft copolymer obtained was homogeneous and suitable for aqueous processing. Irradiation to the required doses was carried out in a Co-60 gamma cell (made in India) at the National Center for Radiation Research and Technology, Cairo, Egypt. The grafting process was carried out at a dose rate of 2.75 kGy/h.

### Dye-sorption Measurements

The percentage sorption of the different dyestuffs and the industrial dye waste by the PVA/CMC-g-PS blend graft copolymer was determined by a general procedure based on spectrophotometric analysis. Standard curves were first made representing a relation between different known concentrations from each dye and the corresponding light absorption as shown in Figures 1 and 2.

The relations representing these standard curves are as follows:

Light absorption

$$= 0.223 \times \text{basic dye concentration (mg/L)}$$

Light absorption

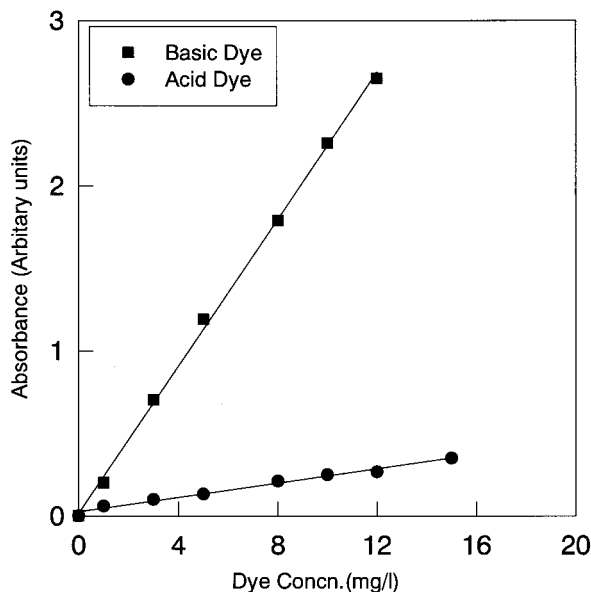
$$= 0.026 \times \text{acid dye concentration (mg/L)}$$

Light absorption

$$= 0.023 \times \text{reactive dye concentration (mg/L)}$$

Light absorption

$$= 0.013 \times \text{direct dye concentration (mg/L)}$$



**Figure 1** UV/vis absorbance of different concentrations of the basic and acid dyes Sandocryl Blue and Sandolan E-3GSL.

In this procedure, a certain concentration from each dye under investigation (20 mg/L) was first dissolved in boiled water and added to the dye solution without any additives. After that, a constant weight of the PVA/CMC blend graft copolymer was then immersed in the different dye solutions and the dye uptake by the graft copolymer was determined by measuring the light absorption of the residual dye solution. The percentage sorption by the blend graft copolymer was determined according to the following equation:

Dye sorption (%)

$$= \frac{\text{Dye concentration on graft copolymer}}{\text{Initial dye concentration}} \times 100$$

The light-absorption measurements were performed using a UV/vis spectrophotometer (Unicam UV2 series).

#### Color-difference Intensity Measurements

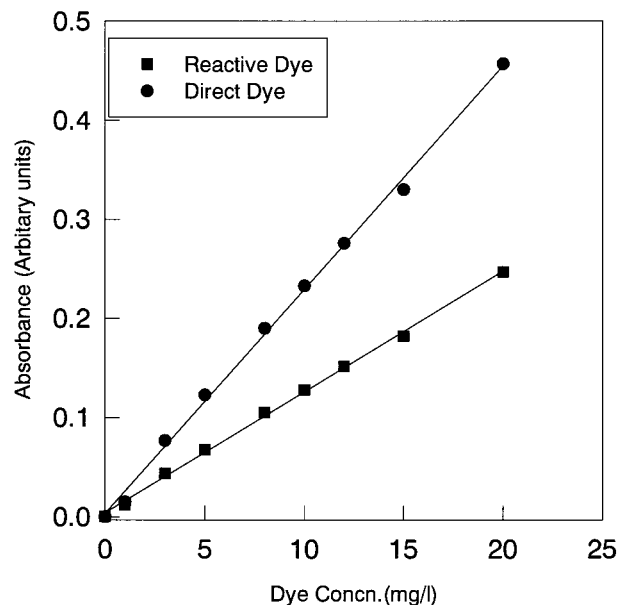
A microcolor unit attached to a data station made by Dr. Lange (Germany) was used for color-strength measurements. The  $L^*$ ,  $a^*$ , and  $b^*$  interceptions used in this system are based on the CIE-color triangle. In this system, the  $L^*$  value represents the dark white axis;  $a^*$ , the green-red axis; and  $b^*$ , the blue-yellow axis. The  $L^*$ ,  $a^*$ , and  $b^*$  values of the PVA/CMC-g-PS blend graft copol-

