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The Wash-off of Reactive Dyes on Cellulosic Fibres. Part 4: The Use of Different Alkalis with Monochlorotriazinyl Dyes on Cotton

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ABSTRACT

One monochlorotriazinyl and two bis-monochlorotriazinyl dyes were applied to cotton fabric and the dyeings then washed-off using aqueous solutions of ammonium hydroxide, sodium bicarbonate, potassium hydroxide, sodium hydroxide or five buffer systems. The effects of varying the amount of each alkali used on both the extent of dye removal and the wash fastness of the dyeings were determined. It was found that potassium hydroxide and sodium bicarbonate were more effective than the two other alkalis used and, also, that the buffer systems were less effective than the alkalis in removing dye. The level of wash-fastness achieved was generally independent of the wash-off method used. © 1997 Elsevier Science Ltd

Keywords: reactive dyes, monochlorotriazinyl dyes, cotton dyeing, wash-off.

INTRODUCTION

Since their introduction forty years ago, reactive dyes have been an increasingly popular dye class for dyeing cellulosic fibres, mainly due to the bright shades and the very good wet fastness that they display on such fibres. However, in order for the dyeings to achieve the characteristically high level of wet fastness it is necessary, in most cases, to employ a series of rinsing and 'soaping' stages which are collectively known as *wash-off* in order to remove unfixed dye [1]. This wash-off process typically accounts for a major portion of the total dyeing cost and also has a major environmental impact owing to the high amount of dye that can be removed during wash-off and also because of the use of surfactants in the process.

The purpose of this study was to consider the role of surfactants in wash-off from the viewpoint of creating a potentially more cost-effective and environmentally friendly wash-off process. In previous parts of this paper [2–4] it was shown that aqueous sodium carbonate solution could replace aqueous solutions of surfactants very successfully in the wash-off of mono- and dichlorotriazinyl reactive dyes on cellulosic fibres. In this part of the work, an exploration was made of the possible use of other alkalis as well as buffer systems in the wash-off of monochlorotriazinyl reactive dyeings on cotton.

EXPERIMENTAL

Materials

Fabric

Scoured and bleached woven cotton (130 g m^{-2}), obtained from Whaleys, was used.

Dyes

Three commercial reactive dyes, namely Procion Red H-EXL (CI Reactive Red 58), Procion Yellow H-EXL (CI Reactive Yellow 138:1) and Procion Royal H-EXL (no available CI number), were used. Each dye was kindly supplied by Zeneca Colours and was not purified prior to use.

Buffer solutions

A stock solution was made up by dissolving 5 g of sodium phosphate monobasic (Na_2HPO_4) and 1 g of potassium phosphate dibasic (KH_2PO_4) in 1 litre of distilled water; the pH of the ensuing solution was 7.6. The pH of the solution was then adjusted to 8, 9, 10, 11 and 12 by the addition of an appropriate volume of 0.1 M aqueous sodium hydroxide solution.

All other reagents were laboratory grade reagents obtained either from Aldrich or BDH.

Procedures

Dyeing

All dyeings were carried out in distilled water, using fabric (2 g) which had been wetted out in cold distilled water, in stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Polycolor laboratory scale dyeing machine, employing a 20:1 liquor ratio. The dyeing method used was the Standard Method recommended by Zeneca Colours [5] shown in Fig. 1. After dyeing, the samples were rinsed and washed-off as described below.

Rinsing and wash-off

At the end of dyeing, the sample was removed from the dyebath, rinsed twice in tap water for 10 min at 70°C and washed-off using the following aqueous solutions:

1. NH_4OH (2 g l^{-1} or 5 g l^{-1}) at 95°C for 30 min;
2. $NaHCO_3$ (2 g l^{-1} or 5 g l^{-1}) at 95°C for 30 min;
3. KOH (1 g l^{-1} or 2 g l^{-1}) at 95°C for 30 min;
4. NaOH (0.1 g l^{-1} or 0.2 g l^{-1}) at 95°C for 30 min;
5. buffer solution (pH 8, 9,10,11 or 12) at 95°C for 30 min.

The pH values of the aqueous alkali solutions (1–5) are given in Table 1. Both rinsing and wash-off were carried out using a 30:1 liquor ratio. At the end of wash-off, the sample was rinsed in tap water at 70°C for 10 min and then in cold tap water for a further 10 min.

