Available online at www.sciencedirect.com
SCIENCE DIRECT
Dyes and Pigments 72 (2007) 23–27
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

The efficiency of washing agents in the post-dyeing removal of hydrolyzed reactive dye

E.P. Akcakoca*, A.T. Ozguney, R. Atav

Department of Textile Engineering, Engineering Faculty, Ege University, Izmir, Turkey

Received 19 November 2004; received in revised form 10 March 2005; accepted 18 July 2005
Available online 15 September 2005

Abstract

The efficiencies of various washing agents (anionic and non-ionic) in removing hydrolyzed reactive dye are evaluated. Hydrolyzed dye was padded onto bleached cotton woven fabric and dried to provide the experimental material. Samples were washed at 95 °C with various washing agents in different concentrations, processing times, and liquor ratios. Removal efficiencies were assessed-spectrophotometrically. The best washing results were obtained with non-ionic washing agent. Liquor ratio has a dominant effect on efficiency on removing the hydrolyzed reactive dye.

Keywords: Reactive dyes; Washing; Hydrolyzed dye; Washing agent

1. Introduction

Reactive dyes always have a significant place in textile dyeing, because of their high colour fastness and wide colour spectrum. In the last years, consumption of this dye has been 4 or 5 times more than the other dyestuff groups. However, hydrolysis of this dye during dyeing decreases the dyeing efficiency. Additionally, substantivity of hydrolyzed dyestuff increases the duration of washing processes realized after dyeing. Also, in reactive dyeing; half of the energy consumption, one third of the effluent (COD) and big portion of total water consumption are related with the washing procedures fulfilled after dyeing [1].

Basic consequences expected from the washing procedure realized after reactive dyeing are as follows:

- to decrease the water consumption without any compromise in product quality; in order to accomplish this, number of washing stages must be decreased or liquor ratios must be reduced. Intense interaction between the product and water must be provided for each case.
- to decrease the utilization of chemicals in washing without any compromise in product quality; because usage of chemicals is an additional cost and also increases the organic effluent rate in the wastewater.
- it is required to decrease the costs of heat and work power and to save on time [2].

The efficiency of washing processes realized after dyeing is associated with various parameters such as substantivity and diffusion rate of dye, hardness of water, pH of washing liquor, type and concentration of washing agent.

Non-ionic and anionic washing agents are used in washing procedures of reactive dyes. Although non-ionic washing agents are recommended for the elimination of hydrolyzed reactive dyes, since they enable the hydrolyzed

* Corresponding author. Tel.: +90 532 208 3588; fax: +90 232 388 7859.
E-mail address: perrin@textil.ege.edu.tr (E.P. Akcakoca).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.07.011

dyes to be expelled from the fibre rapidly, anionic washing agents cannot be recommended, because they make the elimination of hydrolyzed dyes difficult. This disadvantage was also observed in the research of Weible for the dyes having high substantivity. According to the researcher, electrolyte effect of anionic washing agents is sufficient for the wet fastness to decline significantly [3].

Polyphosphate originated washing agents are produced for the washing of reactive dye. However, together with the increasing environmental consciousness, usage of phosphates in washing is highly decreased taking into account the charging of wastewater, instead polyacrylic acids and salts are widely used. Additionally, in some researches it is indicated that washing agents have no contribution to remove hydrolyzed reactive dyes from the fabric [1].

In this article, spectral evaluation of the efficiencies of various washing agents to remove the hydrolyzed dye is the target. Fabric samples impregnated with hydrolyzed dye were washed with five different washing agents – four of them anionic, one of them non-ionic – at various washing times, liquor ratios and washing agent concentrations. Efficiencies of removing the hydrolyzed dyes are compared by evaluating the washed fabrics and washing liquor with the aid of spectral method.

2. Experimental

2.1. Materials

In this study, cotton woven fabric (Ne 30/1, 144 g/m^2) that was bleached and ready for dyeing, and C.I. Reactive Blue 21 dye were used. Five different washing agents (abbreviations: A, B, C, D, E) were used. Their ionic character and chemical structures are given in Table 1.