ymers before dye sorption were measured and taken as a reference. The color-difference intensity ( $\Delta E^*$ ) of the grafted samples after sorption was determined as follows:

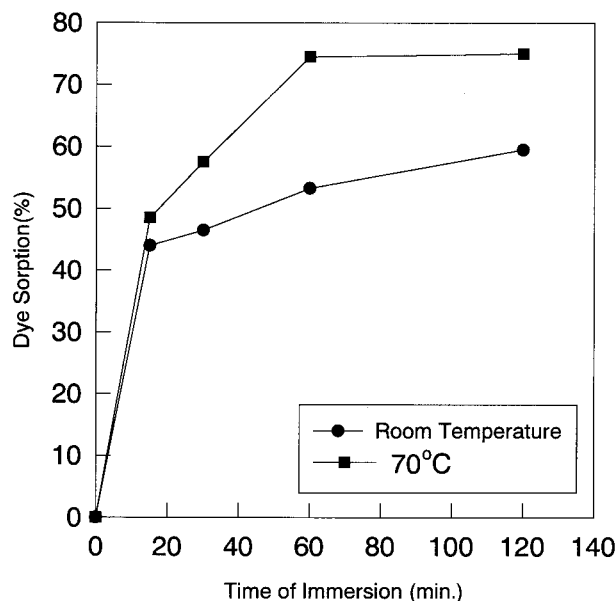
$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

## RESULTS AND DISCUSSION

Although a PVA/CMC blend contains different hydrophilic groups, it cannot be used in aqueous treatments. This is because both blend components are soluble in water. Thus, an attempt was made to convert the PVA/CMC blend to a non-soluble material through radiation-induced grafting with the styrene monomer. The graft polymerization of styrene onto the PVA/CMC polymer blend may be explained by the following points: (1) Since PVA/CMC is a water-soluble blend, methanol was used as a diluent for the styrene monomer and carbon tetrachloride was used as a chain-transfer agent. (2) The PVA/CMC blend used throughout this study contained 20%CMC and 80%PVA. Thus, it is supposed that the grafting process would go mainly onto the PVA component, which represents the major component of the blend. For the CMC component, the reactive hydroxyl groups present on the cellulose molecule

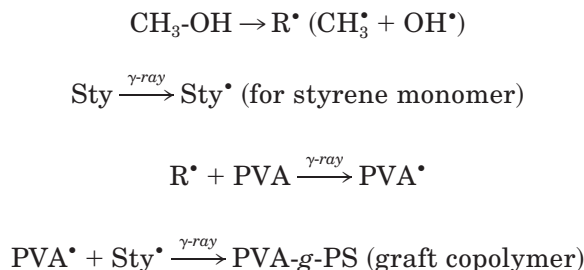


**Figure 2** UV/vis absorbance of different concentrations of the reactive and direct dyes Drimarene Blue K-3GL and Solophenyl Olive EGL.