Colour measurement

The reflectance values of the dry, dyed samples were measured using a Colorgen CS1000 reflectance spectrophotometer interfaced to a personal computer under illuminant D_{65}, using a 10° Standard Observer with specular component excluded and UV component included. The corresponding K/S and L^*, a^*, b^*, C^* and $h°$ values of the samples were calculated at the appropriate λ_{max} of each dye. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric.

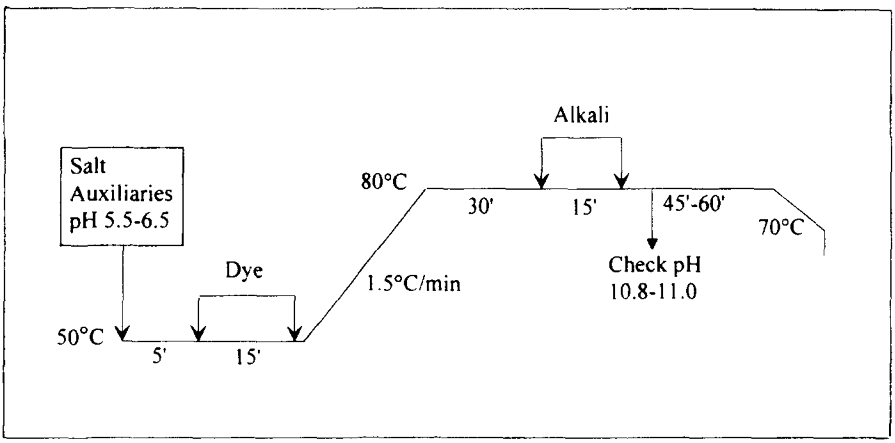


Fig. 1. Dyeing method.

Wash fastness testing
The fastness testing of the dyed samples was carried out in accordance with the ISO C06/C2 method [6].

RESULTS AND DISCUSSION

Instead of using several depths of shade as was done in an earlier study [3], it was decided to employ only 2% omf dye as this was considered to represent a typical, commercial depth of shade. In planning this study, it was decided to examine not only the use of different alkalis in the wash-off of the reactive dyeings but also to determine whether pH had an effect on wash-off. To this latter end, alkali concentrations were selected to provide pH values that ranged from just over neutral to over pH 13 (Table 1); the five buffer pH values used (8–12) were chosen to fit within this pH 7–13 range.

Wash-off

In the tables and figures that follow the colour strength (K/S values) and the colorimetric parameters (L^*, a^*, b^*, C^* and $h°$) of the dyeings are shown, as well as the difference in colour strength ($\Delta K/S$) between dyeings which had not been washed-off and dyeings which had been washed-off. In addition, the percentage difference in colour strength ($\%\Delta K/S$) between unwashed-off and washed-off dyeings are displayed. The latter two parameters were calculated as described previously [2].

CI Reactive Red 58
From the results presented in Table 2 it is evident that the colour strength (K/S values) of the washed-off dyeings was lower than that of the corresponding unwashed-off dyeing, indicating that unfixed reactive dye was removed during wash-off. The $\Delta K/S$ values shown in Table 2 reveal that of

TABLE 1
pH of the Aqueous Alkali Solutions Used

pH	*K/S*
NH_4OH (2 g l^{-1})	11.3
NH_4OH (5 g l^{-1})	11.8
$NaHCO_3$ (2 g l^{-1})	7.4
$NaHCO_3$ (5 g l^{-1})	8.5
KOH (1 g l^{-1})	11.8
KOH (2 g l^{-1})	12.6
NaOH (0.1 g l^{-1})	12.9
NaOH (0.2 g l^{-1})	13.4

the various wash-off methods used, the least effective in removing unfixed dye from the dyeings was that which employed pH 8 buffer and the most effective was that which used 2 g l^{-1} KOH solution. When the effectiveness of the various wash-off methods in removing unfixed dye (%$\Delta K/S$) was plotted as a function of the pH of the wash-off solution used, Fig. 2 was realised from which it is apparent that, in general, the extent of dye removal (which, in turn, is the effectiveness of wash-off) increased with increasing pH of the wash-off solution, as shown by the best-fit line displayed in Fig. 2. For the five buffer systems used (labelled I to M in Fig. 2), the extent of dye removal increased linearly with increasing pH of the buffer used. However, no such simple relationship between wash-off pH and dye removal was obtained for the four alkalis examined in that the effectiveness of KOH and $NaHCO_3$ was much greater than that suggested by the best-fit line, as shown by the shaded bars (labelled C to F) in Fig. 2. Indeed, the difference in the effectiveness of the 13 wash-off systems (Table 2 and Fig. 2) was surprising.

