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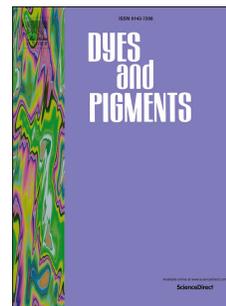


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The wash-off of dyeings using interstitial water Part 5: Residual dyebath and wash-off liquor generated during the application of disperse dyes and reactive dyes to polyester/cotton fabric

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1 **The wash-off of dyeings using interstitial water Part 5: residual dyebath**
2 **and wash-off liquor generated during the application of disperse dyes**
3 **and reactive dyes to polyester/cotton fabric**

4
5 ***Stephen M Burkinshaw, Kangsheng Liu and George Salihu**

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9
10 **Abstract**

11 Both 2% and 5% omf dyeings of polycotton fabric which had been produced using commercial
12 grade disperse dyes and reactive dyes can be washed-off using two, novel processes that utilise
13 polyamide beads. The bead wash-off processes provided dyeings that were of similar colour, depth
14 of shade and fastness compared to those which had been subjected to a conventional reduction
15 clearing process in the case of the disperse dyes and a conventional wash-off in the case of the
16 reactive dyes. The wastewater obtained from the bead wash-off of disperse dyes contained
17 considerably lower concentrations of chloride ion as well as lower TDS compared to that secured
18 using a conventional reduction clearing process, which was attributed to the beads having adsorbed
19 vagrant chloride ions. In contrast, bead wash-off of reactive dyes did not reduce either the chloride
20 ion concentration nor TDS content of the wastewater produced, because of the swamping effect of
21 the very high chloride ion concentration. Bead wash-off also enabled significant reductions in both
22 heat energy and water consumption to be achieved.

23
24 **Highlights**

- 25 • bead wash-off of dyed polycotton was comparable to conventional processing
26 • beads reduced chloride ion and TDS content of wastewater
27 • bead wash-off reduced both heat energy and water consumption

28

29 **keywords:** polycotton dyeing; bead wash-off; disperse dyes; reactive dyes

30

31 **1 introduction**

32 By some margin, polyester (poly(ethylene terephthalate); PES) is the most popular synthetic fibre
33 and cotton the most popular natural fibre, as reflected by PES accounting for 58.6% (53.1×10^6 T)
34 and cotton ~25.3% (22.9×10^6 T) of the 90.6×10^6 T world fibre production in 2015, with other man-
35 made and synthetic fibres comprising ~14.8% (13.4×10^6 T) and wool and silk making up the
36 remaining small proportion (~1.4%; 1.2×10^6 T) (1). Such dominance of global fibre usage enjoyed
37 by PES and cotton can be expected to continue for the conceivable future.

38

39 Unsurprisingly, global dye production is dominated by these two types of fibre namely, disperse
40 dyes in the case of PES fibres and reactive dyes for cotton. Whilst precise dye production figures
41 are unavailable in the public domain, if it is assumed that all textile fibre is dyed to an average depth
42 of shade of 2% omf (2) then an estimate can be made that $\sim 1.8 \times 10^6$ T of dye would have been
43 used to dye the 90.6×10^6 T of fibre produced in 2015. Of this total dye usage, disperse dyes would
44 have accounted for $\sim 1.1 \times 10^6$ T (ie PES fibres = 58.6% of 90.6×10^6 T fibre production), whilst
45 reactive dyes, which make up ~ 55-60% of global dye usage for cellulosic fibres, would have
46 accounted for $\sim 0.27 \times 10^6$ T (ie cotton fibres = 25.3% of 90.6×10^6 T fibre production) of global dye
47 production. Future dye production capacity can be presumed to increase in-line with anticipated
48 increases in PES and cotton fibre production.

49

50 As discussed in the previous part of this paper (3), although both PES and cotton enjoy usage as
51 individual types of fibre in textile materials, the most important commercial use of PES and cotton is
52 in the form of a PES and cotton blend that is commonly known as polycotton. The most popular
53 immersion dyeing method used for dyeing polycotton blend fabrics is a two-bath, multiple-stage
54 process in which the PES component is initially dyed using disperse dyes at $\sim 130^\circ\text{C}$ under acidic
55 conditions and surplus disperse dye is then removed using a wash-off process known as reduction

56 clearing, which involves treating the dyed material in an aqueous, alkaline solution of sodium
57 dithionite ($\text{Na}_2\text{S}_2\text{O}_4$; sodium hydrosulfite). The cotton component is then dyed using reactive dyes at
58 $\sim 60^\circ\text{C}$ under alkaline conditions and surplus dye is once more removed using a multi-stage wash-off
59 process that involves treating the dyed material to several aqueous rinses that use combinations of
60 cold/warm/hot water and which commonly employ a proprietary wash-off agent to expedite reactive
61 dye removal.

62

63 1.1 wash-off processes for polycotton

64 Wash-off is an essential component of each of the two dyeing processes that are used for
65 polycotton materials (ie dyeing the PES component using disperse dyes and dyeing the cotton
66 component using reactive dyes). Wash-off must be carried out in order to not only guarantee that
67 the dyeings display optimum fastness to subsequent wet treatments (eg domestic laundering), but
68 also to avoid any cross-staining of the disperse dyes on cotton and the reactive dyes on PES.

69

70 The exhaust dyeing of polycotton therefore consists of two lengthy, dissimilar, unrelated dyeing
71 stages, each of which is accompanied by a lengthy, dissimilar, unrelated wash-off process that
72 employs considerably different conditions (pH, temperature, type and amount of dyeing auxiliary,
73 etc.) for the two dye/fibre combinations. Indeed, the wash-off of disperse dyes from PES fibres and,
74 especially that of reactive dyes from cotton, routinely consume large amounts of water, as they
75 typically utilise liquor ratios of $\sim 1:10$ for each of the, characteristically, three stages of the reduction
76 clearing process utilised for dyed PES fibres and each of the several (commonly five or more)
77 stages of the conventional wash-off process for dyed cotton fibres. As such, the wash-off of 1 tonne
78 of dyed polycotton will consume somewhere in the region of 30 tonnes of water for the PES
79 component dyed using disperse dyes and a further 50 tonnes for the cotton which had been dyed
80 using reactive dyes (ie a 1:70 total liquor ratio). Should overflow rinsing be used, such already high
81 levels of water consumption in wash-off will be significantly increased.

82

83 1.1.1 polyester component

84 In the case of PES fibres dyed with disperse dyes, the reduction clearing process has especially
85 poor environmental credentials insofar as the dyed material is treated in an aqueous, alkaline
86 solution of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$; sodium hydrosulfite) and a non-ionic surfactant to remove
87 surplus disperse dye as well as surface deposited polyester oligomers (4). The strongly reducing
88 conditions convert anthraquininoid (AQ) disperse dyes to the corresponding water-soluble, low
89 substantivity, ionised variant and result in cleavage of the -N=N- bond in azo dyes, liberating
90 colourless amino compounds. Thus, in addition to the reduction clearing process consuming large
91 amounts of water, energy and chemicals, the highly alkaline wastewater that is generated from
92 reduction clearing will typically comprise the robust reducing agent sodium dithionite, surfactant,
93 residual dyes as well as aromatic amines in the case of azo disperse dyes. Despite persistent
94 attempts over many years to reduce the environmental impact of reduction clearing, the process
95 continues to enjoy widespread usage (5).

96

97 1.1.2 cellulose component

98 Unfortunately, because the immersion application of reactive dyes to cotton and other cellulosic
99 fibres (which account for the majority of contemporary reactive dye usage) is carried out using
100 aqueous alkaline conditions, so as to generate highly nucleophilic ionised hydroxyl groups ($-\text{O}^-$) in
101 the substrate with which the dyes can form a covalent linkage, all exhaust dyeing procedures for
102 reactive dyes are inherent inefficient (~40-60%) since the alkaline application conditions that are
103 necessary to promote dye-fibre reaction also impart alkali-induced dye hydrolysis. Consequently, a
104 rigorous, multi-stage wash-off process must be employed at the end of reactive dye application to
105 remove all unfixed dye, namely both unreacted reactive dye as well as unreactive hydrolysed dye.

106

107 The wash-off process that is used to remove surplus reactive dye from cellulosic fibres has an
108 additional important function that is a corollary of a further inherent deficiency of reactive dyes,
109 namely, that significant quantities of inorganic electrolyte (either sodium sulfate or sodium chloride)
110 must be used in order to achieve acceptable levels of dye uptake during immersion dyeing

111 processes. In this context, between 10-30 gl^{-1} NaCl, with upto 50 gl^{-1} for lower substantivity dyes, 80
112 gl^{-1} for low substantivity vinylsulfone dyes (6) and 100 gl^{-1} of NaCl or Na_2SO_4 in the case of dark
113 shades (7)) are typically added to a reactive dye dyebath to promote dye uptake; the added
114 electrolyte also promotes the extent of dye-fibre fixation (ie covalent fixation of the dye to the
115 substrate. In order to remove all traces of unfixed reactive dye from dyed cellulosic fibres, it is
116 necessary to also remove all residues of inorganic electrolyte from the dyed material that has been
117 adsorbed by the substrate during dyeing. Because of the very high levels of residual inorganic
118 electrolyte that are present in both the dyed fibre and the exhausted dyebath at the end of dyeing,
119 then the dyeing stage and the subsequent wash-off stage each characteristically generate large
120 amounts of wastewater that contains residual hydrolysed dye, unreacted dye, as well as very high
121 levels of NaCl or Na_2SO_4 . Additionally, because proprietary wash-off agents are normally utilised in
122 the wash-off process to expedite unfixed dye removal, the wastewater from reactive dyeing and
123 associated wash-off processes presents considerable environmental and economic challenges.

124

125 1.1.3 polycotton

126 From the foregoing, it is apparent that the wash-off of disperse dyes and reactive dyes from dyed
127 polycotton habitually produces copious amounts of wastewater that is contaminated with residual
128 dyes, inorganic electrolyte, proprietary wash-off agents, reducing agents, alkali, non-ionic
129 surfactants, etc. Despite considerable attention over many decades, no single wastewater treatment
130 method can be utilised for polycotton which has been dyed using disperse dyes and reactive dyes.
131 Indeed, dissimilar, distinctive, and often lengthy, wash-off processes are commonly employed for
132 the diverse range of dye/fibre combinations (eg acid dyes/wool, basic dyes/acrylic, etc.).

133

134 This paper describes a wash-off process for dyeings on polycotton that uses a novel, re-usable and
135 re-cyclable polyamide (PA) bead medium to replace the vast majority of the water and chemicals
136 that are normally employed in wash-off. This novel process (8) employs only the relatively small
137 amount of water that is present within the interstices of both the damp fabric and the bead material
138 to remove residual dye, electrolyte, surfactant, etc; as such, the bead wash-off process does not

139 require the dyed material to be immersed in a large reservoir of water, as employed in conventional
140 wash-off processes. The first part of the paper (9) showed that bead wash-off process was able to
141 remove five different types of dye from three different types of fibre to an extent that was
142 comparable to that achieved using appropriate, conventional wash-off methods. Similar depths of
143 shade and levels of wash fastness were secured in the cases of three, bis(aminochlorotriazine)
144 dyes reactive dyes on cotton (10) and three disperse dyes on PES (5) using bead wash-off
145 processes that utilised fewer treatment stages than the recommended, multi-stage conventional
146 wash-off processes. Less heat energy was consumed during bead wash-off than in conventional
147 wash-off processes (5) and the beads adsorbed vagrant disperse dye liberated during wash-off,
148 thereby presenting the opportunity of a lower effluent load (5, 10). The previous part of the paper (3)
149 demonstrated that in the case of polycotton fabric which had been dyed using reactive dyes and
150 disperse dyes, a novel bead wash-off process furnished dyeings that were comparable, in terms of
151 colour strength, colour and fastness, to those which had been reduction cleared in the case of the
152 disperse dyes and washed-off using a conventional 5-stage wash-off process for the reactive dyes.
153 In addition, the bead wash-off processes enabled reductions of ~70% to be achieved in the amounts
154 of both energy and water consumed during wash-off (3).

155

156 This part of the paper describes the extent to which the use of bead wash-off processes can reduce
157 the environmental impact posed by the wash-off of polycotton which has been dyed using disperse
158 dyes and reactive dyes.

159

160 **2. Experimental**

161 2.1 Materials

162 The materials used were the same as those employed in the previous part of the paper (3) namely
163 scoured, woven 52:48 polyester/cotton fabric (103 gm^{-2}) obtained from Whaley, Bradford, as well as
164 commercial grade samples of the disperse dyes, reactive dyes, dyeing auxiliaries and the
165 proprietary reactive dye wash-off agent shown in Table 1.

166

167 Table 1 dyes and auxiliaries used

chemical	name	supplier
	<i>Dianix Blue ACE</i> (no C.I. Generic Name ascribed)	
disperse dye	<i>Dianix Red E-FB</i> (C.I. Disperse Red 60)	Dystar
	<i>Dianix Yellow S6-G</i> (C.I. Disperse Yellow 114)	
reactive dye	<i>Remazol Red RB</i> (C.I. Reactive Red 198)	Dystar
	<i>Remazol Yellow R</i> (no C.I. Generic Name ascribed)	
	<i>Duractive Black B</i> (C.I. Reactive Black 5)	Town End Chemicals
oxidant	<i>Ludigol AR</i>	Dystar
levelling agent	<i>Levegal DLP</i>	Dystar
reactive dye wash-off agent	<i>Cyclanon XC-W New</i>	BASF

168

169 Owing to commercial confidentiality, details of the bead material used cannot be disclosed. All other
 170 chemicals were of reagent grade purity.

