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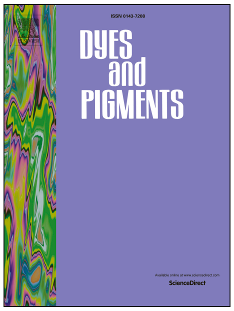

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The wash-off of dyeings using interstitial water Part 5: residual dyebath and wash-off liquor generated during the application of disperse dyes and reactive dyes to polyester/cotton fabric

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Abstract

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

Highlights

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

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

1 introduction

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

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

As discussed in the previous part of this paper (3), although both PES and cotton enjoy usage as individual types of fibre in textile materials, the most important commercial use of PES and cotton is in the form of a PES and cotton blend that is commonly known as polycotton. The most popular immersion dyeing method used for dyeing polycotton blend fabrics is a two-bath, multiple-stage process in which the PES component is initially dyed using disperse dyes at ~130°C under acidic conditions and surplus disperse dye is then removed using a wash-off process known as reduction clearing, which involves treating the dyed material in an aqueous, alkaline solution of sodium dithionite ($Na_2S_2O_4$; sodium hydrosulfite). The cotton component is then dyed using reactive dyes at ~60°C under alkaline conditions and surplus dye is once more removed using a multi-stage wash-off process that involves treating the dyed material to several aqueous rinses that use combinations of cold/warm/hot water and which commonly employ a proprietary wash-off agent to expedite reactive dye removal.

1.1 wash-off processes for polycotton

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

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

1.1.1 polyester component

In the case of PES fibres dyed with disperse dyes, the reduction clearing process has especially poor environmental credentials insofar as the dyed material is treated in an aqueous, alkaline solution of sodium dithionite ($Na_2S_2O_4$; sodium hydrosulfite) and a non-ionic surfactant to remove surplus disperse dye as well as surface deposited polyester oligomers (4). The strongly reducing conditions convert anthraquininoid (AQ) disperse dyes to the corresponding water-soluble, low substantivity, ionised variant and result in cleavage of the -N=N- bond in azo dyes, liberating colourless amino compounds. Thus, in addition to the reduction clearing process consuming large amounts of water, energy and chemicals, the highly alkaline wastewater that is generated from reduction clearing will typically comprise the robust reducing agent sodium dithionite, surfactant, residual dyes as well as aromatic amines in the case of azo disperse dyes. Despite persistent attempts over many years to reduce the environmental impact of reduction clearing, the process continues to enjoy widespread usage (5).

1.1.2 cellulose component

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

The wash-off process that is used to remove surplus reactive dye from cellulosic fibres has an additional important function that is a corollary of a further inherent deficiency of reactive dyes, namely, that significant quantities of inorganic electrolyte (either sodium sulfate or sodium chloride) must be used in order to achieve acceptable levels of dye uptake during immersion dyeing processes. In this context, between 10-30 gl^{-1} NaCl, with upto 50 gl^{-1} for lower substantivity dyes, 80 gl^{-1} for low substantivity vinylsulfone dyes (6) and 100 gl^{-1} of NaCl or Na_2SO_4 in the case of dark shades (7)) are typically added to a reactive dye dyebath to promote dye uptake; the added electrolyte also promotes the extent of dye-fibre fixation (ie covalent fixation of the dye to the substrate. In order to remove all traces of unfixed reactive dye from dyed cellulosic fibres, it is necessary to also remove all residues of inorganic electrolyte from the dyed material that has been adsorbed by the substrate during dyeing. Because of the very high levels of residual inorganic electrolyte that are present in both the dyed fibre and the exhausted dyebath at the end of dyeing, then the dyeing stage and the subsequent wash-off stage each characteristically generate large amounts of wastewater that contains residual hydrolysed dye, unreacted dye, as well as very high levels of NaCl or Na_2SO_4. Additionally, because proprietary wash-off agents are normally utilised in the wash-off process to expedite unfixed dye removal, the wastewater from reactive dyeing and associated wash-off processes presents considerable environmental and economic challenges.

1.1.3 polycotton

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

This paper describes a wash-off process for dyeings on polycotton that uses a novel, re-usable and re-cyclable polyamide (PA) bead medium to replace the vast majority of the water and chemicals that are normally employed in wash-off. This novel process (8) employs only the relatively small amount of water that is present within the interstices of both the damp fabric and the bead material to remove residual dye, electrolyte, surfactant, etc; as such, the bead wash-off process does not require the dyed material to be immersed in a large reservoir of water, as employed in conventional wash-off processes. The first part of the paper (9) showed that bead wash-off process was able to remove five different types of dye from three different types of fibre to an extent that was comparable to that achieved using appropriate, conventional wash-off methods. Similar depths of shade and levels of wash fastness were secured in the cases of three, bis(aminochlorotriazine) dyes reactive dyes on cotton (10) and three disperse dyes on PES (5) using bead wash-off processes that utilised fewer treatment stages than the recommended, multi-stage conventional wash-off processes. Less heat energy was consumed during bead wash-off than in conventional wash-off processes (5) and the beads adsorbed vagrant disperse dye liberated during wash-off, thereby presenting the opportunity of a lower effluent load (5, 10). The previous part of the paper (3) demonstrated that in the case of polycotton fabric which had been dyed using reactive dyes and disperse dyes, a novel bead wash-off process furnished dyeings that were comparable, in terms of colour strength, colour and fastness, to those which had been reduction cleared in the case of the disperse dyes and washed-off using a conventional 5-stage wash-off process for the reactive dyes. In addition, the bead wash-off processes enabled reductions of ~70% to be achieved in the amounts of both energy and water consumed during wash-off (3).