**Figure 3** Dye sorption (%) of the basic dye Sandocryl Blue PVA/CMC-*g*-PS blend graft copolymer at room temperature and 70°C as a function of immersion time. Dye sorption conditions: initial dye concentration, 20 mg; blend graft copolymer weight, 0.17 g; volume of dye, 100 mL.

were partially blocked by carboxymethylation. Thus, it is still possible that styrene can be grafted onto the CMC component through the residual hydroxyl groups. This is because the instability of the PVA/CMC blends in water was greatly increased after the grafting process; otherwise, the CMC component would be dissolved in the aqueous dye-waste solution. (3) The mechanism of grafting the styrene monomer onto PVA or CMC would be initiated through the radiolysis of methanol and styrene as follows:

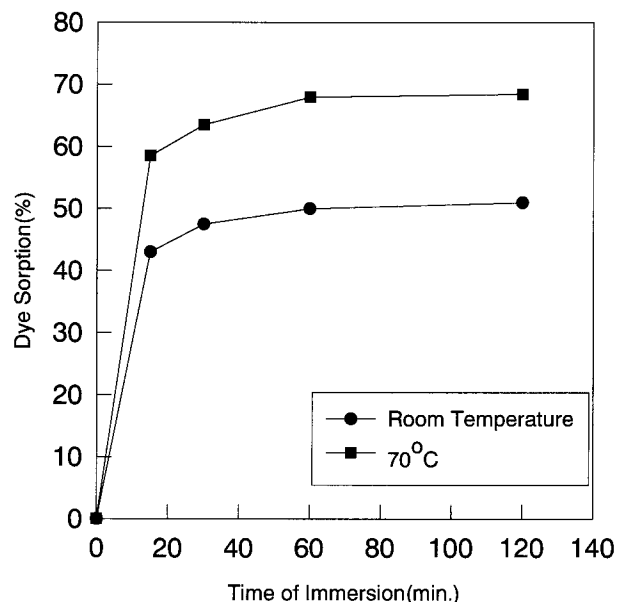


#### Sorption of Dyestuffs by PVA/CMC Blend Graft Copolymer

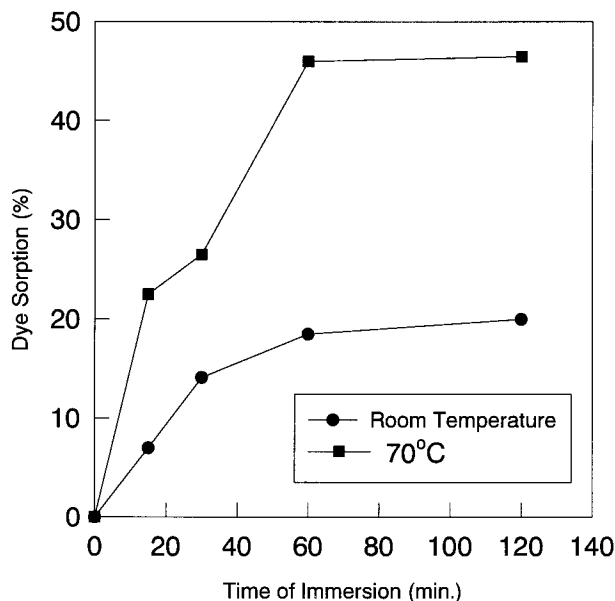
In the textile industry, different dyestuffs, belonging to different classes, are used in dyeing

textile fabrics depending on the kind of fibers. Moreover, among each class of dyestuffs, there are various colors according to the producers. While the reactive and direct dyes are specific for dyeing cotton cellulose fibers, the acid and basic dyes are used for dyeing protein fibers such as wool and silk. Also, disperse dyes are now widely used in dyeing cotton blends with polyester fabrics. In general, the choice of the dyestuff is based on the functional groups on both the fiber and the dyestuffs.

In the present work, a dye bath, containing a constant concentration of 20 mg/L of each dye under investigation, was prepared. The dye sorption of the different dyes by the PVA/CMC blend graft copolymer, as a function of the immersion time at room temperature and 70°C, was investigated as shown in Figures 3–6. It can be seen that the dye sorption–time trend by the blend graft copolymers differs from one dye to another. In the case of basic and acid dyes, the percentage sorption was found to increase significantly after a very short time of 10 min and afterward tended to level off with an increasing time of immersion up to 120 min, as shown in Figures 3 and 4. In the case of the reactive and the direct dyes, the percentage sorption by the blend copolymer increases substantially with an increasing time of immer-



**Figure 4** Dye sorption (%) of the acid dye Sandolan E-3GSL by PVA/CMC-*g*-PS blend graft copolymer at room temperature and 70°C as a function of immersion time. The dye-sorption conditions are the same as in Figure 3.