171

172 2.2 Procedures

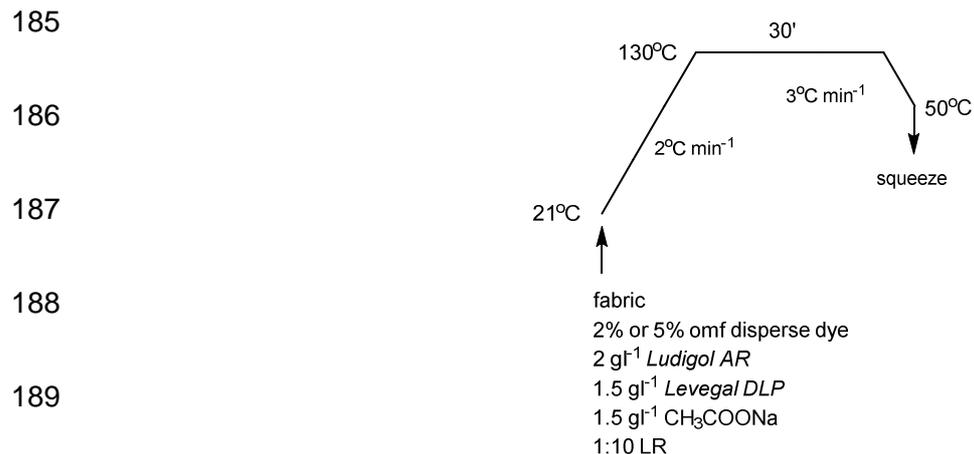
173 The dyeing and wash-off methods used in this part of the paper were similar to those described in
 174 the previous part of the paper (3). However, in this work, a 1:10 liquor ratio was employed for dyeing
 175 and for each of the three stages of the conventional reduction clearing process employed to remove
 176 surplus disperse dye as well as the five stages of the conventional wash-off process used to remove
 177 surplus reactive dye. Both the 2-stage bead wash-off process employed to remove surplus disperse
 178 dye and the 3-stage bead wash-off process used to remove surplus reactive dye utilised a 1:5 liquor
 179 ratio. As recounted previously (3), all dyeing and wash-off processes were undertaken using sealed,
 180 300 cm³ capacity, stainless steel dyepots housed in a Roaches *Pyrotec S* dyeing machine.

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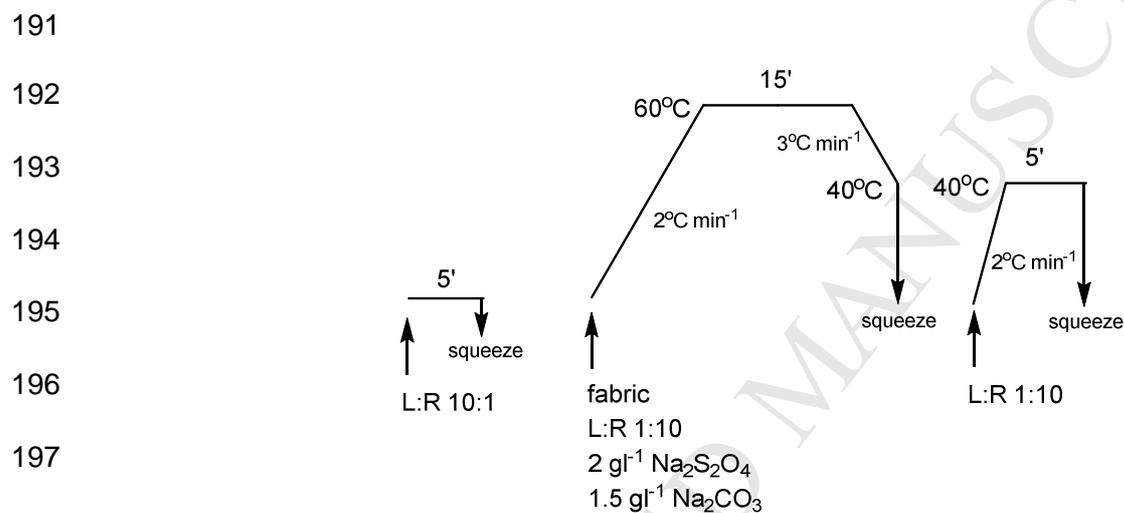
182 2.2.1 Dyeing the PES component of the polycotton blend

183 The three commercial grade disperse dyes were applied using the process shown in Figure 1.

184



190 Figure 1 process for dyeing the PES component using disperse dyes



199 Figure 2 3-stage reduction clearing process

200

201 *2.2.1.1 conventional wash-off of the dyed PES component of the polycotton blend*

202 The PES component of the polycotton fabric which had been dyed using the process recounted in
203 2.2.1 (Figure 1) was subjected to the 3-stage reduction clearing process shown in Figure 2. The
204 reduction cleared dyeing was then either allowed to dry in the open air or was dyed using reactive
205 dye according to the method described in 2.2.4.

206

207 2.2.1.2 bead wash-off of the dyed polyester component of the polycotton blend

208 The PES component of the polycotton fabric which had been dyed using the process recounted in
 209 2.2.1 (Figure 1) was subjected to the 2-stage bead wash-off process shown in Figure 3. The
 210 ensuing washed-off sample allowed to dry in the open air.

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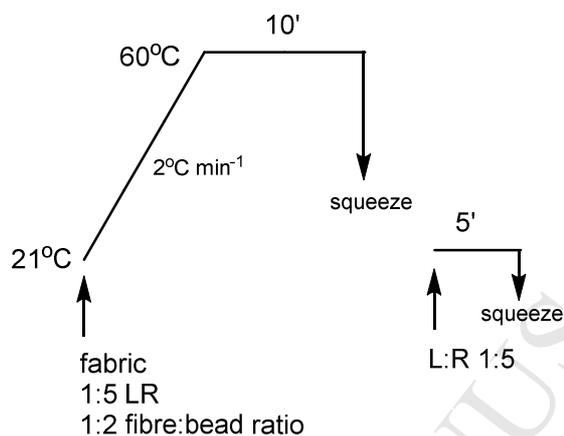


Figure 3 2-stage bead wash-off process

221 2.2.2 Dyeing the cotton component of the polycotton blend

222 The three commercial grade reactive dyes were applied using the process shown in Figure 4.

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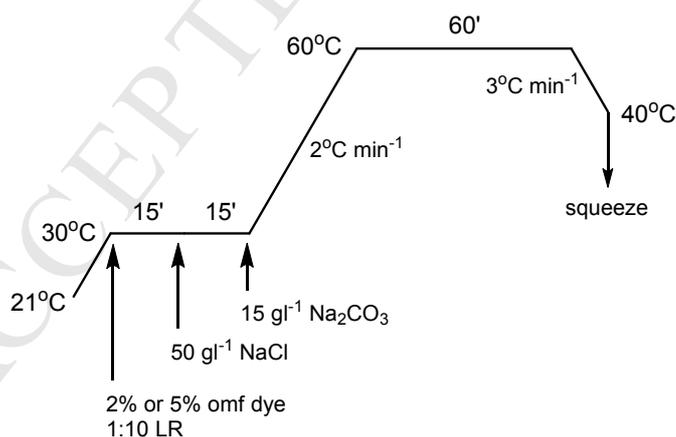


Figure 4 process for dyeing the cotton component using reactive dyes

231 2.2.2.1 conventional wash-off of the dyed cotton component of the polycotton blend

232 The cotton component of the polycotton fabric which had been dyed using the method recounted in
 233 2.2.4 (Figure 4) was subjected to the conventional 5-stage wash-off process shown in Figure 5. The
 234 washed-off dyeing was squeezed and allowed to dry in the open air.

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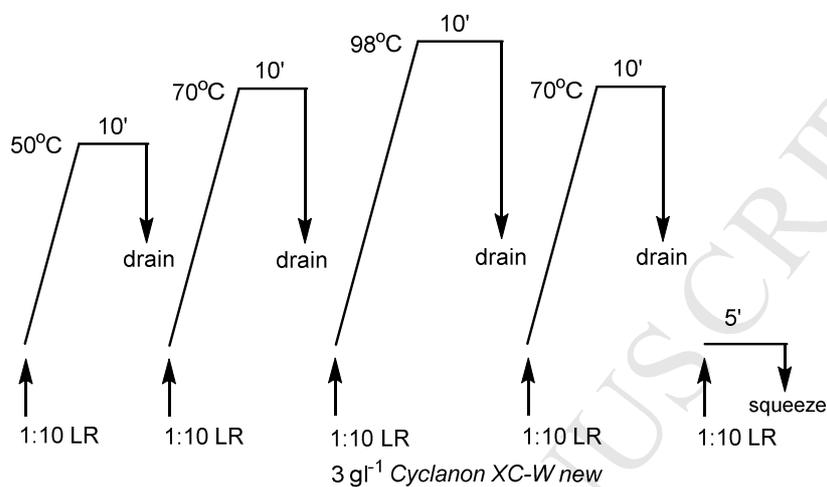


Figure 5 5-stage conventional wash-off process

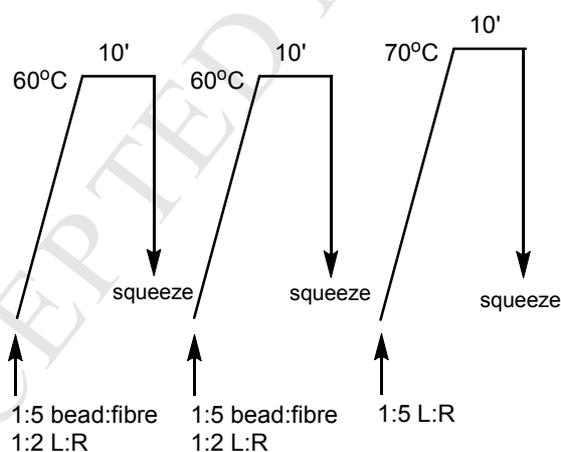


Figure 6 3-stage bead wash-off process

255 2.2.2.2 bead wash-off of the dyed cotton component of the polycotton blend

256 The cotton component of the polycotton blend fabric which had been dyed using the process
 257 recounted in 2.2.4 (Figure 4) was squeezed and subjected to the 4-stage bead wash-off process
 258 shown in Figure 6. In the two bead treatment stages depicted in Figure 6, the same sample of

259 beads was used for both treatment baths. The ensuing washed-off sample allowed to dry in the
260 open air.

261

262 2.2.3 Dyeing the polycotton blend fabric

263 The polyester component of the polycotton blend was first dyed using a disperse dye following the
264 procedure recounted in 2.2.1 (Figure 1) and the ensuing dyeing was subjected to either the 3-stage
265 reduction clearing process described in 2.2.1.1 (Figure 2) or to the 2-stage bead wash-off process
266 described in 2.2.1.2 (Figure 3). At the end of the 3-stage reduction clearing process or the 2-stage
267 bead wash-off process, the ensuing dyeing was dyed using a reactive dye as recounted in 2.2.2
268 (Figure 4). The dyed sample was then subjected to either the conventional 5-stage wash-off process
269 described in 2.2.2.1 (Figure 5) or to the 3-stage bead wash-off process described in 2.2.2.2 (Figure
270 6). The ensuing washed-off dyed polycotton sample was allowed to dry in the open air.

271

272 2.2.4 Colour measurement

273 As described previously (3), the CIE colorimetric co-ordinates and colour strength (f_k values) for
274 each dyeing were calculated from the reflectance values at the appropriate λ_{max} , measured using a
275 *Datacolor Spectroflash 600* spectrophotometer under illuminant D_{65} , employing a 10° Standard
276 Observer with UV component included and specular component excluded. The samples were folded
277 so as to realise four thicknesses and the average of four measurements was taken of each sample.

278

279 2.2.5 determination of chloride ion concentration in residual liquors

280 The concentration of chloride-ions $[Cl^-]$ present in the residual dyebath, wash-off bath and final rinse
281 bath liquors was measured using a *Cole-Parmer* chloride-specific, ion-selective electrode (ISE) (aka
282 chloride-ion electrode) connected to an *Orion Star-A111* pH/mV meter. As the measured electrode
283 potential of such an ion-selective electrode, in mV, is related to the ion concentration in solution (in
284 this case chloride ion) then a quantitative measure of $[Cl^-]$ can be made directly from the measured
285 electrode potential.

286

287 The change in electrode potential observed when the ion concentration changes by a factor of 10 is
288 referred to as the electrode slope; a difference in electrode slope of 56 ± 2 mV indicates correct
289 electrode operation, assuming that the solution temperature lies between 20° and 25°C .
290 Accordingly, a calibration curve was obtained by measuring the electrode potential (mV) of aqueous
291 NaCl solutions whose concentration (mol l^{-1}) varied, in tenfold steps, over the range 0.001 to 1 mol l^{-1} .
292 From the corresponding plot of electrode potential (mV) as a function of NaCl concentration (mol l^{-1})
293 the calibration coefficient was determined so that the NaCl concentration (mol l^{-1}) in liquor
294 samples could be determined from values of measured chloride ion electrode potential (mV). In this
295 work, $[\text{Cl}^-]$ is expressed as mg l^{-1} of Cl^- .