2.2. Application of hydrolyzed reactive dye

Dye solution prepared with 2.5 g/l C.I. Reactive Blue 21 and 10 g/l Soda (Merck) was boiled at 95 °C for 4 h to form hydrolyzed dye, and then cooled to room temperature. Hydrolyzation liquor, that was prepared, was impregnated to the 100% cotton woven fabric at room temperature and by maintaining the pick-up = 80%; and basic fabric was obtained after drying the fabric for 5 min at 120 °C [4].

2.3. Washing tests

Runner cloths of the same type of bleached fabric were sewn to the basic fabric samples, and 3 washing stages of 15 min at 95 °C were realized in Atlas Laundrometer (USA). Washing agents were applied in two different concentrations and liquor ratios (10:1 and 20:1) (Table 2). Additionally, washing process was performed just with water, without using any washing agents, in the same conditions at two different liquor ratios (10:1 and 20:1) in order to determine the efficiency of removing hydrolyzed dyes. At the end of first washing stage of 15 min, samples were removed from the containers, and samples of water were taken from the washing liquor and some of the fabric samples were rinsed under flowing water, then they were squeezed and dried. Remaining fabric samples were squeezed and dried without rinsing, and runner cloths were replaced with new ones. Liquor calculations were made according to the remaining weight, and second washing stage was performed. Same procedures were repeated for the second washing process, and washing was ended after the third washing stage of 15 min. Pure water was used for all washings and trials were repeated two times.

Liquor samples and washed fabric samples were evaluated spectrally after each washing stage. Absorption values of liquor samples were measured with UV-1201 Schimadzu (Japanese) spectrophotometer device, and reflectance values of fabric samples were measured with X-Rite (USA) spectrophotometer, and colour yield was expressed as K/S calculated with the aid of Kubelka Munk equation.

$$K/S = (1-R)^2/2R$$

R = reflectance value in the maximum absorption wave length
K = absorption coefficient
S = scattering coefficient

Table 1
Properties of washing agents used in the experiments

Washing agents	Ionic character	Chemical structure
A	Anionic	Polyacrylate copolymer with saccharides
B	Anionic	Polymeric carbonic acid, containing polyphosphate
C	Anionic	Mixture of organic and inorganic compounds
D	Non-ionic	Combination of polyfunctional nitrogens
E	Anionic	Polycarboxylic acids with modified phosphonates

Table 2
Washing agents and processing conditions

Washing agents	L.R. = 10:1		L.R. = 20:1	
	Concentration (g/l)		Concentration (g/l)	
A	1	3	1	3
B	1	3	1	3
C[a]	0.2	0.5	0.2	0.5
D	1	3	1	3
E	1	3	1	3

[a] Liquor concentration was lower than the others, because low concentration range was especially indicated for this washing agent.

3. Results and discussion

Besides the colour measurements of fabrics, as it is already told, absorbance measurements of washing liquors were also realized. Absorbance measurements of liquor samples taken after each washing stage were performed between 400 and 700 nm with the intervals of 20 nm, and maximum absorption wave length was found as 640 nm. It was accepted that high absorbance values in this wave length indicate that hydrolyzed dye amount in the washing liquor which is removed from the fabric is also high. K/S values of runner cloths can also be a measurement of efficiency in removing the hydrolyzed dyes. However, in the evaluations, values of the runner cloths were not used, and measurement results of basic fabric samples were taken into account, since it was thought that colour fading on the basic fabric will show the efficiency of removing the hydrolyzed dyes in a better way.