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

2. Experimental

2.1 Materials

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

Table 1 dyes and auxiliaries used

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

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

2.2 Procedures

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

2.2.1 Dyeing the PES component of the polycotton blend

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

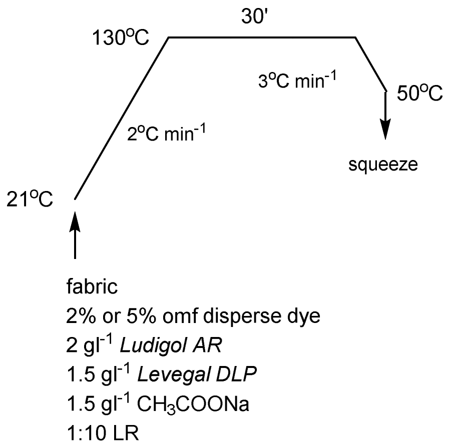


Figure 1 process for dyeing the PES component using disperse dyes

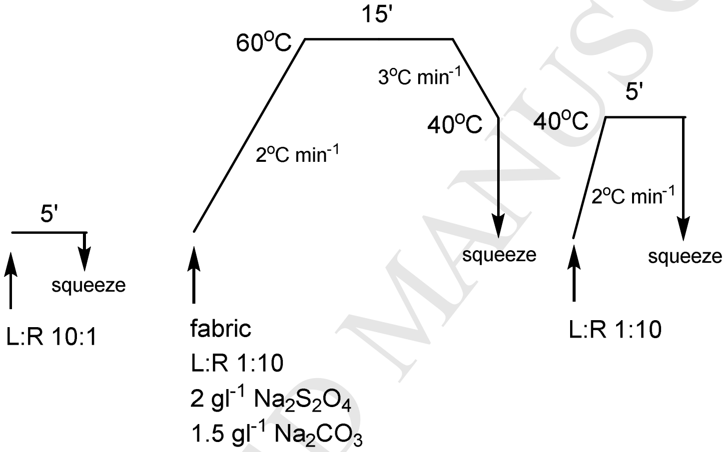


Figure 2 3-stage reduction clearing process

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

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

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

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

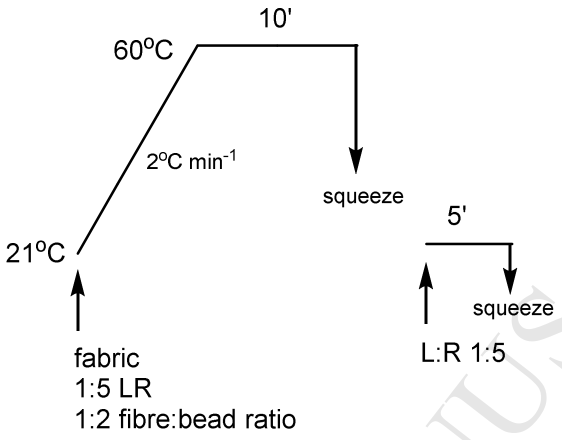


Figure 3 2-stage bead wash-off process

2.2.2 Dyeing the cotton component of the polycotton blend

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

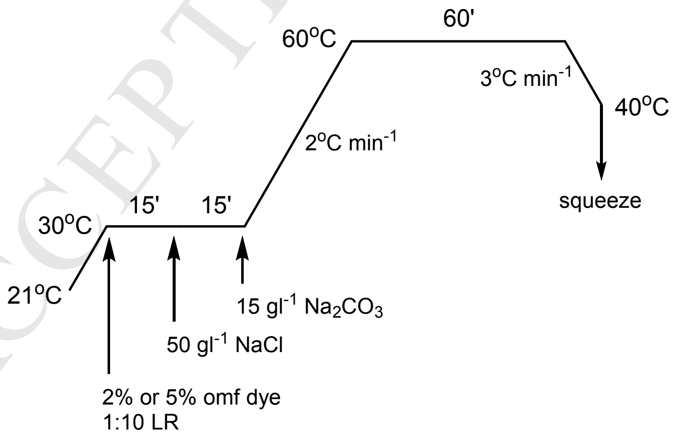


Figure 4 process for dyeing the cotton component using reactive dyes

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

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

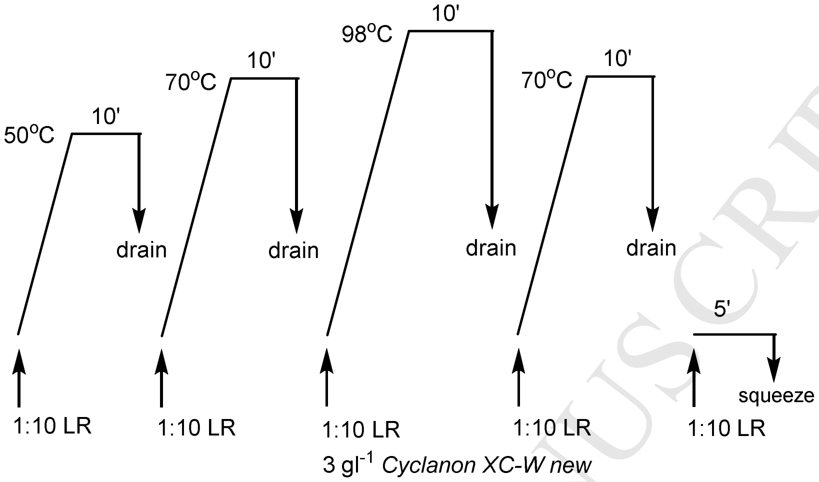


Figure 5 5-stage conventional wash-off process

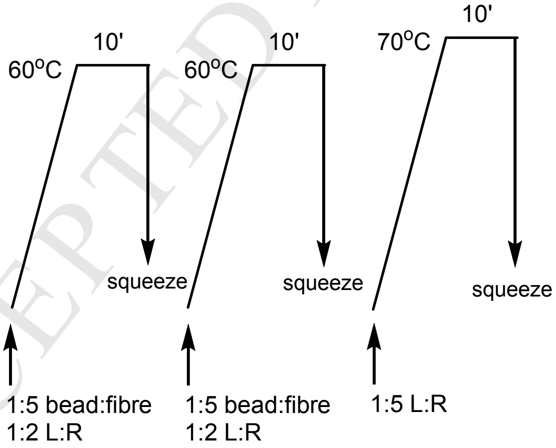


Figure 6 3-stage bead wash-off process

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

The cotton component of the polycotton blend fabric which had been dyed using the process recounted in 2.2.4 (Figure 4) was squeezed and subjected to the 4-stage bead wash-off process shown in Figure 6. In the two bead treatment stages depicted in Figure 6, the same sample of beads was used for both treatment baths. The ensuing washed-off sample allowed to dry in the open air.

2.2.3 Dyeing the polycotton blend fabric

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

2.2.4 Colour measurement

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

2.2.5 determination of chloride ion concentration in residual liquors

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

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

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

2.2.6 determination of total dissolved solids (TDS)

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

Aqueous NaCl solutions of different concentration over the range 0.1 to 100 gl^{-1} were prepared and the TDS of these solutions measured. A calibration curve was constructed by plotting TDS (gl^{-1}) as a function of NaCl concentration (over the range 0.1 to 100 gl^{-1}) from which the calibration coefficient was determined so that the TDS (gl^{-1}) of a given residual liquor sample could be determined from calculated measured values of NaCl concentration.

2.2.7 Fastness determination

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

2.2.8 Photography

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

3. Results and discussion

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

3.1 PES component/disperse dyes

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

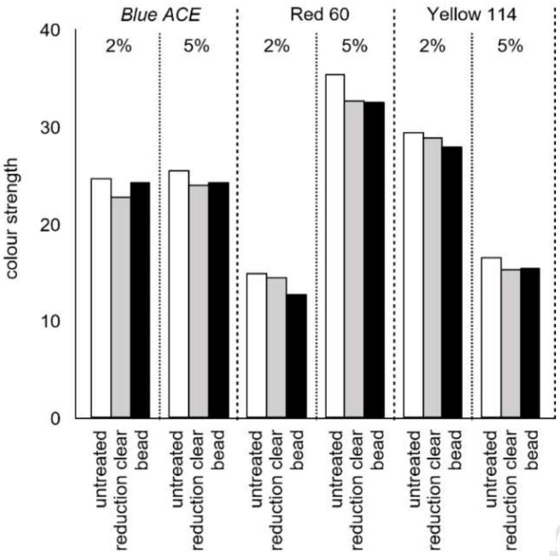


Figure 7 colour strength of PES component dyed using the three disperse dyes and washed-off using the conventional 3-stage reduction clearing process and 2-stage bead wash-off process

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}
Dianix Blue ACE	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
	5	untreated	84.7	-4.4	60.3	60.4	94.1	420
		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