**Figure 5** Dye sorption (%) of the reactive Drimarene Blue K-3GL by PVA/CMC-*g*-PS blend graft copolymer at room temperature and 70°C as a function of immersion time. The dye-sorption conditions are the same as in Figure 3.

sion up to 60 min and then tends to level off. In all cases, the dye sorption was found to increase with increasing of the temperature of the dye solution from room temperature to 70°C. In comparing the maximum dye sorption of the different dyestuffs at 70°C by the blend graft copolymer at 70°C, the affinity for different dyes can be arranged as follows:

Basic dye > Acid dye

> Reactive dye > Direct dye

The respective sorption affinity of the blend graft copolymer for the different dyestuffs may be explained on the basis of the following points:

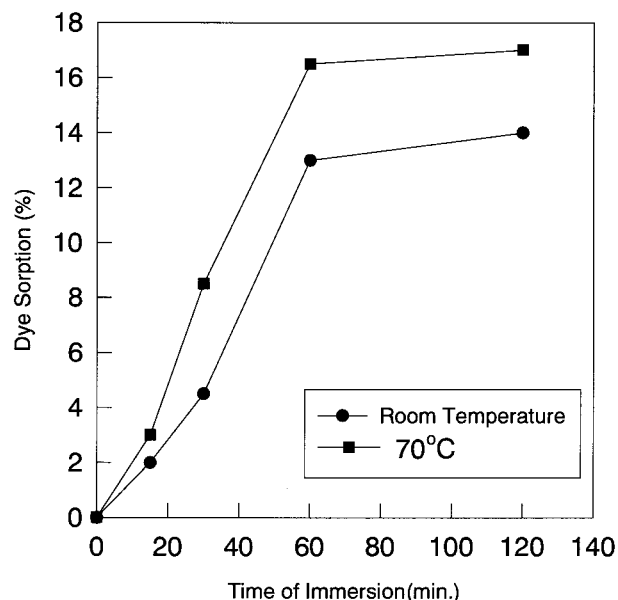
1. The affinity of the blend graft copolymer for the different dyestuffs is essentially dependent on the hydrophilic groups present in the blend. Also, the sorption process will go, eventually, through chemical bonding between the active groups on the different dyes and those of the blend and not through physical absorption. This is because, when the blend graft copolymer was left in the dye solution for a longer time than 120 min, the desorption of dyes did not

occur. Thus, it may be concluded that dyeing of the blend graft copolymer with the different dyestuffs is dependent on the relative affinity for each dye.

2. The mechanism of dyeing with basic dyes implies the presence of an anionic part in the medium to react with the cationic part of the dye through an anionic bond. Therefore, the sorption of the basic dye will go through the reaction with the hydroxyl groups of the PVA component inside the blend.
3. In addition, the opening up of the blend structure during the graft copolymerization with styrene may facilitate the absorption and diffusion into the blend macrostructure.

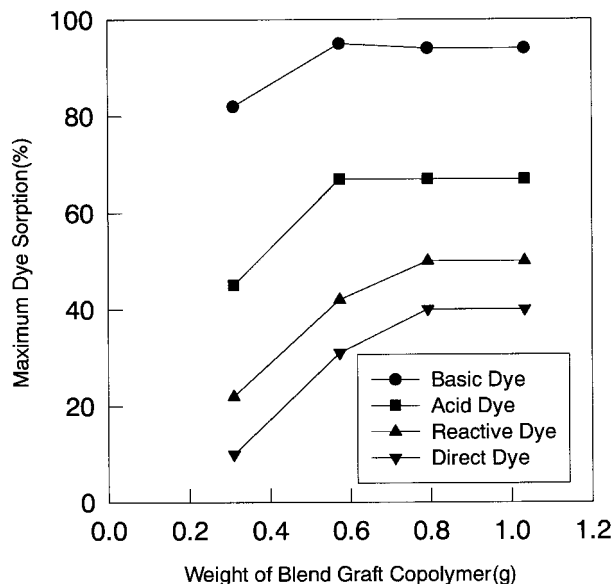
### Factors Affecting Dye Sorption

The economics of treatment and removal of toxic substances from waste waters are very important. From the practical point of view, it is more effective to use a small weight of an absorbent to treat a large volume of waste waters. Therefore, in the present work, sorption of the different dyestuffs by different weights of the PVA/CMC-*g*-PS blend graft copolymer was investigated, as shown