The colorimetric parameters of the washed-off samples (Table 2) show that each of the wash-off treatments caused a slight yellowing of the shade and that this change in shade generally decreased with increasing extent of dye removal.

Procion Royal H-EXL and CI Reactive Yellow 138:1

The results obtained for the wash-off of 2% omf dyeings of Procion Royal H-EXL and CI Reactive Yellow 138:1, are shown in Tables 3 and 4, respectively. In terms of dye removal, the results followed the same pattern as those obtained for CI Reactive Red 58 (Table 2) in that pH 8 buffer was the least effective in removing unfixed dye from the dyeings and 2 g l^{-1} KOH and

TABLE 2

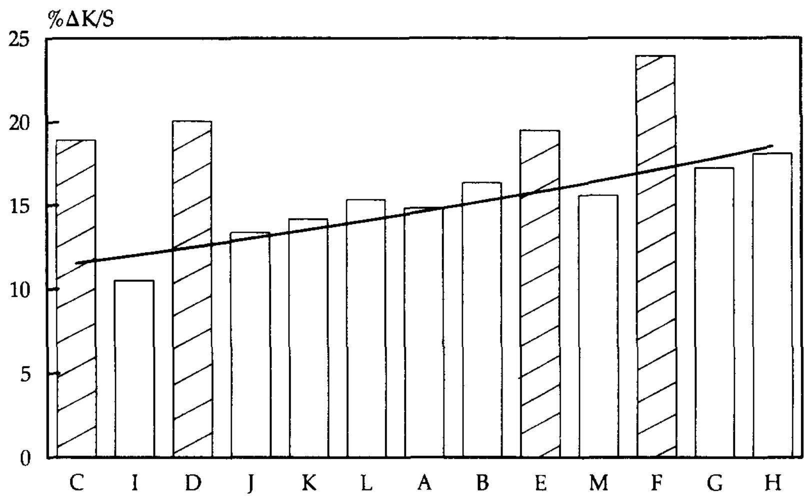
Colorimetric Parameters For 2% omf CI Reactive Red 58

Wash-off method	K/S	$\Delta K/S$	L^*	a^*	b^*	C^*	$h°$
Nil	9.55	—	49.64	50.47	−9.56	51.37	349.3
NH_4OH (2 g l^{-1})	7.82	1.73	45.57	52.15	−7.28	52.66	352.1
NH_4OH (5 g l^{-1})	7.63	1.92	45.60	51.91	−7.43	52.44	351.9
$NaHCO_3$ (2 g l^{-1})	7.34	2.21	45.55	52.40	−7.19	52.89	352.2
$NaHCO_3$ (5 g l^{-1})	7.20	2.35	45.29	51.52	−7.36	52.04	350.2
KOH (1 g l^{-1})	7.27	2.28	45.70	51.35	−7.26	52.27	352.0
KOH (2 g l^{-1})	6.75	2.80	45.37	51.72	−7.59	51.86	351.7
NaOH (0.1 g l^{-1})	7.53	2.02	46.32	52.57	−7.24	53.07	352.2
NaOH (0.2 g l^{-1})	7.43	2.12	47.09	52.26	−7.47	52.79	351.9
Buffer pH 8	8.32	1.23	45.94	53.45	−7.84	54.02	352.4
Buffer pH 9	7.99	1.56	45.87	53.54	−7.63	54.08	352.2
Buffer pH 10	7.89	1.66	45.66	53.62	−7.30	54.11	352.1
Buffer pH 11	7.75	1.80	45.57	53.24	−7.26	53.73	351.9
Buffer pH 12	7.72	1.83	45.29	53.90	−7.22	54.38	351.7

5 g l^{-1} $NaHCO_3$ solutions were the most effective. Furthermore, plots of $\%\Delta K/S$ vs pH of the wash-off solution used (Figs 3 and 4) reveal that the extent of dye removal (effectiveness of wash-off) increased generally with increasing pH of the wash-off solution although the effectiveness of KOH and $NaHCO_3$ was again anomalous as shown by the shaded bars.