296

297 All dyebath, residual dyebath and wash-off liquor samples were measured directly (without any
298 dilution) at room temperature ($\sim 21\text{-}25^\circ\text{C}$). Samples were stirred gently at a constant rate, the
299 electrode tip was lowered into the solution and the stabilised mV readings recorded. The Cl^- ion
300 concentration in each sample was determined by comparing the measured mV readings to that of
301 the calibration curve using the calibration coefficient.

302 2.2.6 determination of total dissolved solids (TDS)

303 The total dissolved solids (g l^{-1}) in the residual dyebath, wash-off bath and final rinse bath liquors
304 were measured using a *Jenway-4510* conductivity/TDS/temperature bench-top meter directly
305 (without any dilution) at room temperature ($\sim 21\text{-}25^\circ\text{C}$). Samples were placed in a 60 cm^3 beaker
306 and stirred gently at a constant rate using a magnetic stirrer; the electrode tip was then lowered into
307 the solution and the stabilised TDS readings recorded.

308

309 Aqueous NaCl solutions of different concentration over the range 0.1 to 100 g l^{-1} were prepared and
310 the TDS of these solutions measured. A calibration curve was constructed by plotting TDS (g l^{-1}) as a
311 function of NaCl concentration (over the range 0.1 to 100 g l^{-1}) from which the calibration coefficient

312 was determined so that the TDS (g l^{-1}) of a given residual liquor sample could be determined from
313 calculated measured values of NaCl concentration.

314

315 2.2.7 Fastness determination

316 The fastness of the dyed samples to the ISO CO6/C2S (60°C) (11) wash test was determined.

317

318 2.2.8 Photography

319 Photographs of glass sample bottles containing wash-off liquors and beads were recorded using a
320 *Canon EOS 550D* digital camera.

321

322 **3. Results and discussion**

323 The six dyes used were chosen arbitrarily as being representative of typical, modern reactive dyes
324 and disperse dyes. A 2% omf depth of shade was used to provide typical pale/medium depth
325 dyeings whilst a 5% omf depth of shade provided a typical medium depth of shade. As mentioned,
326 because in this work, the same materials and similar experimental methods were used as had been
327 employed in the previous part of the paper (3), it was anticipated that the dyeings obtained in this
328 work would be very similar to those secured previously (3), as indeed was observed. However, as
329 the bead wash-off processes utilised in this work differed to those employed previously (3), insofar
330 as a lower liquor ratio was used in the current study, it was expected that the results obtained in this
331 work would differ to those previously secured, as indeed was observed.

332

333 *3.1 PES component/disperse dyes*

334 Figure 7 shows the colour strength (f_k values) of the PES component of the polycotton blend fabric
335 which had been dyed using the three disperse dyes at both 2% and 5% omf depths of shade; the
336 corresponding colorimetric data for the dyeings are shown in Table 2.

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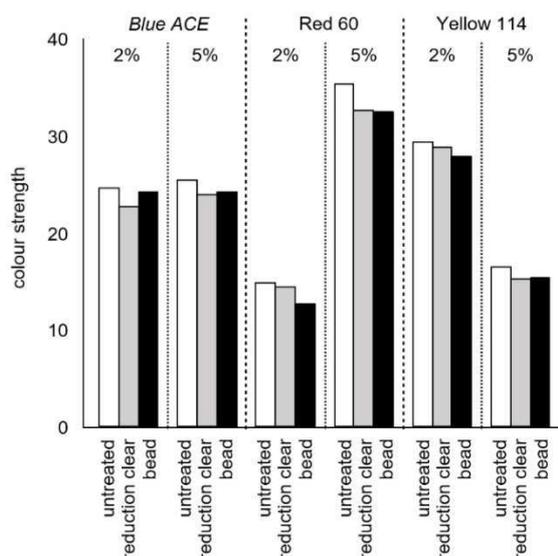


Figure 7 colour strength of PES component dyed using the three disperse dyes and washed-off using the conventional 3-stage reduction clearing process and 2-stage bead wash-off process

Table 2 Colorimetric parameters for dyeings of PES component dyed with disperse dyes and washed-off using the conventional 3-stage reduction clearing process and 2-stage bead wash-off process

dye	% omf	wash-off process	L*	a*	b*	C*	h°	λ_{\max}
<i>Dianix Blue ACE</i>	2	untreated	52.7	-2.2	-23.5	23.6	264.6	640
		reduction clear	53.8	-2.2	-23.3	23.4	264.6	640
		bead	52.9	-2.1	-23.2	23.3	264.8	640
	5	untreated	46.7	0.3	-21.5	21.5	270.9	620
		reduction clear	47.9	0.9	-23.2	23.2	272.2	620
		bead	48.0	0.6	-22.6	22.6	271.6	620
C.I. Disperse Red 60	2	untreated	57.3	43.9	4.6	44.2	5.3	520
		reduction clear	56.6	42.7	3.3	42.8	4.4	520
		bead	56.3	42.8	4.6	43.1	6.1	520
	5	untreated	54.1	40.9	5.3	41.3	7.3	520
		reduction clear	54.3	40.3	5.2	40.6	7.3	520
		bead	54.6	41.4	3.9	41.6	5.4	520
C.I. Disperse Yellow 114	2	untreated	84.9	-1.6	58.4	58.4	91.6	440

	reduction clear	87.0	-5.7	61.1	61.3	95.3	440
	bead	87.1	-6.0	57.6	57.9	96.0	440
	untreated	84.7	-4.4	60.3	60.4	94.1	420
5	reduction clear	83.9	2.3	57.4	57.4	87.7	420
	bead	83.3	-4.2	56.1	56.2	94.3	420

355

356 Two types of wash-off process were used to remove surplus disperse dye from the 2% and 5% omf
 357 dyeings on the PES component of the polycotton blend namely, a conventional a 3-stage reduction
 358 clearing process (Figure 2) and a 2-stage bead process (Figure 3).

359

360 Figure 7 reveals that the f_k values for the 2% and 5% omf untreated dyeings which had not been
 361 subjected to either reduction clearing or bead wash-off but, instead, had been allowed to dry after
 362 excess dye liquor had been removed from the dyeings by squeezing, displayed the highest colour
 363 strength. This was expected, since the primary purpose of both reduction clearing and bead wash-
 364 off is to remove surplus disperse dye and, therefore, both the bead washed-off and reduction
 365 cleared dyeings should be of lower colour strength than their untreated counterparts, as was indeed
 366 observed (Figure 7).

367

368 In this context, Table 2 reveals that the reduction in the colour strength of the dyeings that resulted
 369 from treatment with the hot, aq., alkaline solution of sodium dithionite during reduction clearing, is
 370 reflected in the slightly higher lightness (L^* values) recorded for the reduction cleared samples
 371 compared to the corresponding untreated dyeings. The 3-stage reduction clearing process also had
 372 a small effect upon the hue of the dyeings, as shown by a comparison of the colorimetric
 373 parameters obtained for the untreated dyeings with those which had been subjected to reduction
 374 clearing (Table 2). However, the findings that the λ_{max} of each of the four dyeings was unchanged
 375 by reduction clearing (Table 2) indicates that such changes in colour were moderate.

376

377 Table 3 reveals that when the untreated dyeings (which had received neither reduction clearing nor
378 bead wash-off) were subjected to wash fastness testing at 60°C, only moderate levels of fastness
379 were achieved. This finding was expected because the untreated dyeings contained surplus dye as
380 they had not been subjected to either a reduction clearing or bead wash-off process. When the
381 reduction cleared dyeings were subjected to wash fastness testing, higher levels of fastness were
382 secured in comparison to the corresponding dyeings which had received no treatment at the end of
383 dyeing, especially in the case of the 5% omf depths of shade Table 3). The improved fastness of the
384 dyeings imparted by reduction clearing can be attributed to the hot, aq., alkaline process having
385 removed surplus disperse dye from the dyeings, which obviously also resulted in the reduction
386 clearing dyeings having less dye present for removal during washing, compared to their untreated
387 counterparts.

388

389 Figure 7 also shows that surplus disperse dye was removed from both the 2% and 5% omf dyeings
390 when the dyed polyester component was subjected to the 2-stage bead wash-off process shown in
391 Figure 3, as evidenced by the lower f_k values recorded for the bead washed-off dyeings compared
392 to those of the untreated dyeings (Table 2).

Table 3 fastness of dyeings to ISO 105-C06/C2S

component dyed	dye	%omf dye	wash-off process	change in shade	wool	acrylic	polyester	polyamide	cotton	acetate
	<i>Dianix Blue ACE</i>	2	untreated	1	5	5	4	3/4	5	5
			3-stage reduction clear	1	5	5	4/5	4	5	5
			2-stage bead	1	5	5	4/5	4	5	5
		5	untreated	1	5	5	4	3	3/4	5
			3-stage reduction clear	1	5	5	4/5	3	4	4
			2-stage bead	1	5	5	4/5	3/4	5	4
polyester	C.I. Disperse Red 60	2	untreated	1	5	5	3/4	2/3	4/5	3
			3-stage reduction clear	1	5	5	4/5	3/4	5	4
			2-stage bead	1	5	5	4/5	4	5	4
		5	untreated	1	5	5	4/5	4	4	5
			3-stage reduction clear	1	5	5	5	5	5	5
			2-stage bead	1	5	5	5	4/5	5	5
C.I. Disperse Yellow 114		2	untreated	1	5	5	5	4/5	4	5
			3-stage reduction clear	1	5	5	5	5	5	5
		5	2-stage bead	1	5	5	5	4/5	4	5
			untreated	1	5	5	5	3/4	3/4	5

		3-stage reduction clear	1	5	5	5	5	5	5	
		2-stage bead	1	5	5	5	5	5	5	
		untreated	1	5	5	5	4/5	3/4	5	
	2	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	5	5	5	
	C.I. Reactive Black 5	untreated	1	5	5	5	4/5	4	5	
	5	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	5	5	5	
		untreated	1	5	5	5	4/5	4	5	
	2	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	4/5	4	5	
	cotton	C.I. Reactive Red 198	untreated	1	5	5	5	3/4	3/4	5
	5	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	5	5	5	
		untreated	1	5	5	5	4/5	3/4	5	
	2	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	5	5	5	
	<i>Remazol Yellow R</i>	untreated	1	5	5	5	4/5	4	5	
	5	5-stage conventional	1	5	5	5	5	5	5	
		3-stage bead	1	5	5	5	5	5	5	

		untreated	1	5	5	5	4/5	4	5
	2 + 2	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	4/5	4	5
	<i>Dianix Blue ACE + C.I.</i>								
		untreated	1	5	5	5	3/4	3/4	5
	5 + 5	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	5	5	5
	<i>Reactive Black 5</i>								
		untreated	1	5	5	5	4/5	3/4	5
	2 + 2	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	5	5	5
	<i>Dianix Red + C.I. Reactive</i>								
		untreated	1	5	5	5	4/5	4	5
	5 + 5	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	5	5	5
	<i>Red 198</i>								
		untreated	1	5	5	5	4/5	4	5
	2 + 2	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	4/5	4	5
	<i>Dianix Yellow + Remazol</i>								
		untreated	1	5	5	5	3/4	3/4	5
	5 + 5	reduction clear/conventional	1	5	5	5	5	5	5
		bead/bead	1	5	5	5	5	5	5
	<i>Yellow R</i>								

394

395

396 The lower colour strength recorded for the bead washed-off dyeings was mirrored by higher L*
397 values being obtained for the bead washed-off samples compared to those secured for the
398 untreated dyeings (Table 2). The results presented in Figure 7 and Table 2 show that the bead
399 wash-off process removed generally more surplus dye than the corresponding reduction clearing
400 process; however, bead wash-off imparted less colour change to the dyeings. Table 3 reveals that
401 the bead washed-off dyeings displayed levels of wash fastness that were comparable to or
402 exceeded those secured by reduction clearing, in terms of the extents of shade change and staining
403 of adjacent materials. Such high wash fastness displayed by the bead washed-off dyeings can be
404 attributed to the process having removed surplus disperse dye from the dyeings.

405

406 3.1.1 vagrant disperse dye removal

407 In order to garner information about the relative efficacy of the four wash-off process used in this
408 work to remove surplus disperse dye and reactive dye from the dyed PES and cotton components,
409 respectively, photographs were taken of the residual liquors obtained from both the conventional
410 and bead wash-off processes. Furthermore, as the wastewater that is produced as a result of the
411 wash-off of dyed polycotton will be contaminated with residual chemicals that were used in dye
412 application as well as vagrant reactive dyes and disperse dyes that were removed during wash-off
413 (3, 5, 10), the photographs were also used as means of assessing the extent of such likely coloured
414 contamination.