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

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

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

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

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

Table 3 fastness of dyeings to ISO 105-CO6/C2S

component dyed	dye	%omf dye	wash-off process	change in shade	wool	acrylic	polyester	polyamide	cotton	acetate
polyester	*Dianix Blue ACE*	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
	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
			2-stage bead	1	5	5	5	4/5	4	5
		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
cotton	C.I. Reactive Black 5	2	untreated	1	5	5	5	4/5	3/4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	5	5	5
		5	untreated	1	5	5	5	4/5	4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	5	5	5
	C.I. Reactive Red 198	2	untreated	1	5	5	5	4/5	4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	4/5	4	5
		5	untreated	1	5	5	5	3/4	3/4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	5	5	5
	Remazol Yellow R	2	untreated	1	5	5	5	4/5	3/4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	5	5	5
		5	untreated	1	5	5	5	4/5	4	5
			5-stage conventional	1	5	5	5	5	5	5
			3-stage bead	1	5	5	5	5	5	5

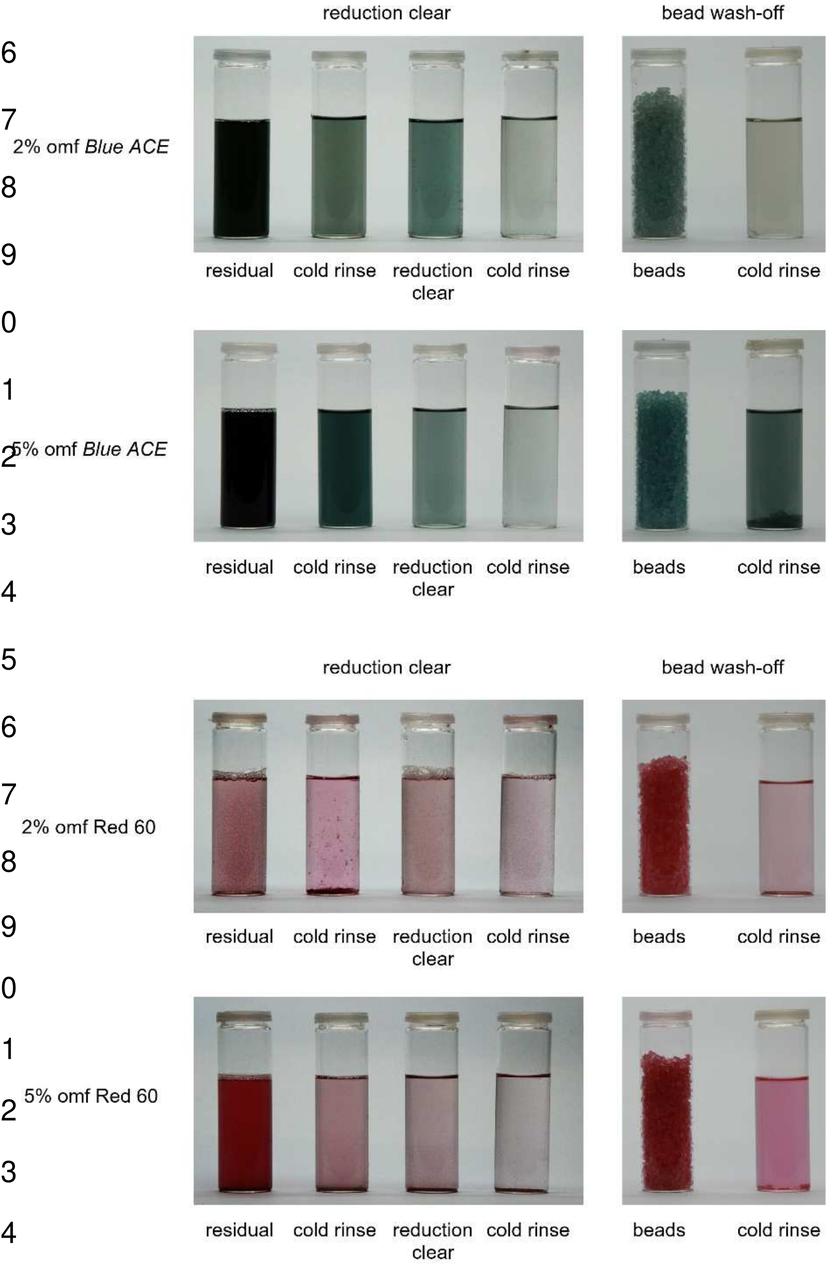
polyester and cotton	*Dianix Blue ACE* + C.I. Reactive Black 5	2 +2	untreated	1	5	5	5	4/5	4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	4/5	4	5
		5 +5	untreated	1	5	5	5	3/4	3/4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	5	5	5
	Dianix Red + C.I. Reactive Red 198	2 + 2	untreated	1	5	5	5	4/5	3/4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	5	5	5
		5 + 5	untreated	1	5	5	5	4/5	4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	5	5	5
	Dianix Yellow + *Remazol Yellow R*	2 + 2	untreated	1	5	5	5	4/5	4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	4/5	4	5
		5 + 5	untreated	1	5	5	5	3/4	3/4	5
			reduction clear/conventional	1	5	5	5	5	5	5
			bead/bead	1	5	5	5	5	5	5

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

3.1.1 vagrant disperse dye removal

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

Figure 8 shows the residual wash-off liquors for both 2% and 5% omf dyeings of the PES component using the three disperse dyes, obtained at the end of both the 3-stage reduction clearing process and the 2-stage bead wash-off process. It is apparent that significant amounts of unexhausted dye were present in the residual dyebath liquors, especially in the case of the 5% omf dyeings. In terms of the conventional 3-stage reduction clearing process, Figure 8 shows that the initial cold water rinse stage of the reduction clearing process removed a substantial amount of vagrant dye, as expected, owing to the marked driving force for dye desorption that accrues from the dye concentration gradient that exists between the dyed fibre and the rinse medium (in this case cold water) (10). Rinsing can be expected to have removed not only unfixed, surplus disperse dye from the dyed sample but also will have reduced the high concentration of residual dispersing agent and other dyeing auxiliaries that will be present within the substrate. Subsequent treatment of the dyed sample with the aqueous $Na_2CO_3/Na_2S_2O_4$ reduction clearing liquor at 60°C removed further dye, as expected, in view of the intended purpose of the $Na_2CO_3/Na_2S_2O_4$ stage of the reduction clear treatment, namely to decolourise azo disperse dyes and solubilise AQ disperse dyes. The finding (Figure 8) that small amounts of vagrant disperse dye was removed during the final cold water rinse stage of the reduction clearing process reveals that not all vagrant disperse dye molecules had been discoloured/removed by treatment with the hot aqueous $Na_2CO_3/Na_2S_2O_4$ solution.



