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The wash-off of dyeings using interstitial water part 2: Bis(aminochlorotriazine) reactive dyes on cotton

S.M. Burkinshaw*, J. Howroyd, N. Kumar, O. Kabambe

University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

2% omf dyeings of three, bis(aminochlorotriazine) reactive dyes on cotton were washed-off using a five-stage process recommended by the dye maker and a novel method that utilised two water rinses and treatment with damp nylon beads. Whilst similar levels of fastness were obtained using four temperatures in the final water rinse stage (ie cold (ambient), 50 °C, 70 °C and 98 °C) of the bead wash-off processes, a final rinse in water at 98 °C imparted levels of staining that were similar to those achieved using the five-stage wash-off process. The depths of shade and colour of the dyeings achieved using the bead wash-off methods were very similar to those obtained for the recommended process. When 5% omf dyeings were washed-off using a bead process that employed a commercial wash-off auxiliary and a cold water final rinse stage, levels of staining and shade change were obtained that were comparable to those secured using a recommended, six-stage, recommended wash-off process. As the beads adsorbed a sizeable amount of vagrant dye that was removed during wash-off, the various bead wash-off processes generated either only one or two coloured rinse liquors compared to the five or six coloured rinse liquors that ensued from the standard wash-off process, thereby constituting a lower effluent load.

1. Introduction

Dyeings and prints are routinely subjected to an aqueous treatment at the end of dyeing/printing that removes surplus dye and dyeing/printing auxiliaries, to which the generic term 'wash-off' has been ascribed [1]. Of the various classes of dye which can be used to dye and print cotton and other cellulosic fibres (ie vat, direct, reactive and azoic colourants), reactive dyes enjoy greatest usage because of their bright, wide shade gamut, relative ease of application and high wet fastness on such fibres. However, the application of reactive dyes has several disadvantages [1], especially from an environmental viewpoint insofar as, immersion (exhaustion) dyeing (which accounts for ~70% of reactive dye usage on cotton [2]) requires the use of sizeable amounts of electrolyte and dye-fibre fixation is always accompanied by alkali-induced dye hydrolysis. As a consequence, in order to achieve the desired level of fastness and correct shade, a stringent wash-off process is required to remove both hydrolysed and unfixed dye as well as dyeing auxiliaries (eg electrolyte) at the end of dyeing/printing. As the commercial wash-off agents that are commonly used to expedite reactive dye wash-off contribute to the effluent load and high volumes of water are routinely consumed during wash-off, such reactive dyeing wash-off processes and the concomitant treatment of the ensuing effluent can account for ~50% of the total dyeing cost [2].

Although the use of reactive dyes for cellulosic fibres has enjoyed seemingly unfettered growth since their commercial introduction in 1956, the wash-off of the dyes has received comparatively little attention, with focus being mostly directed towards attempts to replace the conventional wash-off agents employed with alkalis [3,4,5,6,7] or with processes that employ several water rinses [8,9], as recently exemplified by a three-bath, wash-off method that enabled reductions to be achieved in both the COD and BOD_5 environmental indicators, compared with the conventional wash-off methods [1,2].

This paper describes the use of a wash-off process for dyeings that uses a novel, re-usable and re-cyclable polyamide bead material to replace the vast majority of the water and chemicals that are traditionally used in wash-off. The patented, novel process [10], which is currently being commercialised by Xeros Ltd. [11] does not employ a large reservoir of water to immerse the dyeing/print but, rather, uses only the relatively small amount of water present within the interstices of both the damp fabric and the bead material. The first part of the paper [12] comprised an introduction to the wash-off process, describing the theoretical and empirical considerations behind the selection of the nylon bead material. This part of the paper describes the use of the novel, bead wash-off process for

* Corresponding author. Tel.: +44 113 343 3698; fax: +44 113 343 3704.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

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cotton which had been dyed with bis(aminochlorotriazine) dyes reactive dyes, and compares the colorimetric and fastness data secured for the washed-off dyeings to those which had been obtained in a previous study [1] using the dyemaker's recommended wash-off process which employed a proprietary wash-off agent. The third part of the paper will concentrate on the wash-off of disperse dyes from polyester fibres.