415

416 Figure 8 shows the residual wash-off liquors for both 2% and 5% omf dyeings of the PES
417 component using the three disperse dyes, obtained at the end of both the 3-stage reduction clearing
418 process and the 2-stage bead wash-off process. It is apparent that significant amounts of
419 unexhausted dye were present in the residual dyebath liquors, especially in the case of the 5% omf
420 dyeings. In terms of the conventional 3-stage reduction clearing process, Figure 8 shows that the
421 initial cold water rinse stage of the reduction clearing process removed a substantial amount of
422 vagrant dye, as expected, owing to the marked driving force for dye desorption that accrues from
423 the dye concentration gradient that exists between the dyed fibre and the rinse medium (in this case

424 cold water) (10). Rinsing can be expected to have removed not only unfixed, surplus disperse dye
425 from the dyed sample but also will have reduced the high concentration of residual dispersing agent
426 and other dyeing auxiliaries that will be present within the substrate. Subsequent treatment of the
427 dyed sample with the aqueous $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ reduction clearing liquor at 60°C removed further
428 dye, as expected, in view of the intended purpose of the $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ stage of the reduction
429 clear treatment, namely to decolourise azo disperse dyes and solubilise AQ disperse dyes. The
430 finding (Figure 8) that small amounts of vagrant disperse dye was removed during the final cold
431 water rinse stage of the reduction clearing process reveals that not all vagrant disperse dye
432 molecules had been discoloured/removed by treatment with the hot aqueous $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$
433 solution.

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2% omf Blue ACE

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5% omf Blue ACE

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2% omf Red 60

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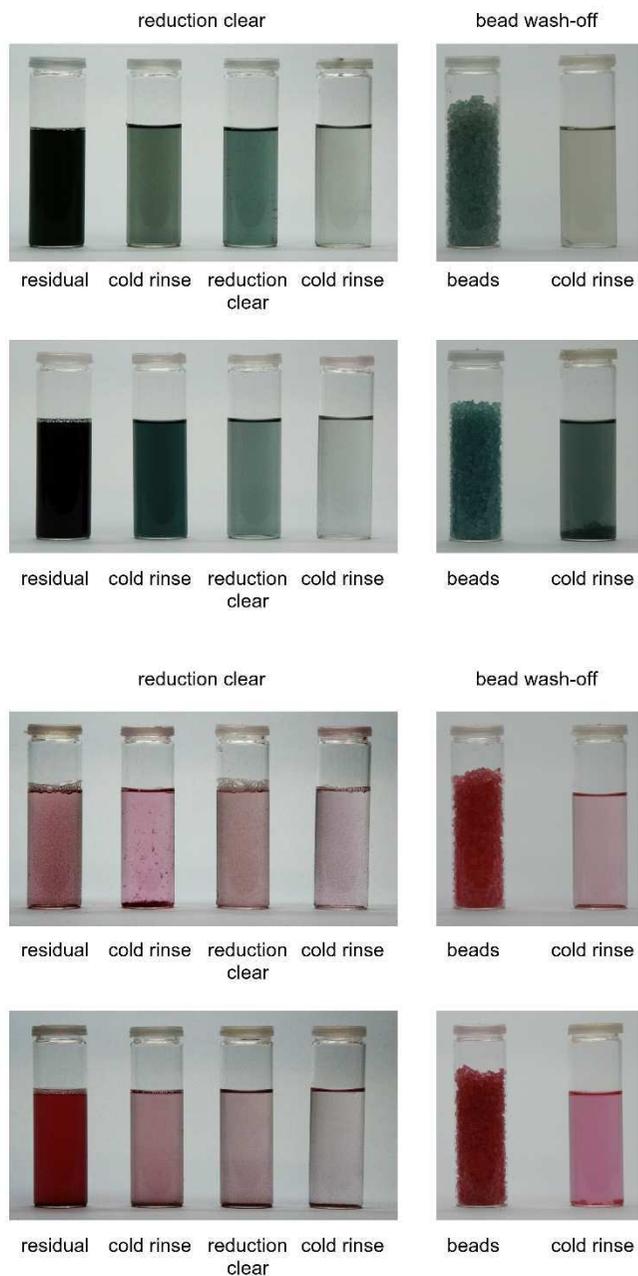
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5% omf Red 60

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2% omf Yellow 114

5% omf Yellow 114

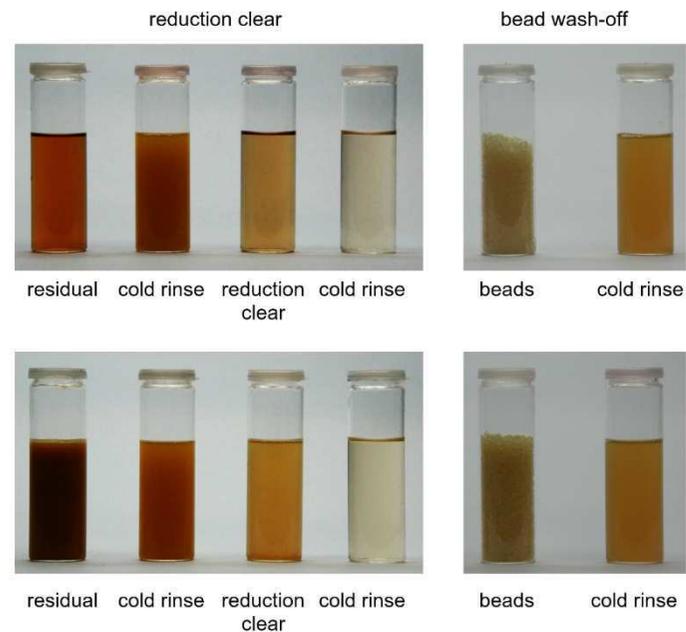


Figure 8 vagrant disperse dye: 2-stage reduction clear and 2-stage bead wash-off

455 The observations that the final cold rinse liquors were coloured may explain why some of the
456 reduction cleared disperse dyeings displayed small shade changes and staining of adjacent
457 materials (Table 3).

458

459 The 2-stage bead wash-off process removed surplus disperse dye (Figure 8) insofar as during the
460 treatment of the dyed sample with the beads, vagrant disperse dye molecules were adsorbed by the
461 beads, and, also, the final cold water rinse liquor obtained at the end of the bead wash-off process
462 contained residual disperse dye. It is considered (3, 5) that the beads remove vagrant disperse dye
463 from dyed PES fabric (and also vagrant reactive dye from dyed cotton) as a consequence of their
464 physical contact with the damp dyeings, in that dye molecules located at the surface of the dyed
465 material transfer to and become adsorbed onto the bead surface and are then retained by the PA
466 substrate. Indeed, Figure 8 shows that a sizeable amount of vagrant disperse dye was adsorbed by
467 the beads. However, the finding that the final cold water rinse liquors obtained from the bead wash-
468 off contained more vagrant disperse dye than the corresponding final cold water rinse liquors
469 obtained at the end of the reduction clearing process (Figure 8), implies that the single treatment of
470 the dyed samples with the beads did not remove as much surplus dye from the dyed PES fibre as
471 did the corresponding two treatments to which the dyeings had been subjected during reduction
472 clearing (ie first cold water rinse and hot aqueous $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ solution).

473

474 Nonetheless, the ensuing bead washed-off dyeings displayed colour strength values that were not
475 too dissimilar to their reduction cleared equivalents (Figure 7) as well as levels of wash fastness that
476 were comparable to that of their reduction cleared counterparts (Table 3). Thus, the findings
477 presented in Figure 7 and Table 3 suggest that a single treatment with the PA beads at 60°C was as
478 effective as the combination of initial cold water rinse and hot aqueous $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ solution in
479 the conventional reduction clearing process.

480

481 The 2-stage bead wash-off process therefore uses less water, does not employ environmentally-
482 challenging chemicals and offers savings in time, compared to the conventional reduction clearing

483 processes. Furthermore, the 2-stage bead wash-off process offers the potential for creating lower
 484 effluent loads than its conventional reduction clearing counterpart because the beads are able to
 485 adsorb significant quantities of vagrant disperse dye which will result in wastewater being much less
 486 contaminated with residual dye.

487

488 3.1.2 chloride ion concentration in residual liquors

489 Figure 9 shows that when each of the three commercial grade disperse dyes had been applied at
 490 2% and 5% omf depths of shade, the residual dyebath and the initial cold water rinse bath of the
 491 reduction clearing process contained Cl^- ion. This finding suggests that the observed residual
 492 chloride ion content may have arisen from diluent that was present in the commercial dye samples.

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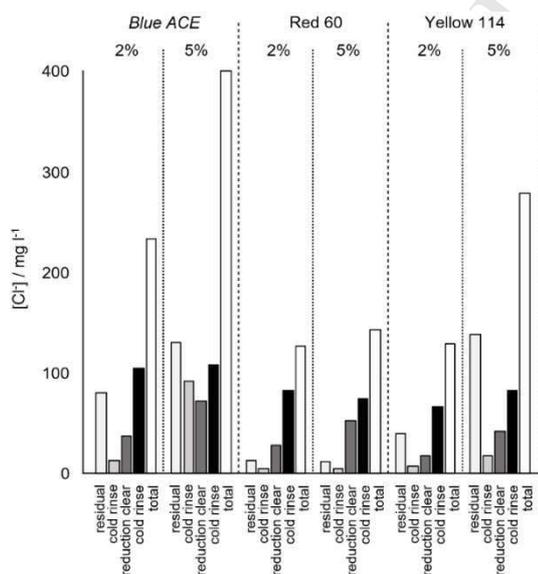
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503 Figure 9 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 3-stage
 504 reduction clearing process

505

506 Commercial grade samples of all most types of dye often contain quantities of shading components
 507 and diluents, the latter frequently being electrolyte such as NaCl, which are used by the dye maker
 508 as part of the dye standardisation process; for example, the dye content of the three contemporary
 509 commercial samples of *Teratop* (Huntsman) disperse dyes was found to vary from 47% to 51% (14).

510

511 As the $[Cl^-]$ of both the residual dyebaths and the cold rinse baths varied for the three dyes used
 512 and, also, the amount of residual chloride ion was greater in the case of the 5% omf dyeings (Figure
 513 9), it seems reasonable to suggest that the origin of the observed chloride ion content was indeed
 514 dye-derived. In a similar vein, the findings (Figure 9) that both the residual $Na_2CO_3/Na_2S_2O_4$ bath
 515 liquor and the final cold rinse bath liquor of the reduction clearing process contained chloride ion
 516 may be due to dye-derived diluent electrolyte having been removed from the dyed fabric. Since it is
 517 well known that cotton readily adsorbs chloride ions during immersion dyeing processes, such as
 518 those using reactive dyes and direct dyes, in which $NaCl$ (or Na_2SO_4) is employed to promote dye
 519 uptake, the $[Cl^-]$ values obtained (Figure 9) may well correspond to chloride ions which had been
 520 adsorbed by the cotton component of the polycotton fabric used; of course, there is no reason why
 521 chloride ions could not also have been adsorbed by the PES component.

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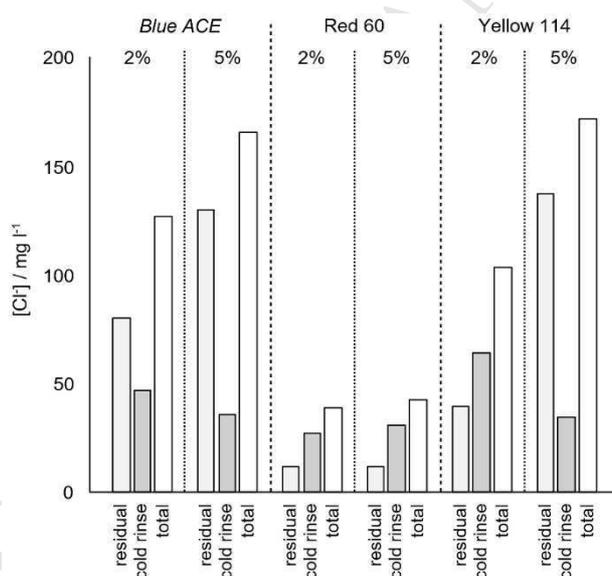


Figure 10 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 2-stage bead wash-off process

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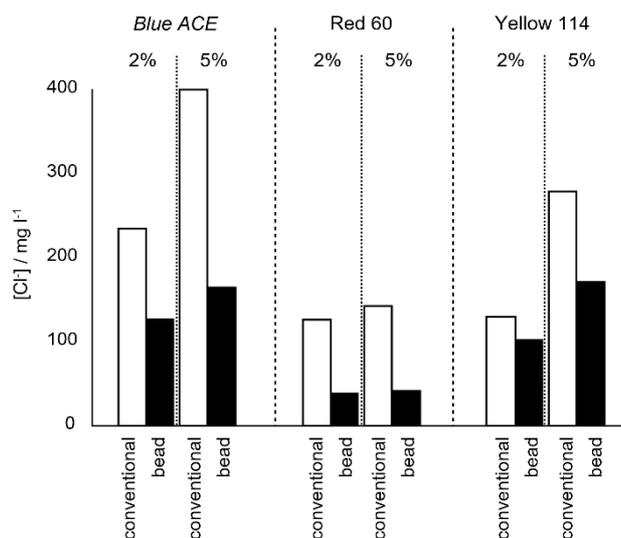
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3.1.3 total dissolved solids of residual liquors

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The term *total dissolved solids*, *TDS*, describes the total amount of inorganic salts and organic matter present in solution in water and the value of TDS recorded for a water sample is often used

565 as a measure of the quality of that water sample. As such, the principal contributors to the TDS in
 566 fresh water are Na^+ , K^+ , Ca^{2+} and Mg^{2+} , CO_3^{2-} , HCO_2^- , Cl^- , SO_4^{2-} and NO_3^- (15-17). The predominant
 567 substances in municipal water that contribute to TDS are inorganic minerals, of which the
 568 component of most concern is NaCl ; as TDS increases the amounts of both Na^+ and Cl^- increase
 569 (16). For benchmark levels, an aesthetic objective of $\leq 500 \text{ mg l}^{-1}$ (ie $\leq 0.5 \text{ g l}^{-1}$) has been established
 570 for TDS in drinking water (18, 19); at higher levels, unpalatability, mineral deposition, corrosion and
 571 excessive hardness may occur (18): the World Health Organisation (WHO) considers drinking water
 572 to be unacceptable if the total dissolved solids content is $>1,200 \text{ ppm}$ (ie $>1.2 \text{ g l}^{-1}$) (17).