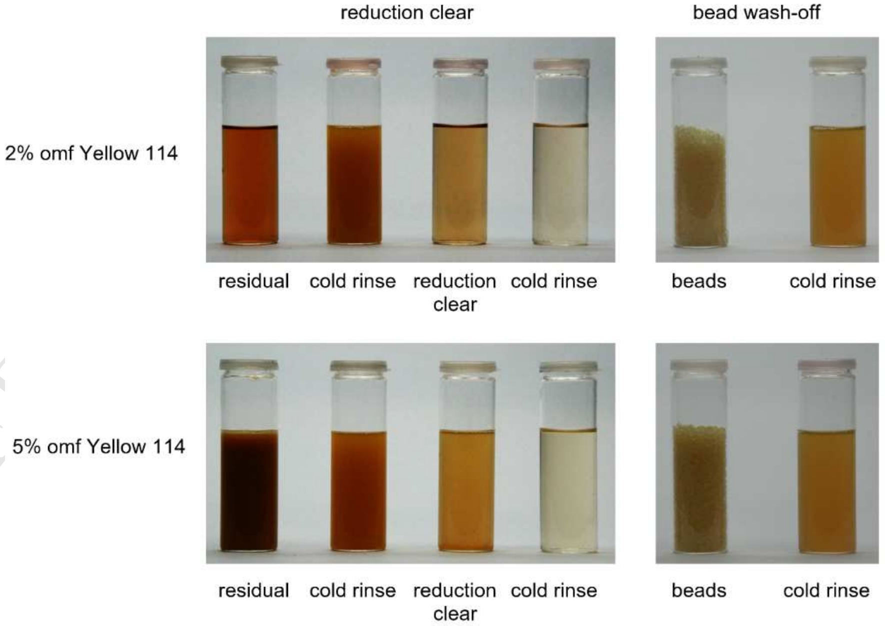


Figure 8 vagrant disperse dye: 2-stage reduction clear and 2-stage bead wash-off

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

The 2-stage bead wash-off process removed surplus disperse dye (Figure 8) insofar as during the treatment of the dyed sample with the beads, vagrant disperse dye molecules were adsorbed by the beads, and, also, the final cold water rinse liquor obtained at the end of the bead wash-off process contained residual disperse dye. It is considered (3, 5) that the beads remove vagrant disperse dye from dyed PES fabric (and also vagrant reactive dye from dyed cotton) as a consequence of their physical contact with the damp dyeings, in that dye molecules located at the surface of the dyed material transfer to and become adsorbed onto the bead surface and are then retained by the PA substrate. Indeed, Figure 8 shows that a sizeable amount of vagrant disperse dye was adsorbed by the beads. However, the finding that the final cold water rinse liquors obtained from the bead wash-off contained more vagrant disperse dye than the corresponding final cold water rinse liquors obtained at the end of the reduction clearing process (Figure 8), implies that the single treatment of the dyed samples with the beads did not remove as much surplus dye from the dyed PES fibre as did the corresponding two treatments to which the dyeings had been subjected during reduction clearing (ie first cold water rinse and hot aqueous $Na_2CO_3/Na_2S_2O_4$ solution).

Nonetheless, the ensuing bead washed-off dyeings displayed colour strength values that were not too dissimilar to their reduction cleared equivalents (Figure 7) as well as levels of wash fastness that were comparable to that of their reduction cleared counterparts (Table 3). Thus, the findings presented in Figure 7 and Table 3 suggest that a single treatment with the PA beads at 60^{o}C was as effective as the combination of initial cold water rinse and hot aqueous $Na_2CO_3/Na_2S_2O_4$ solution in the conventional reduction clearing process.

The 2-stage bead wash-off process therefore uses less water, does not employ environmentally-challenging chemicals and offers savings in time, compared to the conventional reduction clearing processes. Furthermore, the 2-stage bead wash-off process offers the potential for creating lower effluent loads than its conventional reduction clearing counterpart because the beads are able to adsorb significant quantities of vagrant disperse dye which will result in wastewater being much less contaminated with residual dye.

3.1.2 chloride ion concentration in residual liquors

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

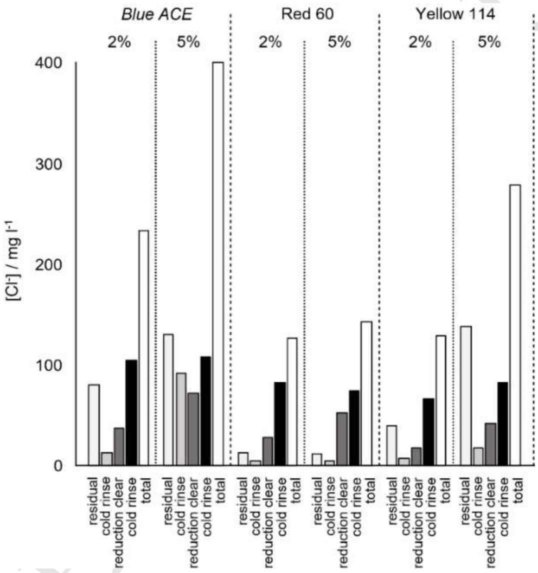


Figure 9 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 3-stage reduction clearing process

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

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

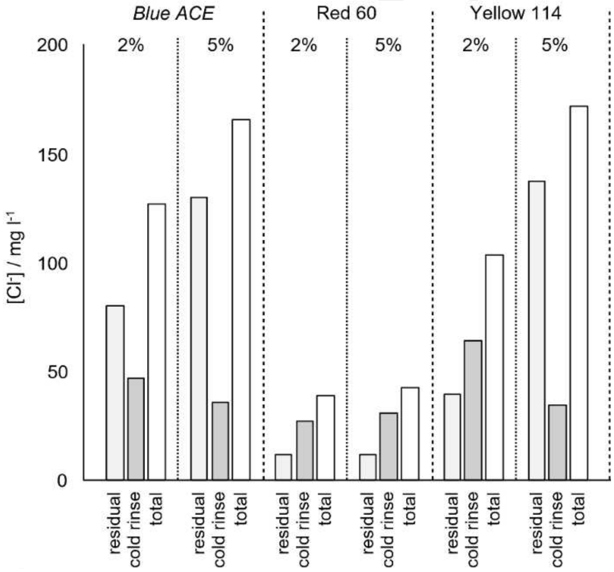


Figure 10 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 2-stage bead wash-off process

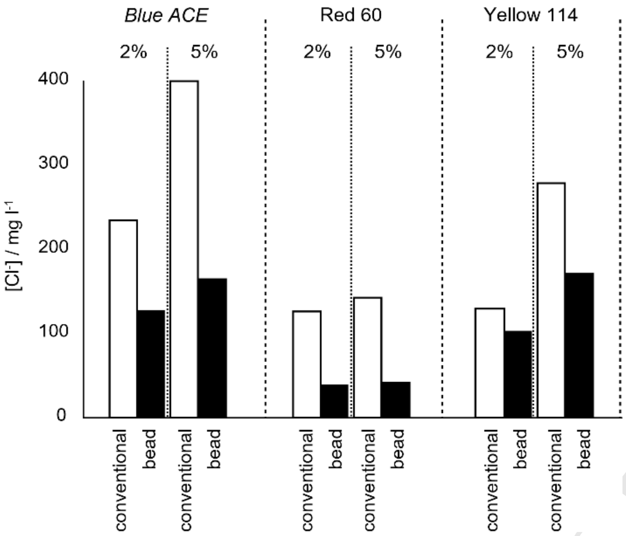


Figure 11 total chloride ion concentration obtained for 2% and 5% omf dyeings washed-off using the 3-bath reduction clearing process and 2-stage bead wash-off process

Figure 10 shows the levels of chloride ion obtained when each of the three commercial grade disperse dyes had been washed-off using the 2-stage bead wash-off process. The final cold water rinse bath liquor contained chloride ions which again, may be attributed to residual disperse dye-derived diluent electrolyte having been removed from the dyed samples. Comparison of the data in Figure 10 with that in Figure 9 reveals that values of the total [Cl$^-$] ion secured using the bead wash-off were much lower than those obtained using the conventional 3-stage reduction clearing process. This is highlighted by the data shown in Figure 11 which clearly shows the large difference between the total [Cl$^-$] obtained for the conventional 3-stage reduction clear process and the 2-stage bead wash-off process. From the previous discussion of the ability of the PA beads to adsorb vagrant disperse dye (section 3.1.1), the findings displayed in Figure 11 can be ascribed to the beads having adsorbed vagrant chloride ions. This particular aspect will be the subject of a future part of the paper.