From the colorimetric parameters of the washed-off samples obtained, it is evident that wash-off caused a slight yellowing of the shade of Procion Royal H-EXL (Table 3) and a slight blueing of the shade of CI Reactive Yellow 138:1 (Table 4); in both cases, the extent of the shade change generally increased with increasing extent of dye removal.

A comparison of the results presented in Figs 2–4 reveals that the results obtained for the three dyes were very similar. Although the absolute extents of dye removal ($\%\Delta K/S$) achieved using a particular wash-off solution



Label	Wash-off solution	pH
A	NH_4OH (2 g l^{-1})	11.3
B	NH_4OH (5 gl^{-1})	11.8
C	$NaHCO_3$ (2 g l^{-1})	7.4
D	$NaHCO_3$ (5 g l^{-1})	8.5
E	KOH (1 g l^{-1})	11.8
F	KOH (2 g l^{-1})	12.6
G	NaOH (0.1 g l^{-1})	12.9
H	NaOH (0.2 gl^{-1})	13.4
I	Buffer	8
J	Buffer	9
K	Buffer	10
L	Buffer	11
M	Buffer	12

Fig. 2. Effectiveness of wash-off as a function of pH.

varied for each dye, the effect of each wash-off solution on the three dyes was remarkably similar as evidenced by the similarity of the gradient of each of the best-fit lines displayed in Figs 2–4.

Discussion

Clearly, each of the aqueous alkaline solutions proved to be capable of removing unfixed dye from the dyeings. In previous parts of this paper [2–4], which showed that aqueous sodium carbonate solution could replace aqueous solutions of surfactants very successfully in the wash-off of mono- and dichlorotriazinyl reactive dyes on cellulosic fibres, several reasons were

TABLE 3
Colorimetric Parameters For 2% omf Procion Royal H-EXL

Wash-off method	K/S	$\Delta K/S$	L^*	a^*	b^*	C^*	$h°$
Nil	11.71	—	38.15	1.86	−41.60	41.64	272.6
NH_4OH (2 g l^{-1})	9.35	2.36	41.28	0.11	−39.84	39.84	270.2
NH_4OH (5 g l^{-1})	9.27	2.44	41.19	0.13	−39.94	39.94	270.2
$NaHCO_3$ (2 g l^{-1})	9.01	2.70	41.93	0.04	−39.39	39.39	270.1
$NaHCO_3$ (5 g l^{-1})	8.64	3.07	41.31	0.45	−39.56	39.56	270.7
KOH (1 g l^{-1})	8.93	2.78	41.78	0.14	−40.35	40.35	270.2
KOH (2 g l^{-1})	8.89	2.82	41.51	0.23	−40.46	40.46	270.3
NaOH (0.1 g l^{-1})	9.31	2.40	42.38	−0.79	−39.66	39.67	268.9
NaOH (0.2 g l^{-1})	9.07	2.64	42.22	−0.77	−40.13	40.14	268.9
Buffer pH 8	10.08	1.63	41.51	−0.51	−40.01	40.01	269.6
Buffer pH 9	9.96	1.75	41.53	−0.53	−40.38	40.38	269.4
Buffer pH 10	9.92	1.79	41.35	−0.44	−40.70	40.70	269.7
Buffer pH 11	9.64	2.07	41.16	−0.31	−40.90	40.90	269.3
Buffer pH 12	9.53	2.18	41.54	−0.23	−41.23	41.23	269.3

TABLE 4
Colorimetric Parameters for 2% omf CI Reactive Yellow 138:1

Wash-off method	K/S	$\Delta K/S$	L^*	a^*	b^*	C^*	$h°$
Nil	8.41	—	67.07	37.44	65.56	75.50	60.3
NH_4OH (2 g l^{-1})	7.43	0.98	66.99	37.23	64.33	74.32	59.9
NH_4OH (5 g l^{-1})	7.34	1.07	67.15	36.79	63.79	73.63	60.0
$NaHCO_3$ (2 g l^{-1})	7.48	0.93	65.83	36.27	63.28	72.94	61.9
$NaHCO_3$ (5 g l^{-1})	7.17	1.24	67.71	32.36	60.50	68.61	60.2
KOH (1 g l^{-1})	7.39	1.02	67.42	36.92	64.00	73.89	60.0
KOH (2 g l^{-1})	7.13	1.28	67.10	36.39	63.02	72.77	60.0
NaOH (0.1 g l^{-1})	7.38	1.03	67.57	36.50	63.92	73.61	60.3
NaOH (0.2 g l^{-1})	7.20	1.21	67.45	36.27	63.47	73.11	60.3
Buffer pH 8	8.04	0.37	67.29	37.00	65.17	74.94	60.4
Buffer pH 9	7.86	0.55	67.36	36.93	65.02	74.78	60.4
Buffer pH 10	7.68	0.73	67.50	36.87	64.96	74.69	60.4
Buffer pH 11	7.62	0.79	67.37	36.29	64.52	74.03	60.7
Buffer pH 12	7.53	0.88	67.41	36.20	64.47	73.94	60.6