3.1. Influence on liquor ratio variation on the washing effect

Variation in the liquor ratio highly changes the washing effect, as it can be seen clearly in Figs. 1–4 (K/S value of basic fabric is 7.47, it was not indicated in the figures to simplify the drawings). K/S values calculated after washing realized in high liquor ratio are lower than the values of washing procedures performed in low liquor ratios, that is higher amount of hydrolyzed dye has been removed from the fabric. Positive effect of increasing the liquor ratio on the washing efficiency is more obvious in comparison to the effect obtained by increasing the processing time. For example, when anionic washing agent, with origin poly-carboxylic acid containing modified phosphonate, is used; K/S value is 0.37 after washing period of 45 min in liquor ratio 10:1, however, when the liquor ratio is increased to 20:1, K/S value is 0.32 after washing for 30 min. That means, efficiency of removing the hydrolyzed dyes that are obtained after a long time in low liquor ratio, can be achieved in a shorter period of time when the liquor ratio is increased. As it can be understood, instead of washing realized in 10:1 liquor ratio for 45 min with anionic washing agent, having origin of poly-carboxylic acid containing modified phosphonate, more or less the same washing effect can be obtained by increasing the liquor ratio to 20:1 and realizing the process for total washing time of 30 min.

Efficiency of removing hydrolyzed dyes, when no washing agent is used in the washing process, is higher than the one obtained by anionic washing agents in the same liquor ratio; however, efficiency is slightly lower than the result achieved with the usage of non-ionic washing agents. Additionally, washing effect of process performed in liquor ratio 20:1 without using any washing agent is better than all other washing procedures realized in 10:1 liquor ratio. This shows us that we

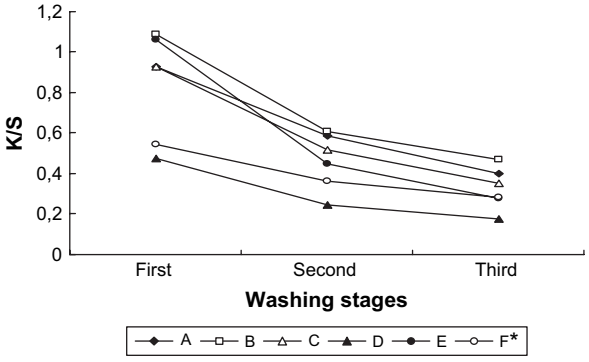

Fig. 2. K/S variance of the fabric with hydrolyzed dyes, with regard to washing time and type of washing agent used in 10:1 liquor ratio and high concentration of washing agent (K/S value of basic fabric = 7.47). *Washing performed only with pure water, without usage of any washing agent.

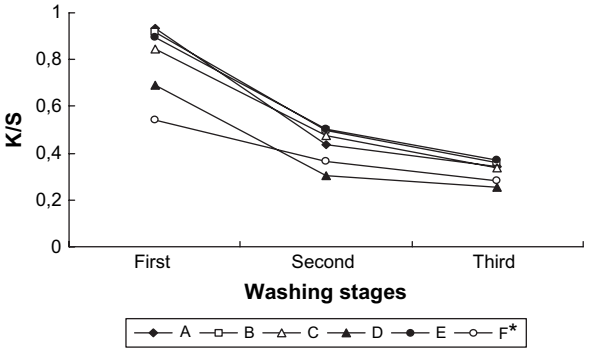

Fig. 1. K/S variance of the fabric with hydrolyzed dyes, with regard to washing time and type of washing agent used in 10:1 liquor ratio and low concentration of washing agent (K/S value of basic fabric = 7.47). *Washing performed only with pure water, without usage of any washing agent.

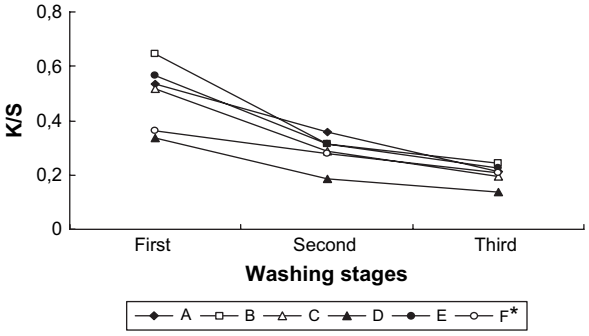

Fig. 3. K/S variance on the fabric with hydrolyzed dyes, with regard to washing time and type of washing agent used in 20:1 liquor ratio and low concentration of washing agent (K/S value of basic fabric = 7.47). *Washing performed only with pure water, without usage of any washing agent.