**Figure 6** Dye sorption (%) of the direct dye Solophenyl Olive EGL by PVA/CMA-*g*-PS blend graft copolymer at room temperature and 70°C as a function of immersion time. The dye-sorption conditions are the same as in Figure 3.

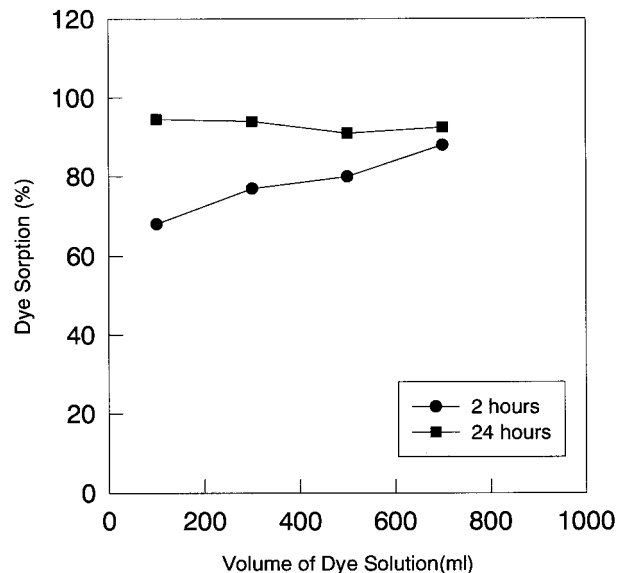




**Figure 7** Effect of changing weight of the blend graft copolymer PVA/CMA-g-PS on the percentage capacity of absorbing different dyestuffs at room temperature immersed in a constant volume of dye solutions of 100 mL for 24 h.

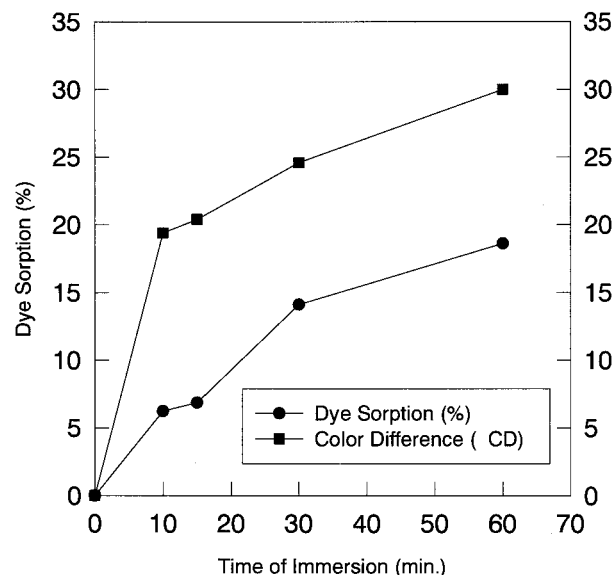
in Figure 7. It should be noted that the sorption was carried out on a constant volume of 100 mL containing a constant concentration from each dye. In general, it can be seen that the sorption of dyes increases with increasing the weight of the blend graft copolymer to a certain weight and then tends to reach a saturation state. This trend is shown to occur with all the dyestuffs under investigation. However, the weight at which maximum sorption was reached differs from one dye to another. It is clear that increasing the weight of the blend graft copolymer has nearly no effect on the sorption of the basic and acid dyes. On the other hand, an increasing weight of the blend graft copolymer seems to affect the sorption of the reactive and direct dyes to some extent.