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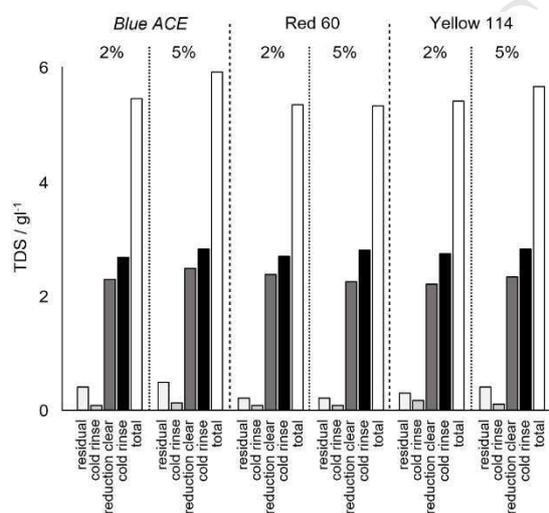
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582

Figure 12 TDS of residual liquors: 2% and 5% of dyeings washed-off using the 3-stage reduction clearing process

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585 The results obtained for the TDS content of the residual dyebath and the various treatment baths of
 586 the reduction clearing process are shown in Figure 12. Whilst the relatively low TDS values obtained
 587 for the residual dyebath may be attributed to dye-derived diluent electrolyte, the much higher TDS
 588 content of the residual $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ bath and final cold rinse bath carried out at the end of the
 589 reduction clearing process exemplify the well-known environmental challenges that arise from the
 590 use of aqueous, alkaline, sodium dithionite in reduction clearing. Indeed, these findings reveal that
 591 the total TDS obtained for the application of each of the three disperse dyes to PES was
 592 considerably greater than not only the aesthetic objective of $\leq 0.5 \text{ g l}^{-1}$ recommended for drinking

593 water (18, 19) but also the limit regarded by the WHO as acceptable for drinking water (ie $<1.2 \text{ g l}^{-1}$)
 594 (17).

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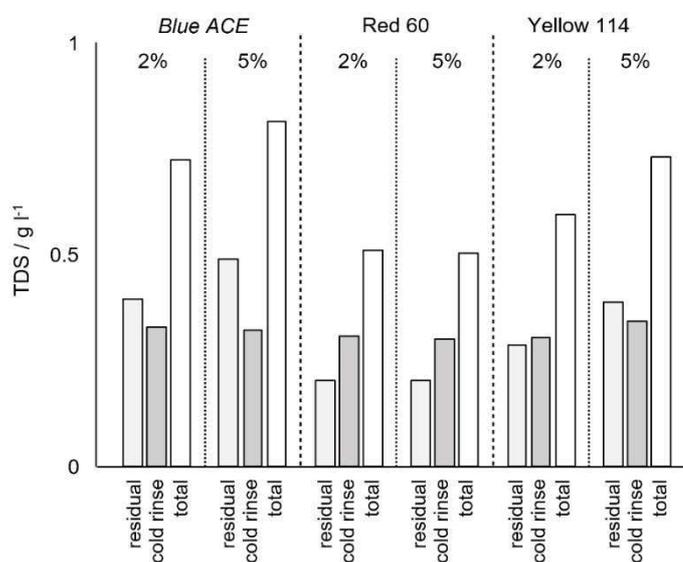


Figure 13 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 2-stage bead wash-off process

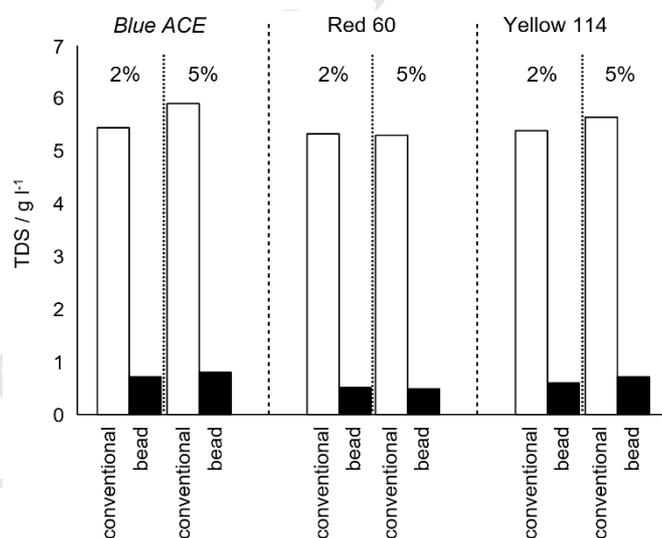


Figure 14 total TDS content obtained for 2% and 5% omf dyeings washed-off using the 3-bath reduction clearing process and 2-stage bead wash-off process

618

619 In terms of the 2-stage bead wash-off process, Figure 13 shows that the TDS content of the final
 620 cold water rinse bath liquor was low which can be attributed to the beads having adsorbed a large

621 proportion of the surplus disperse dye which had been removed from the PES component.
 622 Comparison of the results displayed in Figure 13 with those in Figure 12 reveals that values of TDS
 623 secured using the 2-stage bead wash-off process were considerably lower than those obtained
 624 using the conventional 3-stage reduction clearing process. This is illustrated by Figure 14 which
 625 shows the marked difference in total TDS contents obtained for the conventional 3-stage reduction
 626 clearing process and the 2-stage bead wash-off process. As discussed above, it seems likely that
 627 the findings displayed in Figure 14 can be attributed to the ability of the beads to adsorb vagrant
 628 disperse dye and chloride ions that have been removed from the dyed samples during the bead
 629 wash-off process; this is the subject of a future part of the paper.

630

631 3.2 cotton component/reactive dyes

632 Two types of wash-off process were used to remove surplus reactive dye from the 2% and 5% omf
 633 dyeings on the cotton component of the polycotton blend namely, a conventional 5-stage wash-off
 634 process (Figure 5) and a 3-stage bead process (Figure 6).

635

636 Figure 15 shows the colour strength of 2% and 5% omf dyeings of the cotton component of the
 637 polycotton fabric obtained using the three reactive dyes.

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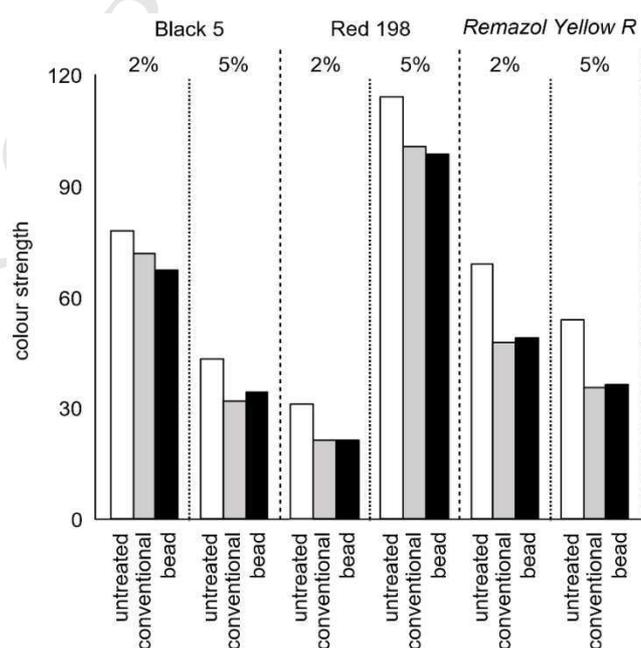
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649 Figure 15 colour strength of cotton component dyed using the three reactive dyes and washed-off using the
 650 conventional 5-stage wash-off process and 3-stage bead wash-off process

651

652 It is apparent that both the 5-stage conventional wash-off method (Figure 5) and the 3-stage bead
 653 wash-off process (Figure 6) removed surplus reactive dye, as shown by the lower f_k values recorded
 654 for the washed-off dyeings compared to those of the untreated dyeings. The lower f_k values
 655 obtained for both the conventional and bead washed-off dyeings (Figure 15) were reflected in higher
 656 L^* values being recorded for the washed-off samples compared to those of the dyeings which had
 657 not been washed-off (Table 4). The results presented in Table 4 also reveal that the two wash-off
 658 processes imparted similar effects upon both the hue and chroma of the dyeings insofar as the
 659 washed-off dyeings were generally duller and yellower than their untreated counterparts. However,
 660 the finding (Table 4) that the λ_{max} of the untreated dyeings was unchanged by either wash-off
 661 processes indicate that the changes in colour imparted by wash-off were small.

662

663 Table 4 Colorimetric parameters for dyeings of cotton component dyed with reactive dyes and washed-off
 664 using the conventional 5-stage wash-off process and 2-stage bead wash-off process

dye	% omf	wash-off process	L^*	a^*	b^*	C^*	h°	λ_{max}
C.I. Reactive Black 5	2	untreated	35.9	-2.7	-18.6	18.8	261.6	640
		reduction clear	37.1	-3.2	-14.2	14.6	257.3	640
		bead	38.2	-3.8	-14.4	14.8	255.3	640
	5	untreated	45.1	35.7	-6.6	36.3	349.5	620
		reduction clear	53.7	51.1	0.2	51.1	0.3	620
		bead	52.3	49.4	-0.5	49.4	359.5	620
C.I. Reactive Red 198	2	untreated	78.7	21.0	68.9	72.0	73.0	520
		reduction clear	81.9	15.2	63.8	65.6	76.6	520
		bead	81.3	15.3	62.9	64.8	76.3	520
	5	untreated	30.0	-0.9	-12.9	12.9	266.1	520
		reduction clear	32.0	-1.6	-10.5	10.6	261.5	520
		bead	32.3	-1.9	-10.6	10.8	259.6	520

		untreated	38.9	34.6	-4.1	34.8	353.2	440
	2	reduction clear	48.4	50.5	3.1	50.6	3.5	440
		bead	47.9	49.8	2.4	49.9	2.7	440
<i>Remazol Yellow R</i>		untreated	72.8	28.3	71.8	77.1	68.5	420
	5	reduction clear	77.9	21.4	70.2	73.4	73.0	420
		bead	77.3	21.5	69.9	73.1	72.9	420

665

666 From the wash fastness results displayed in Table 3, it is evident that the dyeings which had been
667 washed-off displayed higher levels of fastness than those which had received no treatment after
668 dyeing; furthermore, similar levels of fastness were obtained using the two wash-off processes. The
669 improved fastness of the dyeings imparted by both the conventional and bead wash-off processes
670 can be attributed to surplus reactive dye having been removed from the dyeings.

671

672 3.2.1 vagrant reactive dye removal

673 Figure 16 shows the residual wash-off liquors for both 2% and 5% omf reactive dyeings of the
674 cotton component, obtained at the end of the 5-stage conventional wash-off process and the 3-
675 stage bead wash-off process. Substantial amounts of unfixed reactive dye were present in the
676 residual dyebath liquors, especially in the case of the 5% omf dyeings.