proposed to explain the remarkably high ability of Na_2CO_3 to remove unfixed dye. The same reasoning [2–4] may well apply to the findings displayed in Tables 2–4 and Figs 2–4 and so explain the ability of each of the nine aqueous alkaline systems to remove unfixed dye from the dyeings. In terms of the observed general increase in dye removal that accompanied an increase in pH of the wash-off solution (Figs 2–4), previous discussions [2–4] of the wash-off proficiencies of aqueous sodium carbonate solution may well apply to the results secured in the present study. However, no explanation can be given for the marked effectiveness of KOH and, especially, $NaHCO_3$

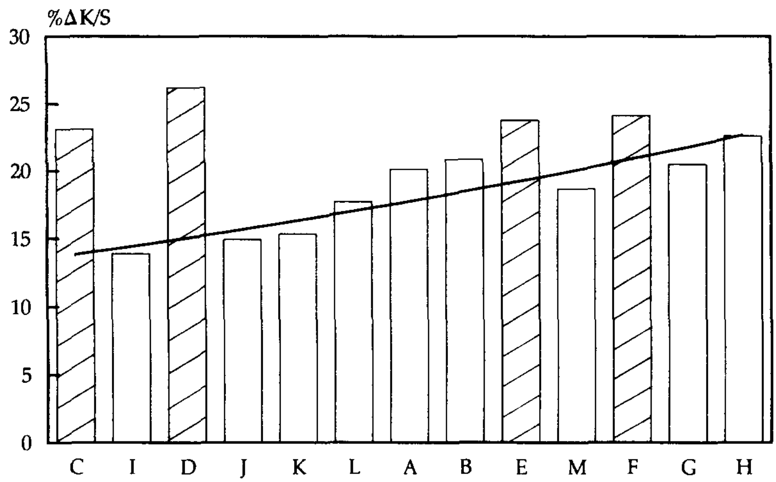


Fig. 3. Effectiveness of wash-off as a function of pH.

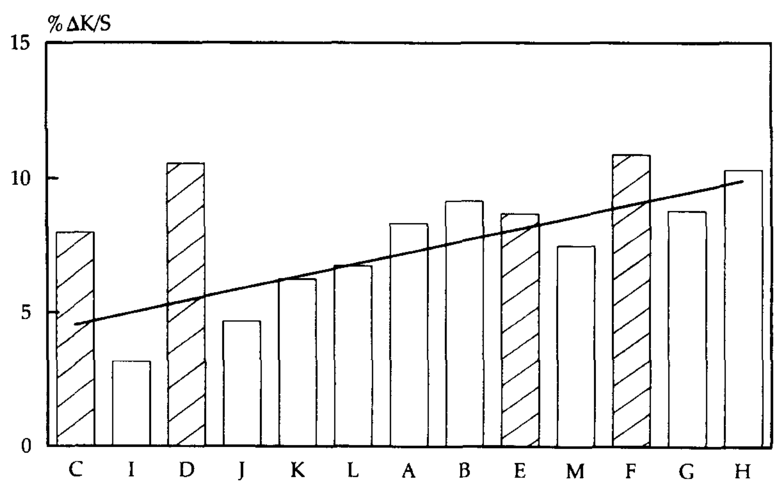


Fig. 4. Effectiveness of wash-off as a function of pH.

in removing unfixed dye. Further work is needed to determine why these two particular alkalis were so effective in washing-off unfixed dye.

