Reactive Dyeing of Cotton in Water-Organic Solvent Mixture

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Abstract : Cotton fabric was dyed with a reactive dye in water/dichloromethane two-phase immiscible solvent media. In order to minimize dye loss due to its hydrolysis, the reactive dyeing was carried out in dichloromethane containing a small amount of water. With only 2 mL of water in 23 mL of dichloromethane, 1 g of cotton fabric could be dyed perfectly. The uptake ratio increased greatly compared with that of normal reactive dyeing in a water medium. It would seem that the hydrophobic solvent, dichloromethane, can assist the even dyeing as it disperses a small amount of dye-dissolved water phase and conveys this water phase to the fabric entirely and uniformly.

(Received 5 June, 2000; Accepted 15 October, 2000)

1. Introduction

As the concern about environmental pollution rises, new technologies in the dyeing industry have become necessary to reduce the waste water produced by the dyeing process. Especially the reactive dyeing of cotton fiber is very serious because of unfixed dyes. Since the reactive dyes can form covalent bonds with a fiber, the dyed fibers exhibit excellent wash-fastness. However, these dyes also react with water molecules competitively; namely they are hydrolyzed. Consequently, as hydrolyzed dyes have no further reactivity to fiber, the uptake ratio is reduced and this brings about water pollution [1-5].

If it could be possible to reduce the water used in the reactive dyeing process, the hydrolysis of the dye would decrease, the fixation would increase, and the water pollution would diminish.

The diminution of water in the dye bath has its own limitations because uneven dyeing may occur. Therefore in the practical reactive dyeing of the cotton fiber in dye houses, it is recommended that the liquor ratio must be around 10:1 [6]. To minimize the quantity of water in the dye bath, the addition of organic solvent, dichloromethane, which is immiscible with water was considered.

In this study, cotton fabrics were dyed with a reactive dye in two-phase immiscible solvents of water and dichloromethane. The dye uptake, uptake ratio, and levelness relative to the amount of water in dichloromethane were investigated.

2. Experimental

2.1 Materials

The substrates were plain-weaved cotton fabric (warp 30S, 72 fil./in., weft 36S, 68 fil./in, 98 g/m²) and nylon fabric (warp 70D, 108 fil./in., weft 70D, 76 fil./in, 60 g/m²) which were completely scoured prior to dyeing. The dyes were C. I. Reactive Red 2 (Procion Red MX-5B, cold type) and C. I. Acid Blue 113 (Nylosan Navy N-RBL) of commercial grade. The organic solvent, dichloromethane, and reagents used in this experiment were first grade and used without further purification.

2.2 Methods

2.2.1 Dyeing

1.0 g samples of cotton fabric were dyed in tightly sealed stainless steel pots containing the dye, sodium carbonate, and 25 mL of immiscible solvent of water and dichloromethane by using an Auto Textile Dyeing Machine (Korea Science Industry Co.) at 50°C for 1 hour.

The nylon fabrics (1.0 g) were dyed with 0.01 g of C. I. Acid Blue 113 and 0.1 mL of acetic acid in water at different liquor ratios using the same dyeing machine at 100°C for 1 hour.

2.2.2 Dye uptake and uptake ratio

At the end of dyeing, the remaining dye inside the pots and on the fiber surface was thoroughly washed away using distilled water at 90°C, and then collected in standard volumetric flasks. The optical density of the washing water was then measured spectrophotometrically in order to determine the amount of dye uptake and uptake ratio by the equations below [7].

Dye uptake = Initial dye – (Dye in residual liquor +
Dye adsorbed on surface of fabric)

Uptake ratio (%) = (Dye uptake / Initial dye) × 100

3. Results and discussion

To evaluate the dye uptake and uptake ratio relative to the amount of water included in 25 mL of the water/dichloromethane immiscible solvent mixture, 1.0 g of cotton fabric was dyed with C. I. Reactive Red 2 at 50°C for 1 hour. The dye and sodium carbonate were controlled at equal concentrations in the water phase of the immiscible solvent. Because the dye and sodium carbonate concentrations were constant in the water phase of the immiscible solvent mixture in each dyeing pot, the net amounts of dye and sodium carbonate in each dyeing pot were increased with the amount of water. In Fig. 1, it is shown that as the amount of water increased, the uptake ratio was rapidly decreased though the dye uptake was increased.