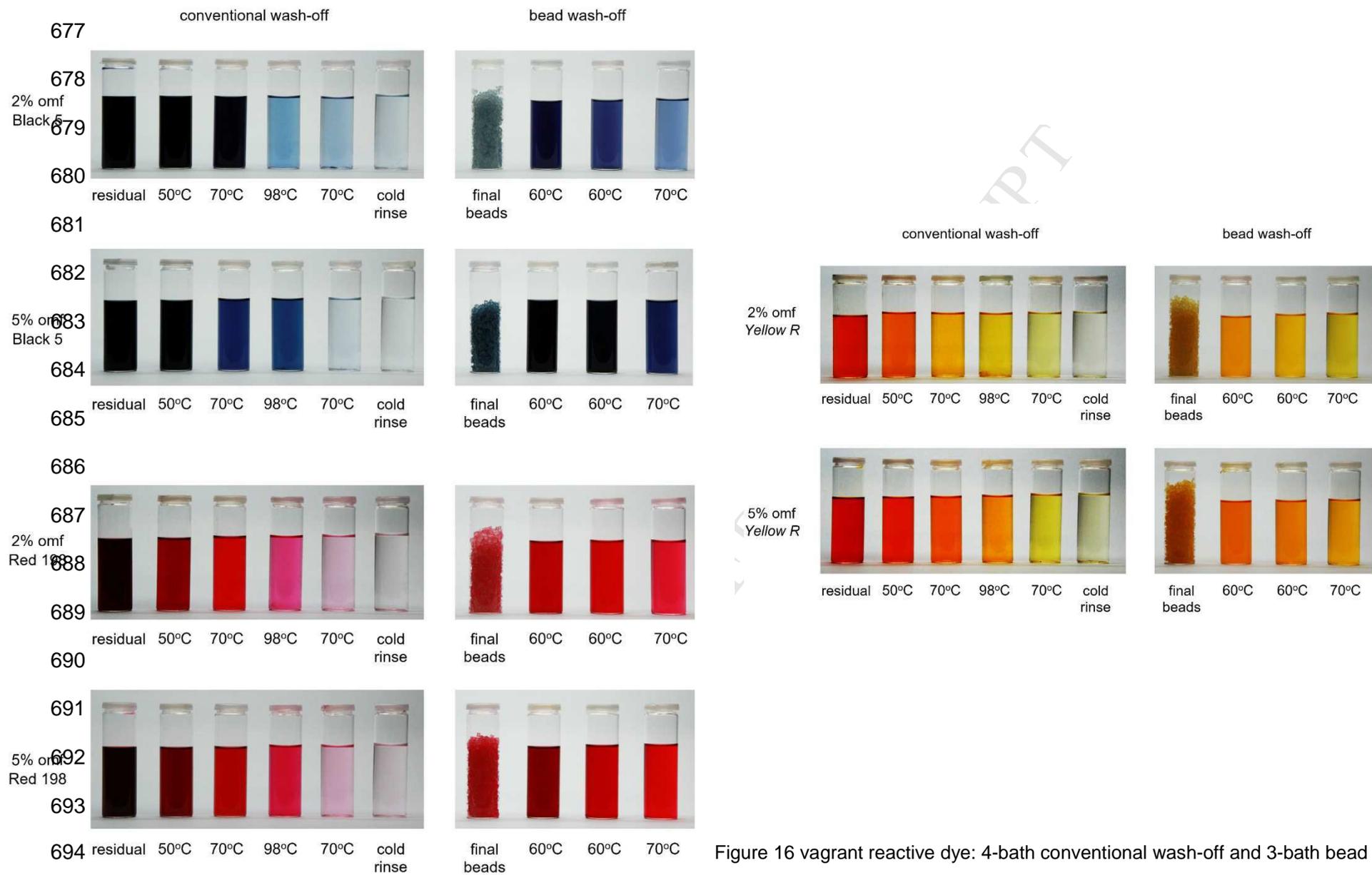


Figure 16 vagrant reactive dye: 4-bath conventional wash-off and 3-bath bead wash-off

696 In the case of the conventional wash-off process, the initial 50°C water rinse removed a large
697 amount of residual dye from the dyed samples. Indeed, in terms of the amount of vagrant dye that
698 was present in the four wash-off baths and the final cold water rinse bath liquors, Figure 64 reveals
699 that for each of the three dyes used, the amount of dye present followed the order:

700

701 first wash-off bath >>> second wash-off bath >> third wash-off bath > fourth wash-off bath > final
702 cold water rinse bath

703

704 These findings agree with the well-known fact that the first wash bath in a conventional wash-off
705 process for reactive dyes on cellulosic fibres removes more easily detached, unfixed dye from the
706 dyed material; dye removal continues during the second and subsequent stages of wash-off, with
707 sequentially lower amounts of dye being removed. It is also widely held that during the first wash-off
708 stage, not only will large amounts of unfixed/hydrolysed reactive be removed but also the very high
709 inorganic electrolyte concentration within the substrate will have been markedly reduced, the latter
710 being an essential pre-requisite of efficient dye removal (10). Treatment at the boil in the presence
711 of the proprietary wash-off agent during the third stage of wash-off was quite effective in removing
712 surplus dye, insofar as only comparatively less dye removal occurred during the fourth wash-off
713 stage at 70°C (Figure 16). For each of the three dyes used at both depths of shade, the final cold
714 water rinse bath liquor contained very little vagrant reactive dye, which illustrates the effectiveness
715 with which the preceding four wash-off stages had removed surplus dye from the dyed samples.

716

717 In the case of the 2% and 5% omf reactive dyeings of the cotton component which had been
718 washed-off using the three-stage, bead process, Figure 16 shows that during the first two stages of
719 the wash-off process, in which the same sample of beads was used for each of two the 60°C bead
720 treatment baths, the beads adsorbed substantial amounts of vagrant reactive dye. In terms of the
721 amount of vagrant dye that was present in the residual wash-off baths and the final cold water rinse
722 bath liquors, for each of the three dyes used, the amount of dye present followed the order:

723

724 first (bead) 60°C wash-off bath >> second (bead) 60°C wash-off bath >>> final 70°C water bath

725

726 These findings once again concur with the above mentioned behaviour of reactive dyes on cellulosic
727 fibres in that the first wash-off bath removes more easily detached, unfixed dye, whilst successive
728 baths continue to remove dye but with sequentially lower amounts being removed; as such, the two
729 bead wash-off stages behaved in a similar manner to that of conventional aqueous wash-off baths. It
730 is apparent that the residual final 70°C water-only wash bath liquors contained considerable
731 amounts of vagrant reactive dye, a finding which contrasted markedly with that secured for the final
732 cold water rinse bath of the conventional wash-off process (Figure 16). This suggests that the 3-
733 stage bead wash-off was less effective in removing hydrolysed/unreacted dye from the dyeings than
734 the conventional 5-stage wash-off process. However, the ensuing bead washed-off dyeings
735 displayed colour strength values that were similar to those of their conventionally washed-off
736 counterparts (Figure 15) and also exhibited similar levels of wash fastness (Table 3). Thus, the
737 findings presented in Figure 15 and Table 3 imply that the 3-stage bead wash-off process was as
738 effective as the 5-stage conventional wash-off process. Furthermore, as the bead process
739 consumes less water and does not require the use of proprietary chemicals to affect efficient
740 vagrant dye removal, it provides a more cost-effective, environmentally-friendly alternative to
741 conventional wash-off processes for reactive dyes on cellulosic fibres. In addition, as the majority of
742 the surplus reactive dye is adsorbed onto the beads, the wastewater that is generated will be far
743 less contaminated with residual dye, unlike conventional wash-off processes.

744

745 3.2.2 chloride ion concentration in residual liquors

746 Figure 17 shows that when each of the three commercial grade reactive dyes had been applied at
747 2% and 5% omf depths of shade, the residual dyebaths contained significant amounts of Cl⁻ ion.
748 Indeed, the [Cl⁻] recorded when the reactive dyes had been applied to the cotton component (Figure
749 15) were ~100 times greater than those obtained when the three disperse dyes had been applied to
750 the PES component (Figure 9). This finding was expected, because the three reactive dyes had
751 been applied in the presence of 50 g l⁻¹ added NaCl to promote dye uptake.

752

753 The highest $[Cl^-]$ was observed for the residual dyebaths and the first wash-off bath, for each of the
 754 three commercial grade reactive dyes used. The very high $[Cl^-]$ of the residual dyebath liquors
 755 reflects the 50 g l^{-1} of added NaCl that was used during dyeing. In terms of the chloride ion content of
 756 the four wash-off baths and final rinse bath, as mentioned, it is generally considered that during the
 757 first stage of reactive dye wash-off, the often very high inorganic electrolyte content of the dyeing is
 758 markedly reduced and that the level of inorganic electrolyte in the dyed fibre is further lowered
 759 during subsequent wash-off stages. The results displayed in Figure 17 support this view insofar as,
 760 in the cases of both the 2% and 5% omf dyeings, the largest amount of Cl^- ion was removed during
 761 the first wash-off bath, which employed water at 50°C . NaCl continued to be removed from the
 762 dyeing during each of the remaining wash-off baths as well as the final cold water rinse bath. The
 763 results presented in Figure 17 clearly illustrate the magnitude of the severe environmental problem
 764 that is caused by the routinely very high amounts of residual chloride ion in reactive dye wastewater,
 765 which stem from having to use added inorganic electrolyte in the application of reactive dyes to
 766 cotton and other cellulosic fibres.

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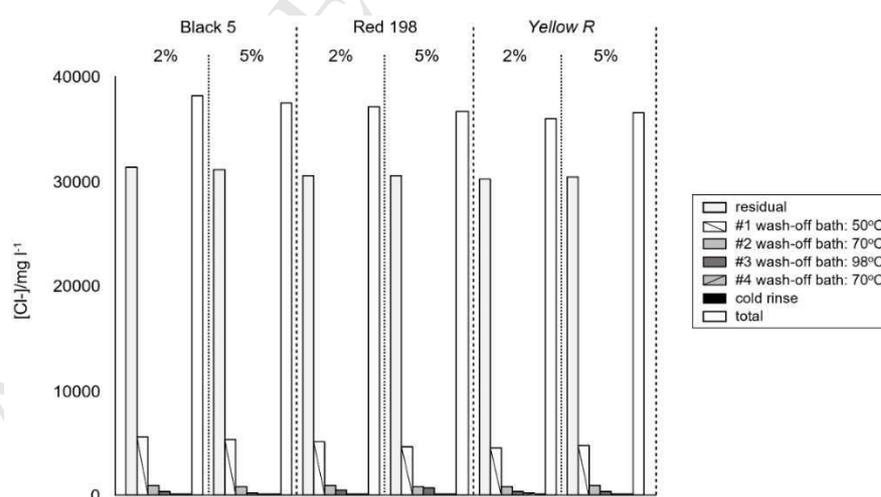
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776 Figure 17 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 5-bath
 777 conventional wash-off process

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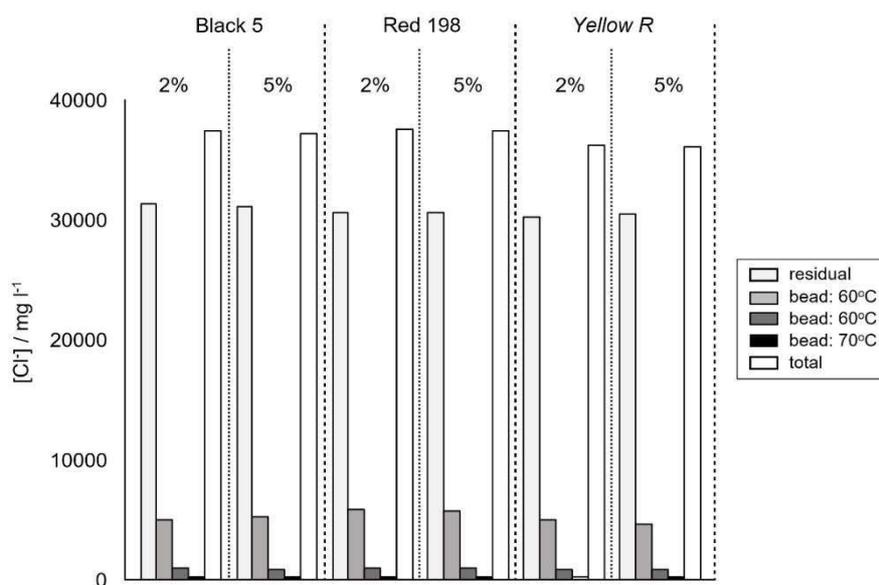


Figure 18 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 3-bath bead wash-off process

Figure 18 shows the levels of chloride ion obtained when the three commercial grade reactive dyes had been washed-off using the 3-stage bead wash-off process. Each of the three bead treatment stages removed chloride ions, the highest $[Cl^-]$ being recorded for the first bead wash-off bath, with the amount of chloride ion decreasing during the two subsequent bead wash-off baths. Comparison of the results displayed in Figure 18 with those in Figure 17 reveals that there was little difference between values of the total chloride ion concentration secured using the 5-stage conventional wash-off process and the 3-stage bead wash-off process. This finding contrasts with that made in the case of disperse dyes applied to the PES component (section 3.1.2), for which it was found that values of total $[Cl^-]$ secured using the 2-stage bead wash-off were much lower than those obtained using the conventional 3-stage reduction clearing process, which was attributed to the PA beads having adsorbed vagrant chloride ions. As mentioned, the levels of residual Cl^- ion recorded for the three reactive dyes (Figures 17 and 18) were ~100 times greater than those obtained when the three disperse dyes had been applied to the PES component (Figures 9 and 10). Such very high chloride ion concentration obtained for the three reactive dyes may be the reason why there was so little difference between values of total $[Cl^-]$ obtained using the 5-stage conventional wash-off

807 process and the 3-stage bead wash-off process (Figures 17 and 18). Assuming that the beads
 808 adsorbed chloride ions, as was suggested in the case of the disperse dyes, perhaps the extent of
 809 such adsorption was essentially negligible in comparison to the very high $[Cl^-]$ involved.

810

811 3.2.3 total dissolved solids of residual liquors

812 The results obtained for the TDS of the residual dyebath, each of the four wash-off and the final cold
 813 rinse liquors are shown in Figure 19.