Wash fastness

The effect of wash-off on the wash fastness of samples dyed using 2% omf CI Reactive Red 58, Procion Royal H-EXL as well as CI Reactive Yellow 138:1

TABLE 5
Wash Fastness of 2% omf Dyeings of CI Reactive Red 58

		Staining of adjacent	
Wash-off method	*Shade change*	*cotton*	*viscose*
Nil	3–4	3–4	3–4
NH_4OH (2 g l^{-1})	4–5	4–5	5
NH_4OH (5 g l^{-1})	4–5	4–5	5
$NaHCO_3$ (2 g l^{-1})	4–5	4–5	5
$NaHCO_3$ (5 g l^{-1})	4–5	4–5	5
KOH (1 g l^{-1})	4–5	4–5	5
KOH (2 g l^{-1})	4–5	4–5	5
NaOH (0.1 g l^{-1})	4–5	4–5	5
NaOH (0.2 g l^{-1})	4–5	4–5	5
Buffer pH 8	4–5	4–5	5
Buffer pH 9	4–5	4–5	5
Buffer pH 10	4–5	4–5	5
Buffer pH 11	4–5	4–5	5
Buffer pH 12	4–5	4–5	5

TABLE 6
Wash Fastness of 2% omf Dyeings of Procion Royal H-EXL

		Staining of adjacent	
Wash-off method	*Shade change*	*cotton*	*viscose*
Nil	4	3–4	4–5
NH_4OH (2 g l^{-1})	4–5	4	4–5
NH_4OH (5 g l^{-1})	4–5	4	4–5
$NaHCO_3$ (2 g l^{-1})	4–5	4	4–5
$NaHCO_3$ (5 g l^{-1})	4–5	4	4–5
KOH (1 g l^{-1})	4–5	4	4–5
KOH (2 g l^{-1})	4–5	4	4–5
NaOH (0.1 g l^{-1})	4–5	4	4–5
NaOH (0.2 g l^{-1})	4–5	4	4–5
Buffer pH 8	4–5	4	4–5
Buffer pH 9	4–5	4	4–5
Buffer pH 10	4–5	4	4–5
Buffer pH 11	4–5	4	4–5
Buffer pH 12	4–5	4	4–5

TABLE 7
Wash Fastness 2% omf Dyeings of CI Reactive Yellow 138:1

Wash-off method	*Shade change*	*Staining of adjacent*	
		cotton	*viscose*
Nil	3–4	3–4	4
NH_4OH (2 g l^{-1})	4–5	4–5	5
NH_4OH (5 g l^{-1})	4–5	4–5	5
$NaHCO_3$ (2 g l^{-1})	4–5	4–5	5
$NaHCO_3$ (5 g l^{-1})	4–5	4–5	5
KOH (1 g l^{-1})	4–5	4–5	5
KOH (2 g l^{-1})	4–5	4–5	5
NaOH (0.1 g l^{-1})	4–5	4–5	5
NaOH (0.2 g l^{-1})	4–5	4–5	5
Buffer pH 8	4–5	4–5	5
Buffer pH 9	4–5	4–5	5
Buffer pH 10	4–5	4–5	5
Buffer pH 11	4–5	4–5	5
Buffer pH 12	4–5	4–5	5

are shown in Tables 5–7. Lowest wash fastness was, not surprisingly, displayed by the dyeings which had not been washed-off. Interestingly enough, each of the wash-off methods employed imparted practically identical wash-fastness to the dyeings. However, none of dyeings exhibited excellent wash fastness (i.e. ratings of 5 for shade change, staining of cotton adjacent and staining of viscose adjacent) which implies that not all unfixed reactive dye had been washed-off, which, in turn, implies that none of the wash-off methods used was fully effective in removing all unfixed dye from the dyeings.

CONCLUSIONS

While each of the four alkalis and five buffers proved to be capable of removing unfixed dye from 2% omf dyeings, the effectiveness of the nine wash-off systems varied, with KOH and $NaHCO_3$ being the most effective and pH 8 buffer the least effective. Although in general, the extent of dye removal (and, thus, the effectiveness of wash-off) increased with increasing pH of the wash-off solution, the marked effectiveness of KOH and $NaHCO_3$ was not explainable in terms of pH. Each of the wash-off methods imparted virtually identical wash-fastness to the dyeings, although none exhibited excellent wash fastness.

These findings further those made in a previous part [3] of this paper which suggested that sodium carbonate presented an attractive alternative to the use of surfactants in the wash-off of the three dyes used in the present study.

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