Fig. 1 The dye uptake and uptake ratio of C. I. Reactive Red 2 on cotton fabrics in water/dichloromethane at 50°C for 1 hour. The concentrations of both the dye and sodium carbonate were constant (1.0 g/l) in the water phase, but their net amounts were different (0.001 g/1 ml ~ 0.025 g/25 ml).

Both the reactive dye and sodium carbonate are water-soluble and, therefore, will dissolve in the water phase of the immiscible solvent mixture. Because each concentration of dye and sodium carbonate was maintained equally in the water phase, it was entirely predictable that as the amount of water reduced, the dye uptake would decrease because the net amount of dye reduced. However, the more important issue is the uptake ratio. That is, the less the amount of water used,

the higher the uptake ratio observed, and it seems that the reduction in the hydrolysis of the dye might increase the chance of reaction between the dye and the fiber.

When an extremely small amount of water, less than 2 mL, was used, the uptake ratio increased greatly, but the shortage of dye-dissolved liquor resulted in uneven dyeing. As shown in Fig. 1, in the presence of dichloromethane the minimum amount of water required for even dyeing in this study was 2 mL, corresponding to a very low liquor ratio of 2:1. This would be impossible in normal exhaustion dyeing methods using only water as a dyeing medium. If dichloromethane was used without water as a dyeing medium, the dye and sodium carbonate would not be dissolved and the fiber would remain undyed.

Figs 2 and 3 illustrate the dye uptake and uptake ratio relative to the amount of water for equal amounts of net dye. The amounts of dye were varied to be 0.01, 0.025, and 0.05 g, corresponding to 1.0, 2.5, and 5.0% owf, but the amount of sodium carbonate was fixed at 0.05 g in each dyeing pot. In Fig. 2, it is not strange that the higher the amount of dye used, the higher the dye uptake revealed. But regardless to the amount of dye used, it is shown that the lower the amount of water in mixed solvent used, the higher the dye uptake. This is due to the increasing concentration of dye in water by reducing the water in the mixed solvent. Fig. 3 shows the uptake ratio. In this case, as the amount of water was reduced, the uptake ratio increased rapidly from 15–25% in 10/25 mL up to 38–48% in 2/25 mL. In contrast to the dye uptake in Fig. 2, less dye was used, the uptake ratio was higher.

Fig. 2 The dye uptake of C. I. Reactive Red 2 on cotton fabrics in water/dichloromethane at 50°C for 1 hour. The net amount of sodium carbonate was 0.05 g.

Fig. 3 The uptake ratio of C. I. Reactive Red 2 on cotton fabrics in water/dichloromethane at 50°C for 1 hour. The net amount of sodium carbonate was 0.05 g.

The increased uptake ratio with a reduced amount of water might be due to the decreased hydrolysis of the dye because of the reduced amount of water rather than the increased concentration of dye and sodium carbonate in the water phase.

To clarify this matter, the effect of the liquor ratio on the adsorption of acid dye onto nylon fiber using equal net amounts of dye and acetic acid in different amount of water was estimated. The dyeing mechanism of acid dye to nylon fiber would be similar to that of reactive dye to cotton because dyes are fixed on specific dyeing sites of fibers. Using only water, 1.0 g of nylon fabric was dyed with 0.01 g of C. I. Acid Blue 113 and 0.1 mL of acetic acid at 100°C for 1 hour, and the liquor ratio was varied from 2:1 to 25:1. The results are shown in Fig. 4.