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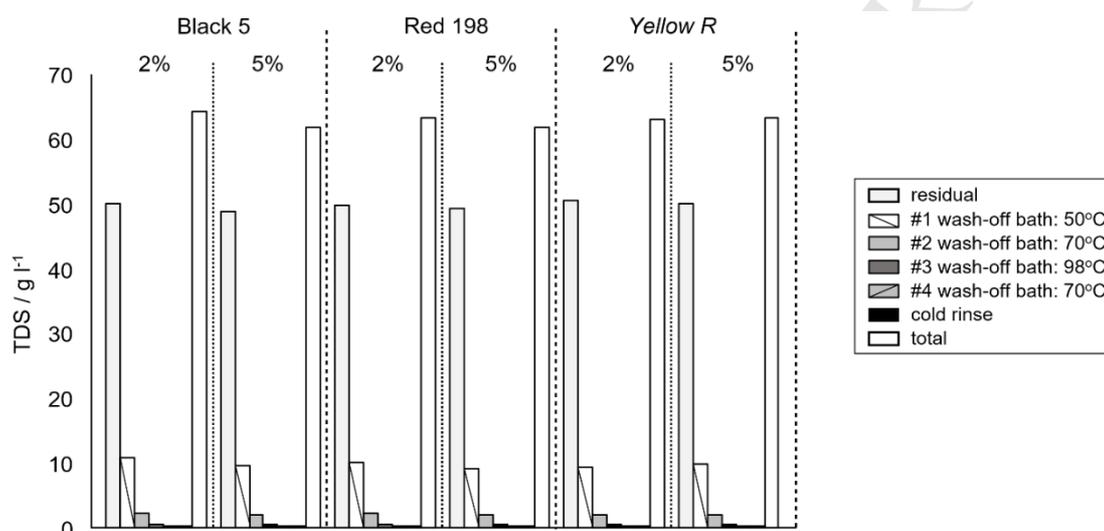
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823 Figure 19 TDS of residual liquors: 2% and 5% of dyeings washed-off using the 5-bath conventional wash-off
 824 process

825

826 The very high TDS content of the residual dye bath can be attributed to presence of chloride ion that
 827 stemmed from the use of 50 g l^{-1} added NaCl in dyeing. Similar levels of TDS content were obtained
 828 for the residual dyebaths for each of the three reactive dyes used, which reflects the fact that the
 829 same amount of added NaCl (ie 50 g l^{-1}) had been used for dyeing. Commercial grade samples of
 830 reactive dyes often contain quantities of shading components and diluents, the latter frequently
 831 being electrolyte such as NaCl, which are used by the dye maker as part of the dye standardisation
 832 process. In this context, it has been reported that the amount of standardising constituents in
 833 commercial grade reactive dyes ranged from 34% to 73% (20-22); in the case of the three
 834 commercial grade reactive dyes employed in this work, the amount of diluent NaCl present in the

835 commercial samples ranged from 11.6% to 12.3% (14). Thus, the slight variation in the TDS content
 836 of the residual dyebaths observed for the three dyes (Figure 19) can be attributed to different levels
 837 of diluent electrolyte in the commercial dye samples.

838

839 It is evident that the TDS content of the first wash-off bath was very high (Figure 19) which was
 840 expected, since it had been observed (Figure 17) that during this particular stage of the
 841 conventional wash-off process, large amounts of Cl^- ion had been detected, which implied that large
 842 amounts of residual NaCl had been removed from the dyeings; the high TDS values recorded for
 843 the first wash-off bath therefore reflect their high chloride ion content. Furthermore, for each of the
 844 three dyes, the TDS content of the residual wash-off baths decreased with each successive stage in
 845 the 5-bath wash-off process, including the final cold water rinse bath. These observations once
 846 again reflect the trends in $[\text{Cl}^-]$ of the wash-off baths previously recounted (Figure 17) and, therefore,
 847 can be attributed to NaCl having been removed from the dyeings.

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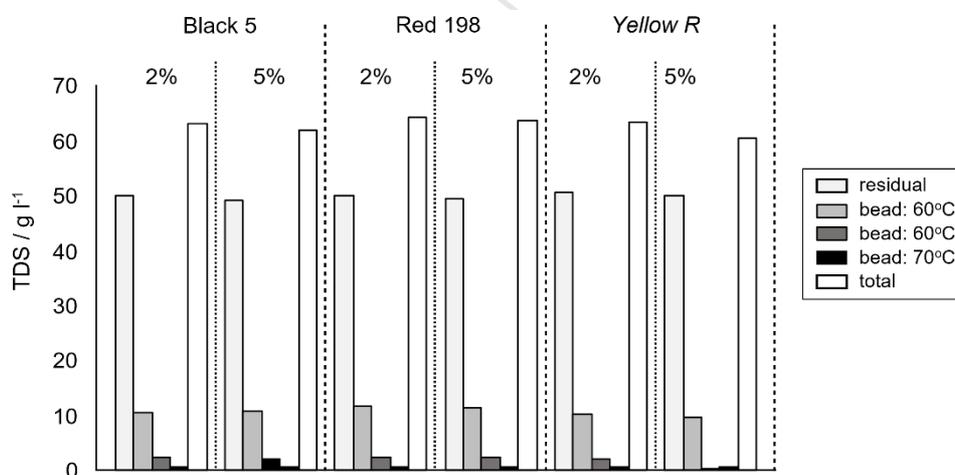
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857 Figure 20 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 3-bath bead wash-off
 858 process

859

860 Interestingly, in terms of the previously mentioned relationship between drinking water quality and
 861 TDS content, only the residual liquors obtained from the final one or two wash-off baths and the final
 862 rinse bath displayed TDS levels $\leq 0.5 \text{ g l}^{-1}$ (Figure 19). The results displayed in Figure 19 therefore

863 illustrate the inherent, severe environmental challenges that reactive dyeing wastewater presents,
864 because of the routine usage of outrageously high levels of added inorganic electrolyte in immersion
865 dyeing of cellulosic fibres.

866

867 In terms of the 3-stage bead wash-off process that was employed for the three reactive dyes, Figure
868 20 shows that the first of the three bead treatment baths recorded the highest TDS content, and that
869 TDS values decreased sequentially during the two subsequent bead wash-off baths. As such, these
870 findings reflect those obtained for the chloride ion content of the three bead wash-off baths (Figure
871 18) and, therefore, the TDS values observed can be attributed to the presence of residual chloride
872 ion. Comparison of the results displayed in Figure 20 with those in Figure 19 show that there was
873 little difference between the TDS values obtained for the 5-stage conventional wash-off process and
874 the 3-stage bead wash-off process, as was previously observed in the case of chloride ion values
875 (Figures 17 and 18). This latter finding was anticipated because the TDS values displayed in Figure
876 20 closely reflect the values of [Cl⁻] presented in Figure 18.

877

878 *3.3 PES and cotton components of the polycotton blend dyed with disperse and reactive dyes*

879 The PES component of the polycotton blend was first dyed using a disperse dye and the ensuing
880 dyeing subjected to either the conventional 2-stage reduction clearing method (Figure 2) or 2-stage
881 bead wash-off process (Figure 3). At the end of the reduction clearing process or bead wash-off
882 process, the ensuing dyeing was dyed using a reactive dye and the ensuing dyed sample subjected
883 to either the conventional 5-bath wash-off process (Figure 5) or 3-bath bead wash-off process
884 (Figure 6).

885

886 Figure 21 shows the f_k values obtained for 2% and 5% omf dyeings, produced on both the polyester
887 and cotton components of the polycotton blend fabric using each of the three disperse and three
888 reactive dyes. Results are presented for untreated dyeings (which had not been reduction cleared,
889 or washed-off using either the 2-stage bead process, 3-stage bead process or conventional 5-stage
890 process) as well as dyeings which had been subjected to the combined treatments of the 2-stage

891 reduction clearing to remove surplus disperse dye (Figure 2) and the conventional 5-stage wash-off
 892 (Figure 5) to remove surplus reactive dye from the dyed polycotton; also shown are the results
 893 obtained for dyeings which had been subjected to the combined treatments of the 2-stage bead
 894 wash-off process to remove surplus disperse dye (Figure 3) and the 3-stage bead wash-off to
 895 remove surplus reactive dye (Figure 6) from the dyed polycotton.

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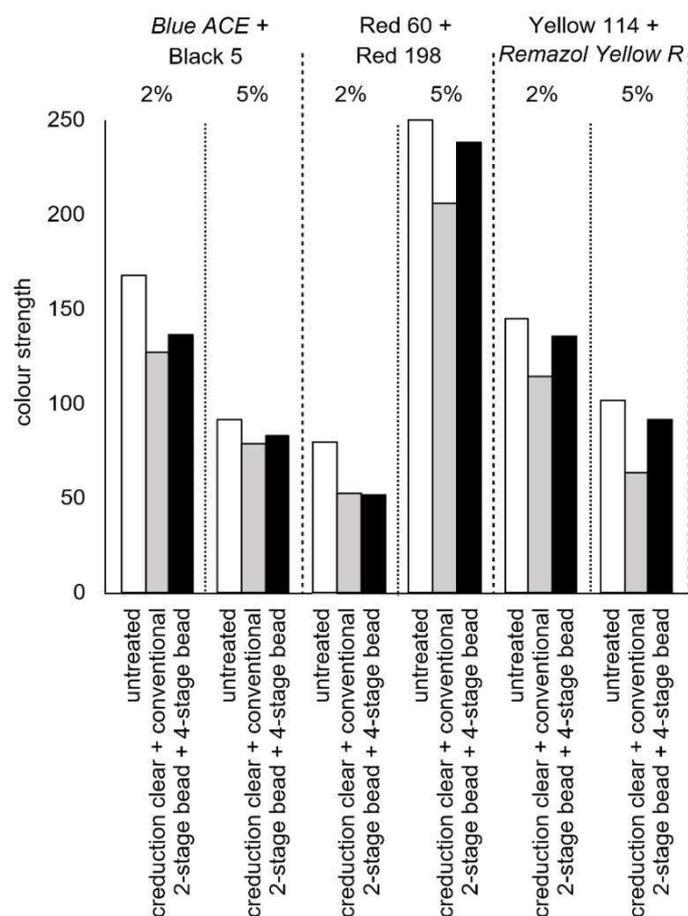
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911 Figure 21 colour strength of PES and cotton component dyed using the three disperse dyes and three
 912 dyes

913 It is evident that the combined 2-stage reduction clearing/5-stage conventional wash-off removed
 914 surplus dye, as shown by the lower f_k values recorded for the washed-off dyeings compared to
 915 those of the untreated dyeings (Figure 21). The lower colour strength of the reduction
 916 cleared/conventionally washed-off dyeings resulted in higher L^* values being secured for the
 917 washed-off samples compared to those of the dyeings which had not been washed-off (Table 6).
 918 When the polycotton fabric which had been dyed with both disperse and reactive dyes was washed-

919 off using the combination of the 2-stage process for disperse dyes and the 5-stage conventional
 920 wash-off process for reactive dyes, surplus dye was again removed, as shown by the lower colour
 921 strength (Figure 21) and higher lightness values observed (Table 6).

922

923 Table 6 Colorimetric parameters for dyeings of PES and cotton component dyed with disperse and reactive
 924 dyes

dye	% omf	wash-off process	L*	a*	b*	C*	h°	λ_{\max}
<i>Dianix Blue ACE +</i>	2	untreated	26.8	-1.8	-23.8	23.9	265.8	640
		reduction clear	30.4	-3.4	-22.0	22.3	261.2	640
		bead	29.5	-2.7	-23.2	23.3	263.3	640
C.I. Reactive Black 5	5	untreated	38.7	48.1	-1.2	48.1	358.5	620
		reduction clear	45.3	58.9	6.4	59.2	6.2	620
		bead	43.6	56.6	4.6	56.8	4.6	620
C.I. Disperse Red 60 +	2	untreated	73.6	19.2	80.7	82.9	76.6	520
		reduction clear	79.9	12.7	80.4	81.3	81.0	520
		bead	78.2	15.8	78.8	80.4	78.7	520
C.I. Reactive Red 198	5	untreated	20.7	0.8	-19.7	19.7	272.4	520
		reduction clear	23.5	-0.4	-20.3	20.3	269.0	520
		bead	21.5	0.3	-19.4	19.4	271.0	520
C.I. Disperse Yellow 114 +	2	untreated	73.6	19.2	80.7	82.9	76.6	440
		reduction clear	41.1	57.9	9.3	58.6	9.1	440
		bead	38.5	56.0	9.1	56.7	9.2	440
<i>Remazol Yellow R</i>	5	untreated	71.5	16.8	79.8	81.5	78.1	420
		reduction clear	77.2	19.1	80.6	82.9	76.7	420
		bead	75.9	18.9	86.3	88.4	77.6	420

925

926 Figure 21 also reveals that dissimilar levels of dye removal were obtained using the reduction
 927 clear/conventional wash-off and bead/bead wash-off processes, this being reflected in the different
 928 lightness values recorded for the respective dyeings (Table 6). The results presented in Table 6 also
 929 show that the reduction clear/conventional wash-off processes generally imparted greater changes

930 in both the hue and chroma of the dyeings than did the corresponding bead/bead wash-off
931 processes; the finding that the λ_{\max} of the dyeings was unchanged by both combined wash-off
932 processes showed that the changes imparted by wash-off were small.