The effect of the volume of the dye solution on the sorption (%) of the basic dye Remacryl Blue, as an example, at different immersion times at room temperature is shown in Figure 8. It is to be noted that the dye-sorption process was carried out at a constant weight of the blend graft copolymer of ~0.75 g. It is obvious that the dependency of the sorption on the volume of the dye solution displayed different trends depending on the time of immersion. When the immersion time was carried out for 24 h, the volume of the dye solution had nearly no effect on the percentage sorption. When the blend graft was immersed for 2 h, the



**Figure 8** Effect of volume of dye solution on the sorption (%) of the basic dye Remacryl Blue at different immersion times at room temperature.

dye sorption was affected by the volume of the dye solution to some extent. In conclusion, the sorption of the basic dye, in particular, by the blend graft copolymer, is shown not to depend on either the weight of the absorbent or the volume of the dye solution when immersed for longer times.



**Figure 9** Dye sorption (%) of the reactive dye Drimarine Blue by PVA/CMA-g-PS blend graft copolymer and the corresponding color-difference intensity on the blend graft copolymer at different immersion times at room temperature.

### Treatment of Industrial Dye Waste

The radiation-induced degradation of dyestuffs has been extensively reported.<sup>4-6</sup> Even though ionizing radiation may be promising in this field, the radiochemical yield products of the degraded dye wastes are still toxic. This is because most dyestuffs are aromatic compounds having at least two fused benzene rings or sometimes are polynucleides. As a matter of fact, the discoloration of dyestuffs, as a result of irradiation, is mostly due to the degradation of the chromophore group responsible for the coloring and not to the main structure of the dyes. In some cases, high-energy radiation may cause a partial degradation to the main structure of small aromatic fragments. The toxicity of these fragments may cause more dangerous effects than the original structure. The treatment and purification of dye waste by sorption using graft copolymers with active groups may be considered a more efficient practical method.

In the present work, the PVA/CMC-*g*-PS blend graft copolymer was utilized in the treatment of industrial waste normally released from some textile factories in Cairo. It should be noted that the dye-waste sample was taken from the drain of the dye bath at the end of the dyeing process. This dye bath contains, beside the reactive dyes used for dyeing cotton fabrics, the usual additives used during dyeing such as salts, wetting agents, and alkalis. In practice, it is difficult to determine the amount of absorbed dye by the graft copolymer because the concentration of dyes in the waste drains is unknown. Therefore, the sorption of the industrial dye waste was determined by comparing the percentage sorption of a similar class of dyestuff by the same blend graft copolymer. Figure 9 shows the sorption (%) of the reactive dye Drimarene Blue (taken from Fig. 5) by PVA/CMC-*g*-PS and the corresponding color difference ( $\Delta E^*$ ) on the blend graft copolymer at different immersion times. It should be noted that the color difference ( $\Delta E^*$ ) was measured after the sorption process had been completed. In this case,  $\Delta E^*$  is proportional to the sorption (%). It can be seen that, at any time of immersion, the difference between the percentage sorption by the blend

**Table I** Color Difference Intensity on PVA/CMC-*g*-PS Blend Graft Copolymer as a Result of Immersion for Different Lengths of Time in an Industrial Dye Waste

	Time of Immersion (min)					
	5	10	20	30	40	60
Color-difference intensity ( $\Delta E^*$ )	72	74	75	75	76	76

The industrial dye waste contains different colors of reactive dye: Remacryl Red 2BS, Remazol Black, and Remazol Blue RSP at different concentrations according to the factory recipe.

graft copolymer and the corresponding color difference on the graft copolymer is nearly constant. Therefore, it can be concluded that the color-difference intensity is proportional to the dye sorption for the same sample.

Table I shows the color difference  $\Delta E^*$  on the PVA/CMC-*g*-PS blend graft copolymer after it had been immersed in the industrial dye waste for different immersion times. It is obvious that the blend graft copolymer displayed a remarkable sorption behavior, higher than its sorption capacity for the identical laboratory-prepared dyestuffs. Moreover, the blend graft copolymer showed a high sorption behavior for the industrial sample after a very short time.

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