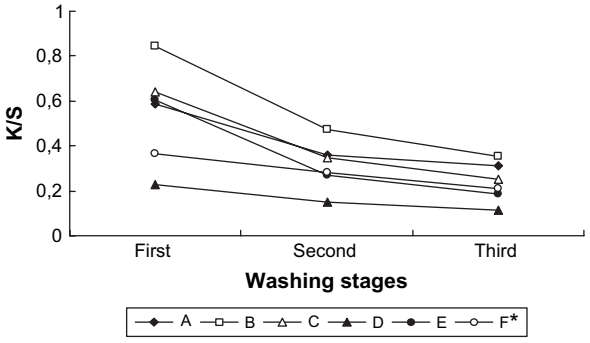

Fig. 4. K/S variance on the fabric with hydrolyzed dyes, with regard to washing time and type of washing agent used in 20:1 liquor ratio and high concentration of washing agent (K/S value of basic fabric = 7.47). *Washing performed only with pure water, without usage of any washing agent.

can make more efficient washing by using more water, instead of using washing agents.

In Figs. 5 and 6, the effect of liquor ratio on the efficiency of removing hydrolyzed dyes is given from the viewpoint of absorbance values. Absorbance values of washing liquor increases as the liquor ratio increases. This means that more hydrolyzed dye has been removed during washing and more efficient washing has been performed.

3.2. Influence of processing time on the washing effect

Results obtained from the repetitive washings show that as the processing time extends washing effect also increases. However, hydrolyzed dye amount found in the water after 15 min of 1st washing stage is much more than the amount that passes to the water after 30 and 45 min (Figs. 5 and 6). This show us that main effect is built in the first 15 min. In the second interval of 15 min still some hydrolyzed dye can be removed, however, when the washing continues further, no clear benefit is obtained from the viewpoint of washing effect.

3.3. Influence of washing agent type on the washing effect

The non-ionic washing agent (D) examined removes hydrolyzed dye more efficiently than all anionic washing agents used here. This can be clearly seen from Figs. 1–4. When the absorbance values are considered, the results parallel those found with the fabric: most hydrolyzed dye is removed in the first 15 min with the non-ionic washing agent (D) (Figs. 5 and 6).

Non-ionic washing agents have a slight cationic property in certain mediums. Furthermore, the alteration occurs only in the reactive groups during hydrolyzation. Anionic groups which enable solubility in water are not affected by the hydrolyzation. Thus slight cationic property of non-ionic agent may promote the removal of hydrolyzed reactive dye.

3.4. Influence of concentration of washing agent on the washing effect

Increasing the concentration of the washing agent brings to light an interesting result. Relationship between the concentration and washing effect changes according to the ionic character of the washing agent. When the concentration of non-ionic washing agent is increased, efficiency of removing hydrolyzed dyes also improves. However, the reverse is valid for anionic washing agents, as the concentration of the washing agent increases, washing effect decreases (Figs. 5 and 6). Ionic character of the liquor is an important factor for the washing process realized after reactive dyeing. It is also indicated in the research of Weible [3] that ionic character of the liquor increases when anionic washing

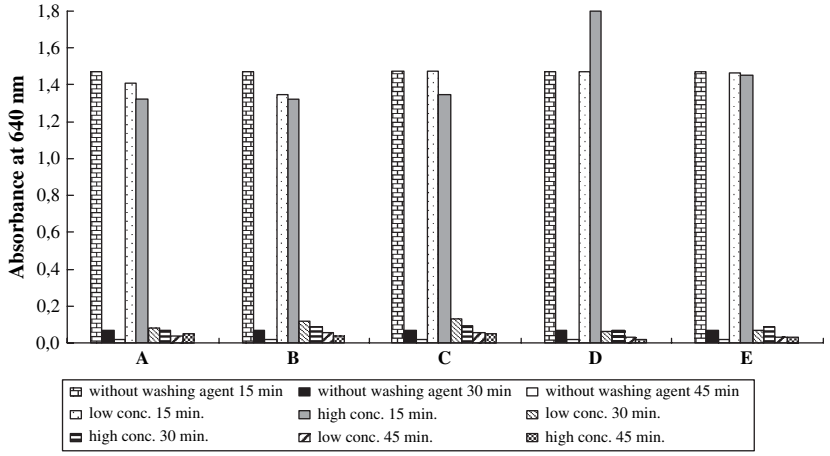

Fig. 5. The relation between the type of washing agent, concentration, washing time, and absorbance value when the liquor ratio is constant (10:1).