3.1.3 total dissolved solids of residual liquors

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 as a measure of the quality of that water sample. As such, the principal contributors to the TDS in 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 substances in municipal water that contribute to TDS are inorganic minerals, of which the component of most concern is NaCl; as TDS increases the amounts of both Na^+ and Cl^- increase (16). For benchmark levels, an aesthetic objective of ≤500 mg l^{-1} (ie ≤0.5 gl^{-1}) has been established for TDS in drinking water (18, 19); at higher levels, unpalatability, mineral deposition, corrosion and excessive hardness may occur (18): the World Health Organisation (WHO) considers drinking water to be unacceptable if the total dissolved solids content is >1,200 ppm (ie >1.2 gl^{-1}) (17).

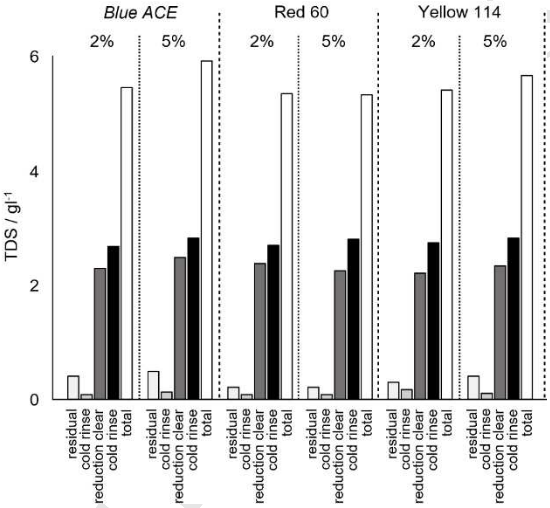


Figure 12 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 3-stage reduction clearing process

The results obtained for the TDS content of the residual dyebath and the various treatment baths of the reduction clearing process are shown in Figure 12. Whilst the relatively low TDS values obtained for the residual dyebath may be attributed to dye-derived diluent electrolyte, the much higher TDS content of the residual $Na_2CO_3/Na_2S_2O_4$ bath and final cold rinse bath carried out at the end of the reduction clearing process exemplify the well-known environmental challenges that arise from the use of aqueous, alkaline, sodium dithionite in reduction clearing. Indeed, these findings reveal that the total TDS obtained for the application of each of the three disperse dyes to PES was considerably greater than not only the aesthetic objective of ≤0.5 gl^{-1} recommended for drinking water (18, 19) but also the limit regarded by the WHO as acceptable for drinking water (ie <1.2 gl^{-1}) (17).

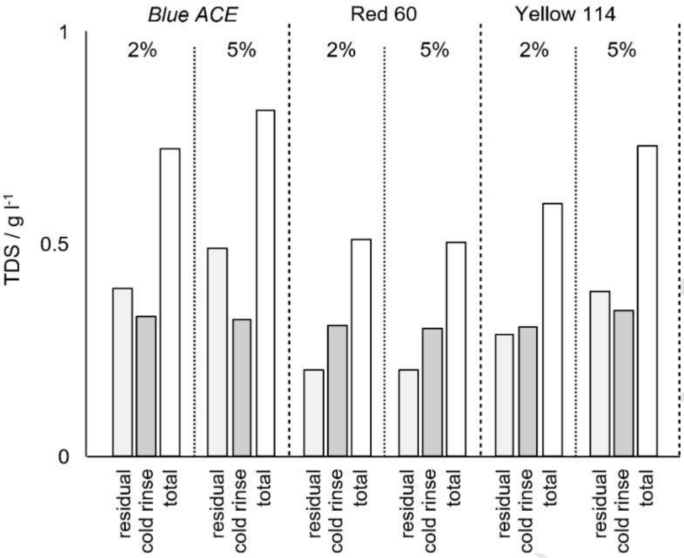


Figure 13 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 2-stage bead wash-off process

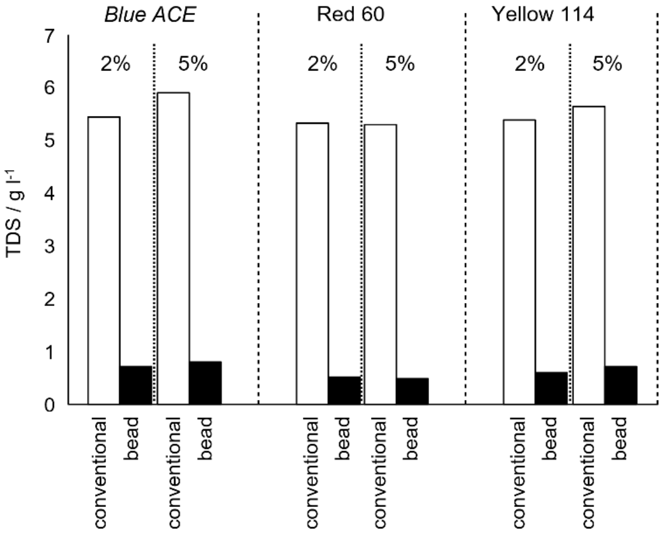


Figure 14 total TDS content obtained for 2% and 5% omf dyeings washed-off using the 3-bath reduction clearing process and 2-stage bead wash-off process

In terms of the 2-stage bead wash-off process, Figure 13 shows that the TDS content of the final cold water rinse bath liquor was low which can be attributed to the beads having adsorbed a large proportion of the surplus disperse dye which had been removed from the PES component. Comparison of the results displayed in Figure 13 with those in Figure 12 reveals that values of TDS secured using the 2-stage bead wash-off process were considerably lower than those obtained using the conventional 3-stage reduction clearing process. This is illustrated by Figure 14 which shows the marked difference in total TDS contents obtained for the conventional 3-stage reduction clearing process and the 2-stage bead wash-off process. As discussed above, it seems likely that the findings displayed in Figure 14 can be attributed to the ability of the beads to adsorb vagrant disperse dye and chloride ions that have been removed from the dyed samples during the bead wash-off process; this is the subject of a future part of the paper.

3.2 cotton component/reactive dyes

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

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

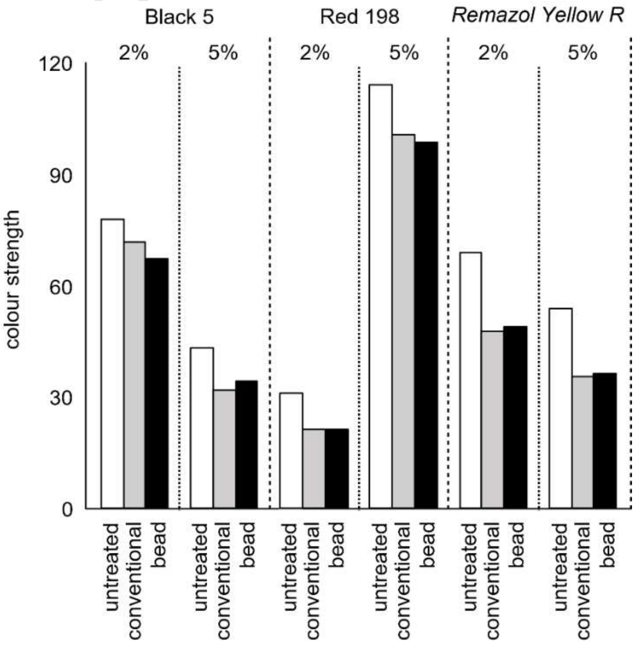


Figure15 colour strength of cotton component dyed using the three reactive dyes and washed-off using the conventional 5-stage wash-off process and 3-stage bead wash-off process