933

934 Table 3 shows that when the polycotton dyeings were subjected to wash fastness testing, the
935 washed-off dyeings displayed higher levels of fastness than those which had received no treatment
936 after dyeing, as expected. Similar levels of fastness were obtained for the dyeings which had been
937 washed-off using the two types of combined wash-off process (Table 3). The improved fastness of
938 the dyeings imparted by the both the reduction clear/conventional wash-off and bead/bead wash-off
939 processes can be attributed to each combination having removed surplus disperse dye and reactive
940 dye from the dyeings.

941

942 It is widely accepted that the level of fastness displayed by a given dye on a particular type of fibre
943 to aqueous agencies (eg water, perspiration, domestic laundering, etc.) generally decreases with
944 increasing amount of dye present within the dyed substrate (ie increasing depth of shade), simply
945 because more dye molecules are available within the dyed material to desorb when the dyeing is
946 exposed to laundering, etc., and so result in both fading (ie loss of depth of shade) and staining (ie
947 transfer of vagrant dye molecules to adjacent materials. Interestingly, the data shown in Figure 21
948 and Table 3 imply that the level of wash fastness recorded for the washed-off polycotton dyeings
949 (Table 3) was not directly related to the depth of shade of the dyed polycotton fabric insofar as
950 whilst the bead/bead washed-off dyeings were generally of greater colour strength than their
951 respective reduction cleared/conventional washed counterparts (Figure 21), the dyeings displayed
952 quite similar levels of fastness (Table 3). Indeed, quite large differences were observed between the
953 colour strength of the respective bead/bead and reduction clear/conventional washed-off dyeings,
954 which can be expressed using the parameter Δf_k which is calculated using Eq 2 where f_{k1} is the
955 colour strength of the reduction cleared/conventional washed-off dyeing and f_{k2} that of the
956 corresponding bead/bead washed-off dyeing.

957

$$\Delta f_k = \frac{f_{k1} - f_{k2}}{f_{k1}} \times 100$$

2

959

960 As Figure 22 shows, quite large differences were observed between the colour strength of the
 961 respective bead/bead and reduction clear/conventional washed-off dyeings. Thus, it would be
 962 expected that as the f_k values of the polycotton dyeings which had been washed-off using the
 963 bead/bead wash-off combination were noticeably greater than those of corresponding dyeings
 964 which had been washed-off using the reduction clearing/conventional wash-off processes (Figures
 965 21 and 22), the fastness of the bead washed-off dyeings to washing at 60°C should have been
 966 noticeably lower than their reduction cleared/conventionally washed-off counterparts. However, this
 967 was not the case since the fastness of the variously washed-off polycotton dyeings was quite similar
 968 (Table 3).

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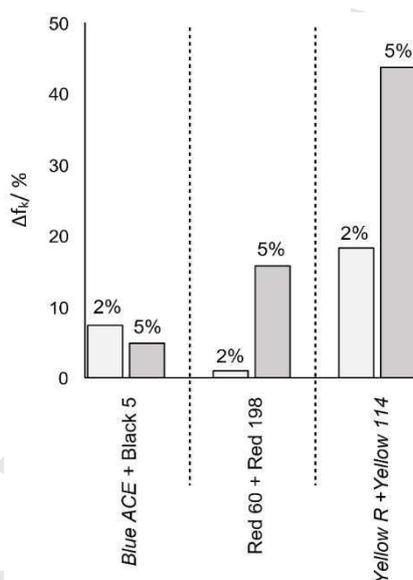
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Figure 22 Δf_k for dyed polycotton

981

982 This implies that not all surplus dye must be removed from dyed polycotton in order to achieve
 983 reasonable levels of wash fastness, which, in turn, has implications in terms of the rigorousness of
 the wash-off processes employed. This aspect of wash-off is the focus of a future part of the paper.

984

985 **4. Energy, water and chemical usage**

986 As discussed in previous parts of the paper (3, 5, 10), Eqs 3 and 4 can be employed to obtain an
 987 approximate measure of the amount of heat energy consumed in each of the four different wash-off
 988 processes that were used in this work, where Q is the amount of heat required (kJ) to raise the
 989 temperature of w kg of water or n kg of PA beads, from 21°C (T_1) to the final temperature (T_2) of the
 990 particular wash-off stage, c_w being the specific heat capacity of water at 21°C ($4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$) and
 991 c_{PA} the specific heat capacity of PA 6 at 20°C ($1.67 \text{ kJ kg}^{-1} \text{ K}^{-1}$) (23):

992

$$993 \quad Q = w \cdot c_w (T_2 - T_1) \quad 3$$

$$994 \quad Q = n \cdot c_{PA} (T_2 - T_1) \quad 4$$

995

996 As Table 7 shows, in the case of the 2-stage reduction clearing process (Figure 2) that was utilised
 997 to remove surplus disperse dye from the dyed PES component of the polycotton fabric, more energy
 998 was consumed during the 60°C $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_4$ treatment stage than the subsequent 40°C water
 999 rinse stage because of the higher temperature of the aq. alkaline stage; it is assumed that the final
 1000 cold water rinse stage (Figure 2) would consume no energy. The 2-stage bead wash-off process for
 1001 disperse dyes depicted in Figure 5 consumed much less energy than the reduction clearing process
 1002 (Table 7) because the 60°C bead treatment stage employed only a 1:2 liquor ratio (compared to the
 1003 1:10 liquor ratio utilised in the first stage of the reduction clearing process) and, therefore, less
 1004 energy was needed to heat the lower amount of water used in the bead wash-off process.

1005

1006 However, in the bead wash-off process, as PA beads were also used at a 1:5 bead:fibre ratio
 1007 (Figure 5), additional heat energy was therefore consumed in heating the beads from ambient
 1008 temperature to 60°C (Table 7). As the calculations in Table 7 assumed a 1 kg fibre mass, then the
 1009 respective masses of water and PA beads utilised in the bead wash-off were, respectively, 2 kg (of
 1010 water) owing to the use of a 1:2 water:fibre ratio and 5 kg (of PA beads) because of the 1:5
 1011 bead:fibre ratio. However, as the specific heat capacity of polyamide is only $\sim 1/3$ that of water (1.67
 1012 $\text{kJ kg}^{-1} \text{ K}^{-1}$ compared to $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$), the same amount of heat energy (326 kJ) was required to

1013 heat both the 5 kg of PA beads and the 2 kg of water to 60°C. The total amount of heat energy used
 1014 in the bead wash-off process (ie 651 kJ) was therefore much lower than that used in the reduction
 1015 clearing process (2424 kJ); indeed, the energy consumption of the bead wash-off process was only
 1016 ~27% of that of the reduction clearing process (Table 7).

1017
 1018 In the case of the two wash-off processes that had been used for reactive dyes on the cotton
 1019 component of the polycotton fabric, Table 7 shows that a total of 8527 kJ of heat energy was
 1020 consumed during the 4-bath conventional wash-off process (Figure 5); this figure contrasted
 1021 markedly with the 2123 kJ of energy that was consumed in the 3-bath bead wash-off process
 1022 (Figure 6). Indeed, the energy consumption of the bead wash-off process was only ~25% of that of
 1023 the conventional 4-bath wash-off process.

1024
 1025 Thus, from the data shown in Table 7, it follows that if polycotton fabric which had been dyed using
 1026 both disperse dyes and reactive dyes was washed-off using the two bead wash-off processes
 1027 (Figures 3 and 6) rather than the 2-stage reduction clear process (Figure 2) and conventional 5-bath
 1028 wash-off process (Figure 5), then the total amount of heat energy consumed in wash-off would be
 1029 reduced by some 75%, from 10951 kJ (2424 + 8527) to 2774 kJ (652 + 2122).

1030 **Table 7** Amount of heat energy and water used

dye	wash-off	stage	temp./°C	liquor ratio*	bead ratio*	Q/ kJ	water used*/kg
		Na ₂ CO ₃ /Na ₂ S ₂ O ₄	60	1:10	-	1630	10
	reduction clear	rinse	40	1:10	-	794	10
		total				2424	20
disperse		wash-off	60	1:2	-	326	2
	bead			-	1:5	326	-
		rinse	room	1:5	-	0	5
		total				651	7

	1 st wash-off	50	1:10	-	1212	10	
	1 st rinse	room	1:10	-	0	10	
	2 nd wash-off	70	1:10	-	2048	10	
	2 nd rinse	room	1:10	-	0	10	
conventional	3 rd wash-off	98	1:10	-	3219	10	
	3 rd rinse	room	1:10	-	0	10	
	4 th wash-off	70	1:10	-	2048	10	
	4 th rinse	room	1:10	-	0	10	
	total				8527	80	
reactive	1 st wash-off	60	1:2	-	326	2	
				-	1:5	326	-
	1 st rinse	room	1:5	-	0	10	
	2 nd wash-off	60	1:2	-	326	2	
				-	1:5	326	-
bead	2 nd rinse	room	1:5	-	0	10	
	3 rd wash-off	70	1:2	-	409	2	
					1:5	409	-
	3 rd rinse	21	1:5	-	0	5	
	total				2123	31	

*assumes a 1 kg fibre mass resulting in 10 kg of water in the case of a 1:10 L:R and 2 kg water for a 1:2 L:R as well as 5 kg beads in the case of a 1:5 bead:fibre ratio

1032

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1035

1036 It is apparent that in the case of the 2-stage reduction clearing process that was utilised to remove
 1037 surplus disperse dye from the dyed PES component of the dyed polycotton fabric, a total of 20 kg of
 1038 water was consumed per kg of fabric, whilst a sizeable 80 kg of water was employed to remove the
 1039 surplus reactive dye from the dyed cotton component of the dyed polycotton fabric. Such water
 1040 usage contrasts to that displayed by the two bead wash-off processes employed, namely 7 kg and
 1041 31 kg of water per kg of fabric, respectively. Thus, if polycotton fabric which had been dyed using
 1042 both disperse dyes and reactive dyes was washed-off using the two bead wash-off processes

1043 (Figures 3 and 6) rather than the 2-stage reduction clear process (Figure 2) and conventional 4-bath
1044 wash-off process (Figure 5), then the total amount of water consumed in wash-off would be reduced
1045 by 62%, from 100 kg (ie 20 + 80) to 38 kg (ie 7 + 31).

1046
1047 In the context of the amount of chemicals used in the four wash-off processes employed in this
1048 work, Table 7 demonstrates that for every Tonne of polycotton dyed using disperse dyes and
1049 reactive dyes, the 20 T of wastewater that would be generated using the reduction clearing process
1050 depicted in Figure 2 would be contaminated with 20 kg of residual Na_2CO_3 and 15 kg of $\text{Na}_2\text{S}_2\text{O}_4$,
1051 whilst the 80 T of wastewater that could be produced using the conventional wash-off process for
1052 reactive dyes (Figure 5) would contain 240 kg of wash-off agent. In sharp contrast, as no chemicals
1053 were employed in either of the two bead wash-off processes detailed in Figures 5 and 6, then the
1054 wastewater generated would not contain residual added chemicals.

1055

1056 **5 conclusions**

1057 Polycotton fabric which had been dyed using commercial grade disperse dyes and reactive dyes
1058 can be washed-off using a process that employs beads. The use of the 2-stage and 3-stage bead
1059 wash-off processes afforded dyeings that were of similar colour strength and colour to those which
1060 had been washed-off using a 5-stage conventional process in the case of reactive dyes and a 3-
1061 stage reduction clearing process in the case of disperse dyes. The fastness to washing at 60°C of
1062 dyeings which had been washed-off using the bead processes was comparable to that obtained for
1063 dyeings which had been washed-off using reduction clearing and a conventionally wash-off process.

1064

1065 The use of both the 2-stage and 3-stage bead wash-off processes in place of the conventional
1066 wash-off processes enable savings of >70% and >60% in the amounts of energy and water,
1067 respectively, consumed in conventional wash-off and reduction clearing processes. In addition,
1068 neither of the bead wash-off processes require the use of auxiliary chemicals (eg proprietary wash-
1069 off agents, Na_2CO_3 , $\text{Na}_2\text{S}_2\text{O}_4$) and therefore offer more environmentally acceptable processes for
1070 dye removal from dyed materials. As a major proportion of both the reactive dye and disperse dye

1071 that is removed during bead wash-off is adsorbed by the beads, the ensuing wastewater generated
1072 during wash-off is far less contaminated with residual dye, unlike conventional wash-off processes.

1073

1074 In the case of the wash-off of disperse dyes from the dyed PES component of polycotton using the
1075 2-stage bead wash-off process, the residual wash-off baths contained much lower amounts of
1076 chloride ions and TDS than those obtained using the conventional 3-stage reduction clearing
1077 process. This was attributed to the PA beads having adsorbed vagrant chloride ions. In the case of
1078 the wash-off of reactive dyes from the cotton component of dyed polycotton, the use of a 3-bath
1079 bead wash-off process rather than a 5-stage conventional wash-off process did not result in such a
1080 reduction in either [Cl⁻] or TDS content, which was ascribed to the swamping effect of the very high
1081 levels of chloride ion that resulted from 50 g l⁻¹ added NaCl having been employed in the reactive
1082 dyeing process.

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