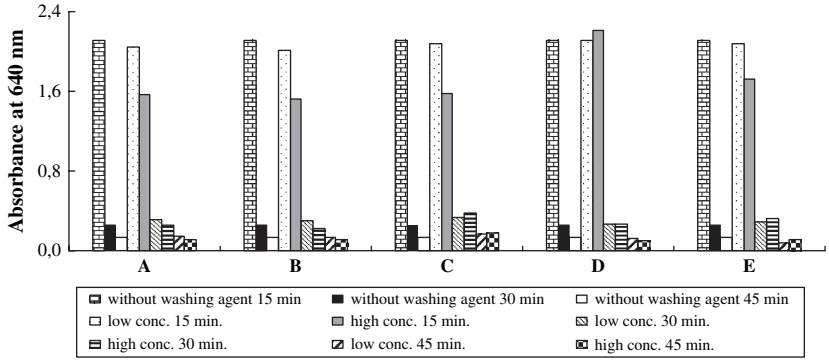

Fig. 6. The relation between the type of washing agent, concentration, washing time, and absorbance value when the liquor ratio is constant (20:1).

agents are used, thus the washing effect is influenced in a negative way.

4. Conclusion

In this research, it is observed that removal of hydrolyzed dyes efficiently took place in the first 15 min of the washing process, in the second 15 min small amount of hydrolyzed dye could be removed, however, in the last 15 min hydrolyzed dye amount that is removed was unimportant with regard to the first and second stages. For this reason, extending the washing time will cause an increase in the energy and water consumption, and also in the over-all costs, instead of improving the washing effect. Additionally, the effect achieved in high liquor ratio cannot be obtained regardless of the increase we make in washing time. Thus, instead of extending the washing time, increasing the liquor ratio slightly will improve the washing effect more efficiently.

Also, the type of washing agent used in the washing process has an important part on the efficiency of removing hydrolyzed dyes. For this reason, this fact must be taken into consideration when deciding on the washing agent. If we compare the washing effects of non-ionic and anionic washing agents used in the washing process realized after reactive dyeing; it is seen that a better result is achieved with non-ionic washing agents in the same concentration. On the other hand, increasing the concentration of washing agent can be a good alternative for non-ionic washing agents, which is not the case for anionic washing agents. Efficiency of removing hydrolyzed dyes, obtained by washing without using any washing agent, is higher than the washing done with anionic washing agents; however, it is slightly lower than the efficiency achieved with the usage of non-ionic washing agents. In addition, in the washing performed without using any washing agent in high liquor ratio, better washing effect is achieved with regard to all other washing processes realized with washing agent in low liquor ratio. This shows us that more efficient washings can be made by using more water, instead of using washing agents in the process. Thus, when we consider environmental protection and energy consumption factors, to enable the contact of the goods with abundant water in high liquor ratios will give better results as long as it is possible and economic.

References

[1] Cleaner technology in reactive dyeing of cotton. <http://www.\2_Cleaner technology in reactive dyeing of cotton, Danish Environmental Protection Agency.htm>.
[2] Yurdakul A. Comparison of washing effects of classic and thermo-flush methods in reactive dyeing. Tekstil ve Konfeksiyon 1999;6:444–6.
[3] Weible K-H. The influence of calcium when washing off reactive dyes. Melliand English 1990;10:E 361–2. Original German pages: Melliand Textilberichte 1990;10:772–4.
[4] CHT R. BEITLEIH GMBH, Product catalogues of washing agents.