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

Table 4 Colorimetric parameters for dyeings of cotton component dyed with reactive dyes and washed-off 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

Remazol Yellow R	2	untreated	38.9	34.6	-4.1	34.8	353.2	440
		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
	5	untreated	72.8	28.3	71.8	77.1	68.5	420
		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

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

3.2.1 vagrant reactive dye removal

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

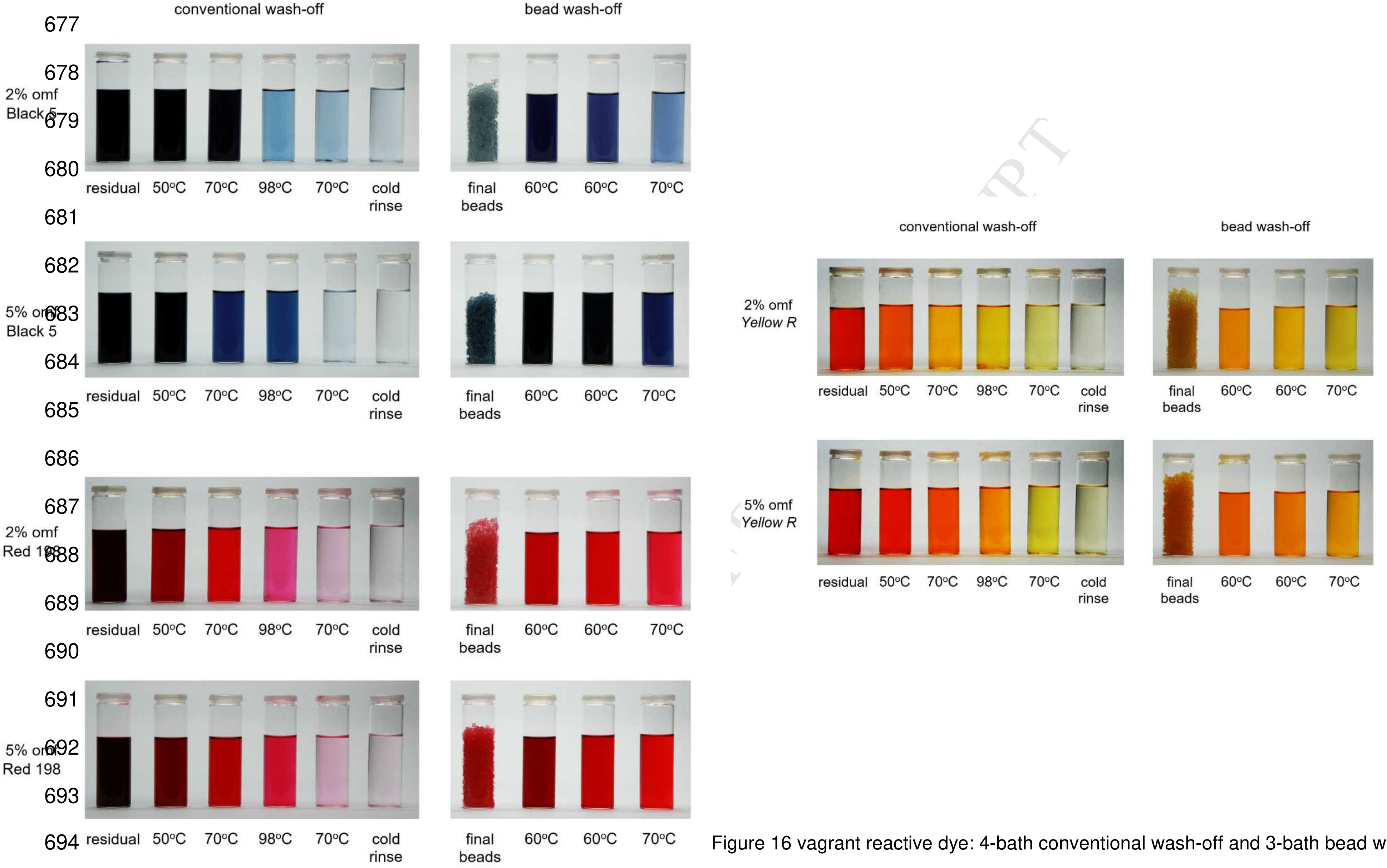


Figure 16 vagrant reactive dye: 4-bath conventional wash-off and 3-bath bead wash-off

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

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

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

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

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

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

3.2.2 chloride ion concentration in residual liquors

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

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

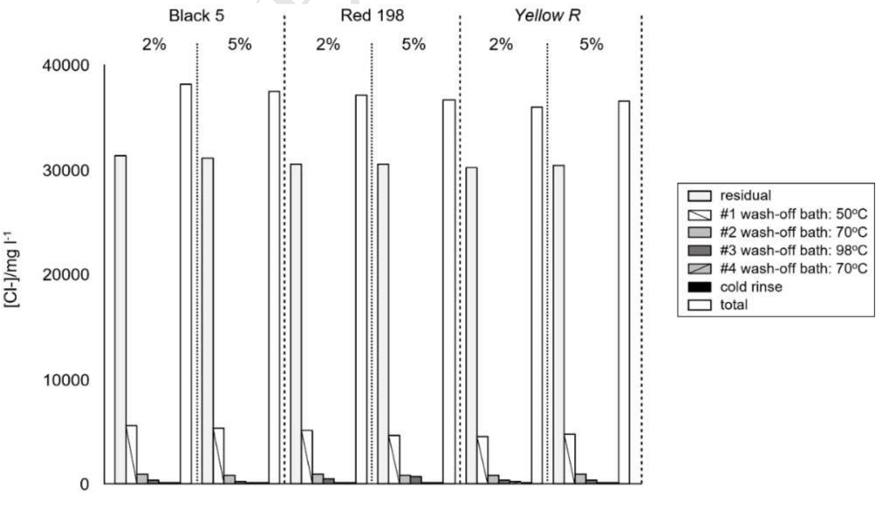


Figure 17 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 5-bath conventional wash-off process

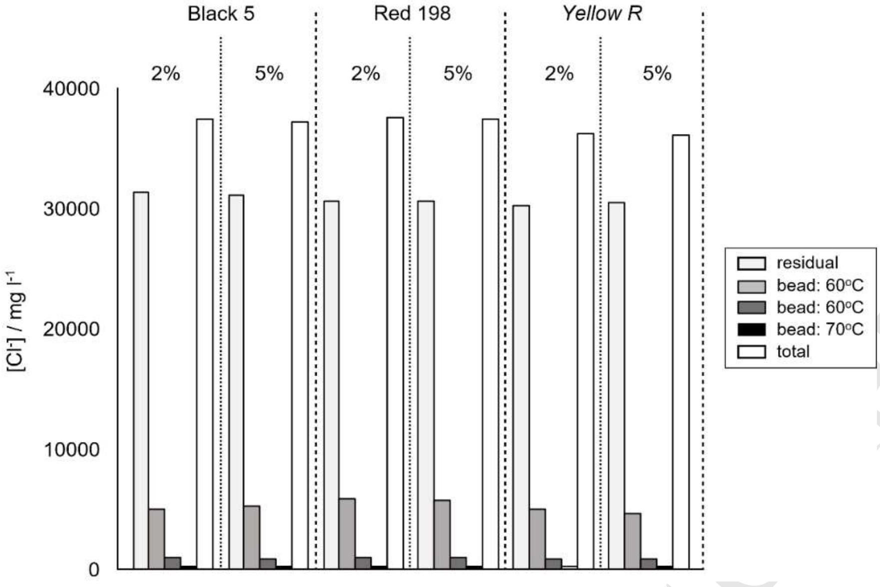


Figure 18 chloride ion concentration of residual liquors: 2% and 5% omf dyeings washed-off using the 3-bath bead wash-off process