The levelness at the lower liquor ratio was not good. Although the concentrations of dye and acetic acid varied according to the variation of liquor ratio, the fixations were all 100% for the entire range of liquor ratios. An acid dye, unlike a reactive dye, is not hydrolyzed, thus all the dye is adsorbed to the nylon fiber even at the highest liquor ratio of 25:1. Consequently, if the reactive dyes were not hydrolyzed, there would be no difference in the uptake ratios according to the amount of water in solvent mixture.

To investigate the effect of the sodium carbonate concentration on the uptake ratio, cotton was dyed with 0.05 g of C. I. Reactive Red 2 in a constant amount of water, 2 mL, in 25 mL of the solvent mixture at 50°C for 1 hour with varying quantities of sodium carbonate from 0 to 0.1 g.

Fig. 4 The effect of liquor ratio on the uptake ratio of C. I. Acid Blue 113 on nylon. 1.0 g samples of nylon were dyed with 0.01 g of the acid dye and 0.1 ml of acetic acid at 100°C for 1 hour.

As shown in Fig. 5, the maximum uptake ratio already appeared at 0.01 g of sodium carbonate. The amount of sodium carbonate, 0.05 g, in 10 mL of water which corresponds to the maximum water content in Fig. 3 is equal to 0.01 g / 2 mL in Fig. 5. From this result it can be concluded that the increased uptake ratio with a reduced amount of water, less than 10 mL in Fig. 3, does not come from an increased concentration of sodium carbonate. Figs 4 and 5 confirm that the increased uptake ratio with reduced water is due to the decreased hydrolysis of the dye rather than the increased concentrations of the dye and sodium carbonate.

Fig. 5 The effect of sodium carbonate on uptake ratio of C. I. Reactive Red 2 on cotton fabrics in 2 ml of water and 23 ml of dichloromethane at 50°C for 1 hour. The amount of the dye was 0.05 g.

In this experiment, what is the role of dichloromethane in the mixed solvent? In order to know this, dyeing was carried out in 2 mL of water with and without dichloromethane. As shown in Fig. 6, with 2 mL of water and 23 mL of dichloromethane perfectly-even dyeing was obtained, but with 2 mL of water without dichloromethane, all of the dyeing liquor was absorbed on only some part of the fabric and this resulted quite uneven dyeing. Accordingly, the role of non-solvent dichloromethane in facilitating even dyeing can be considered as follows: Dichloromethane is at first competitively absorbed on the fiber with water. It then disperses a small amount of dye-dissolved water phase and conveys this water phase throughout the fiber uniformly, playing the role of a dyeing vehicle.

Fig. 6 Dyed cotton fabrics with 0.05 g net weight of C. I. Reactive Red 2 and 0.05 g of sodium carbonate at 50°C for 1 hour. The concentrations of the dye and sodium carbonate in the water phase decreased as the amount of water increased.

As dichloromethane is advantageous in the aspect of energy because of its low boiling point, and furthermore is hardly flammable, it is a very good medium for the reactive dyeing as shown in this experiment. But it may be restricted because it contains chlorine.

First, the result of this experiment is very interesting and is reported. On the basis of this result, the researches using non-chlorinated solvent media will be continued.

4. Conclusion

In order to minimize dye loss due to its hydrolysis during the reactive dyeing process, 1.0 g of cotton fabric was dyed with C. I. Reactive Red 2 in dichloromethane containing a small amount of water. Perfectly-even dyeing was still obtained with a combination of 23 mL of dichloromethane and 2 mL of water. This amount of water is corresponding to a liquor ratio of 2:1. In addition, the uptake ratio increased greatly compared with that of normal reactive dyeing. Accordingly, it would seem that the hydrophobic solvent dichloromethane can facilitate even dyeing as it disperses a small amount of dye-dissolved water phase and conveys this water phase to fiber entirely and uniformly.

The requirement for solvent used in dyeing is that the solvent must be non-flammable and recovered easily after use. Almost all the organic solvents are flammable, but dichloromethane is hardly flammable. In view of the recovery of solvent, its lower boiling point, 39.8°C, is advantageous.

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