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

3.2.3 total dissolved solids of residual liquors

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

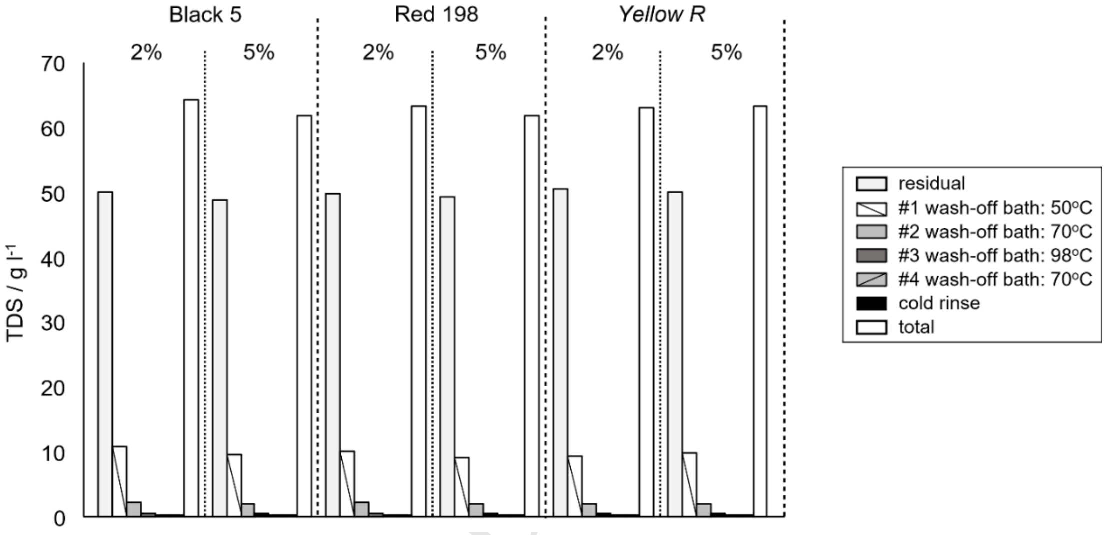


Figure 19 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 5-bath conventional wash-off process

The very high TDS content of the residual dyebath can be attributed to presence of chloride ion that stemmed from the use of 50 gl^{-1} added NaCl in dyeing. Similar levels of TDS content were obtained for the residual dyebaths for each of the three reactive dyes used, which reflects the fact that the same amount of added NaCl (ie 50 gl^{-1}) had been used for dyeing. Commercial grade samples of reactive dyes often contain quantities of shading components and diluents, the latter frequently being electrolyte such as NaCl, which are used by the dye maker as part of the dye standardisation process. In this context, it has been reported that the amount of standardising constituents in commercial grade reactive dyes ranged from 34% to 73% (20-22); in the case of the three commercial grade reactive dyes employed in this work, the amount of diluent NaCl present in the commercial samples ranged from 11.6% to 12.3% (14).Thus, the slight variation in the TDS content of the residual dyebaths observed for the three dyes (Figure 19) can be attributed to different levels of diluent electrolyte in the commercial dye samples.

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

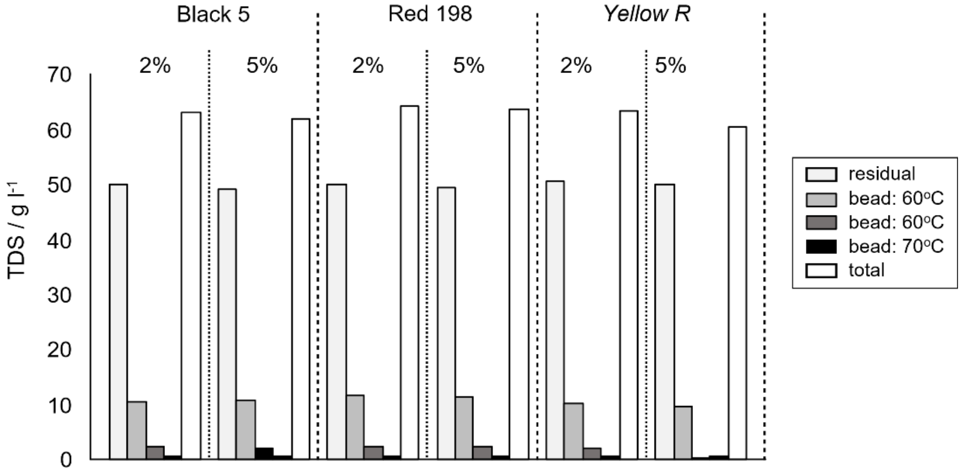


Figure 20 TDS of residual liquors: 2% and 5% omf dyeings washed-off using the 3-bath bead wash-off process

Interestingly, in terms of the previously mentioned relationship between drinking water quality and TDS content, only the residual liquors obtained from the final one or two wash-off baths and the final rinse bath displayed TDS levels ≤0.5 gl^{-1} (Figure 19). The results displayed in Figure 19 therefore illustrate the inherent, severe environmental challenges that reactive dyeing wastewater presents, because of the routine usage of outrageously high levels of added inorganic electrolyte in immersion dyeing of cellulosic fibres.

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

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

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

Figure 21 shows the f_k values obtained for 2% and 5% omf dyeings, produced on both the polyester and cotton components of the polycotton blend fabric using each of the three disperse and three reactive dyes. Results are presented for untreated dyeings (which had not been reduction cleared, or washed-off using either the 2-stage bead process, 3-stage bead process or conventional 5-stage process) as well as dyeings which had been subjected to the combined treatments of the 2-stage reduction clearing to remove surplus disperse dye (Figure 2) and the conventional 5-stage wash-off (Figure 5) to remove surplus reactive dye from the dyed polycotton; also shown are the results obtained for dyeings which had been subjected to the combined treatments of the 2-stage bead wash-off process to remove surplus disperse dye (Figure 3) and the 3-stage bead wash-off to remove surplus reactive dye (Figure 6) from the dyed polycotton.

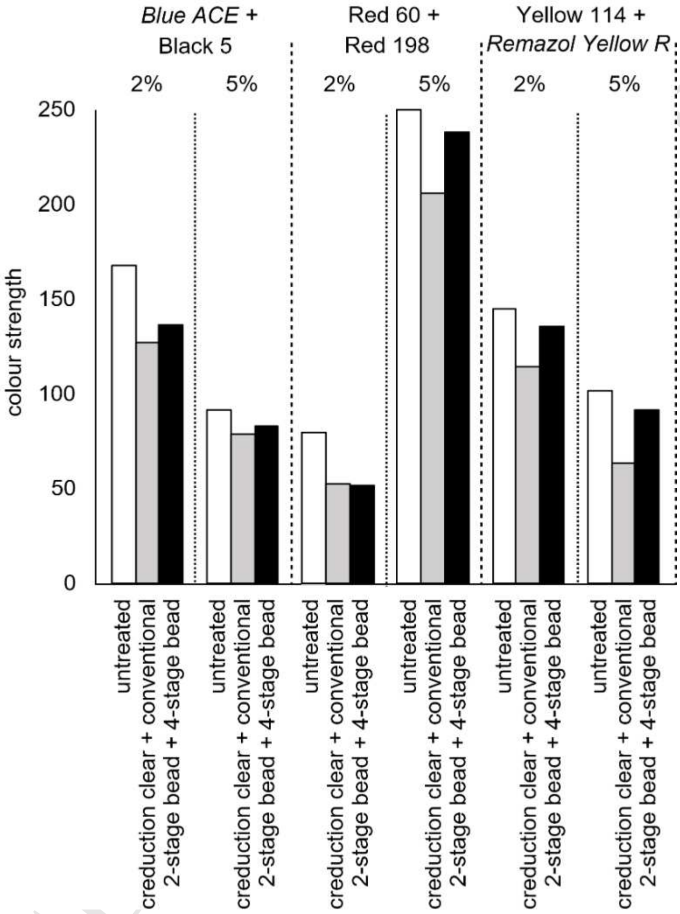


Figure 21 colour strength of PES and cotton component dyed using the three disperse dyes and three reactive dyes

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

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

dye	% omf	wash-off process	L*	a*	b*	C*	h°	λ_{max}
Dianix Blue ACE + C.I. Reactive Black 5	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
	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 + C.I. Reactive Red 198	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
	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 + *Remazol Yellow R*	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
	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

Figure 21 also reveals that dissimilar levels of dye removal were obtained using the reduction clear/conventional wash-off and bead/bead wash-off processes, this being reflected in the different lightness values recorded for the respective dyeings (Table 6). The results presented in Table 6 also show that the reduction clear/conventional wash-off processes generally imparted greater changes in both the hue and chroma of the dyeings than did the corresponding bead/bead wash-off processes; the finding that the $\lambda_{max.}$ of the dyeings was unchanged by both combined wash-off processes showed that the changes imparted by wash-off were small.

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

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

$$\Delta f_k = \frac{f_{k1} - f_{k2}}{f_{k1}} \times 100 \qquad 2$$

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

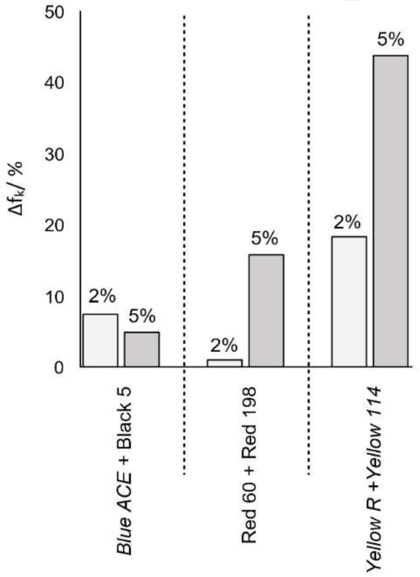


Figure 22 Δf_k for dyed polycotton

This implies that not all surplus dye must be removed from dyed polycotton in order to achieve 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.

4. Energy, water and chemical usage

As discussed in previous parts of the paper (3, 5, 10), Eqs 3 and 4 can be employed to obtain an approximate measure of the amount of heat energy consumed in each of the four different wash-off processes that were used in this work, where *Q* is the amount of heat required (kJ) to raise the 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 particular wash-off stage, c_w being the specific heat capacity of water at 21°C (4.18 kJ kg^{-1} K^{-1}) and c_{PA} the specific heat capacity of PA 6 at 20°C (1.67 kJ kg^{-1} K^{-1} (23)):

$$Q = w.c_w\ (T_2\text{-}T_1) \qquad 3$$

$$Q = n.c_{PA}\ (T_2\text{-}T_1) \qquad 4$$

As Table 7 shows, in the case of the 2-stage reduction clearing process (Figure 2) that was utilised to remove surplus disperse dye from the dyed PES component of the polycotton fabric, more energy was consumed during the 60°C $Na_2CO_3/Na_2S_2O_4$ treatment stage than the subsequent 40°C water rinse stage because of the higher temperature of the aq. alkaline stage; it is assumed that the final cold water rinse stage (Figure 2) would consume no energy. The 2-stage bead wash-off process for disperse dyes depicted in Figure 5 consumed much less energy than the reduction clearing process (Table 7) because the 60°C bead treatment stage employed only a 1:2 liquor ratio (compared to the 1:10 liquor ratio utilised in the first stage of the reduction clearing process) and, therefore, less energy was needed to heat the lower amount of water used in the bead wash-off process.

However, in the bead wash-off process, as PA beads were also used at a 1:5 bead:fibre ratio (Figure 5), additional heat energy was therefore consumed in heating the beads from ambient temperature to 60°C (Table 7). As the calculations in Table 7 assumed a 1 kg fibre mass, then the respective masses of water and PA beads utilised I the bead wash-off were, respectively, 2 kg (of water) owing to the use of a 1:2 water:fibre ratio and 5 kg (of PA beads) because of the 1:5 bead:fibre ratio. However, as the specific heat capacity of polyamide is only ~1/3 that of water (1.67 kJ kg^{-1} K^{-1} compared to 4.18 kJ kg^{-1} K^{-1}), the same amount of heat energy (326 kJ) was required to heat both the 5 kg of PA beads and the 2 kg of water to 60°C. The total amount of heat energy used in the bead wash-off process (ie 651 kJ) was therefore much lower than that used in the reduction clearing process (2424 kJ); indeed, the energy consumption of the bead wash-off process was only ~27% of that of the reduction clearing process (Table 7).

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

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

Table 7 Amount of heat energy and water used

dye	wash-off	stage	temp./°C	liquor ratio*	bead ratio*	Q/ kJ	water used*/kg
disperse	reduction clear	$Na_2CO_3/Na_2S_2O_4$	60	1:10	-	1630	10
		rinse	40	1:10	-	794	10
		total				**2424**	**20**
	bead	wash-off	60	1:2	-	326	2
				-	1:5	326	-
		rinse	room	1:5	-	0	5
		total				**651**	**7**

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

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

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

In the context of the amount of chemicals used in the four wash-off processes employed in this work, Table 7 demonstrates that for every Tonne of polycotton dyed using disperse dyes and reactive dyes, the 20 T of wastewater that would be generated using the reduction clearing process depicted in Figure 2 would be contaminated with 20 kg of residual Na_2CO_3 and 15 kg of $Na_2S_2O_4$, whilst the 80 T of wastewater that could be produced using the conventional wash-off process for reactive dyes (Figure 5) would contain 240 kg of wash-off agent. In sharp contrast, as no chemicals were employed in either of the two bead wash-off processes detailed in Figures 5 and 6, then the wastewater generated would not contain residual added chemicals.

5 conclusions

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

The use of both the 2-stage and 3-stage bead wash-off processes in place of the conventional wash-off processes enable savings of >70% and >60% in the amounts of energy and water, respectively, consumed in conventional wash-off and reduction clearing processes. In addition, neither of the bead wash-off processes require the use of auxiliary chemicals (eg proprietary wash-off agents, Na_2CO_3, $Na_2S_2O_4$) and therefore offer more environmentally acceptable processes for dye removal form dyed materials. As a major proportion of both the reactive dye and disperse dye that is removed during bead wash-off is adsorbed by the beads, the ensuing wastewater generated during wash-off is far less contaminated with residual dye, unlike conventional wash-off processes.

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

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