2. Experimental

2.1. Materials

The scoured and bleached, plain weave cotton fabric (150 g m^{-2}; Whaleys) together with the dyeing auxiliary *Sera Sperse C-SN* (DyStar) and commercial samples of *Procion Yellow H-E4R* (C.I. Reactive Yellow 84; **1**), *Procion Red H-E7B* (C.I. Reactive Red 141; no structure disclosed in the Colour Index [13]) and *Procion Navy H-ER 150%* (C.I. Reactive Blue 171, **2**) (DyStar), described previously [1], were used. A commercial sample the anionic wash-off agent, *Sandopur RSK Liq*, was generously provided by Clariant.

Owing to commercial confidentiality, details of the polyamide bead material used cannot be disclosed.

2.2. Dyeing

2% and 5% omf dyeings were carried out in sealed, 300 cm^3 capacity, stainless steel dyepots housed in a Roaches *Pyrotec S* dyeing machine using the method shown in Fig. 1 as described earlier [1].

2.3. Wash-off

At the end of dyeing, the samples were removed from the dyebath, squeezed to remove surplus dye liquor and then subjected to the wash-off processes described below. At the end of each of the three different wash-off processes, the washed-off dyeings were allowed to dry in the open air.

2.3.1. Standard wash-off

This was the dye maker's recommended method (Fig. 2) which employed the proprietary wash-off agent, *Sera Sperse C-SN* (DyStar); a 10:1 L:R was used [1]. In Fig. 2, the 98 °C rinse stage shown

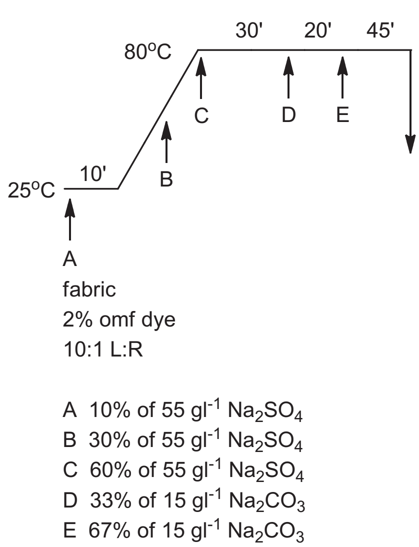

Fig. 1. Dyeing method for *Procion HE* dyes.

after that in which the wash-off agent had been employed, was used only in the case of the 5% omf dyeings.

2.3.2. Bead wash-off

2.3.2.1. Water based. Dyeings were treated, using the method shown in Fig. 3, in a sealed polypropylene container using sufficient beads to provide a 1:15 dyed fabric:bead ratio and sufficient tap water to provide a 2:1 water:dyed fabric ratio. The rinsed, treated dyeings were allowed to dry in the open air.

2.3.2.2. Wash-off agent based. Dyeings were treated, using the method shown in Fig. 4, in a sealed polypropylene container using sufficient beads to provide a 1:15 dyed fabric:bead ratio and sufficient aq 2 g l^{-1} *Sandopur RSK Liq* solution to provide a 2:1 liquor ratio. The rinsed, treated dyeings were allowed to dry in the open air.

2.4. Colour measurement

The equipment and procedures recounted previously [1] were employed.

2.5. Photography

Photographs of glass sample bottles containing wash-off liquors and beads were recorded using a Nikon *Coolpix 995* digital camera.

2.6. Wash fastness

The modified ISO 105:C06/C2 method described earlier [1] was used, dyeings being subjected to five, consecutive wash tests at 60 °C and, at the end of each wash test, the washed sample was rinsed thoroughly in tap water (but was not dried) and a fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests. The change in shade that the dyed sample underwent was determined at the end of the repeated washing process.

3. Results and discussion

3.1. Background

The conventional, multi-stage, immersion wash-off process for removing unfixed/hydrolysed reactive dye from cotton and other cellulosic fibres, as used herein (Fig. 2), entails submersing the dyed substrate in a series of agitated, heated water baths, at least one of which normally contains a surfactant, so as to abstract, solubilise and remove dye from the dyeing. In this context, as previously suggested in the case of generic dye wash-off processes [12], reactive dye wash-off can be considered as being analogous to domestic laundering insofar as, both reactive dye wash-off and domestic laundering are multi-stage processes which rely upon the combination of mechanical action, time and temperature to expedite dye removal/laundering and, in both processes, auxiliaries are employed, namely wash-off agents (surfactants) in the case of reduction clearing and detergent, alkali, etc. [14] in the case of domestic laundering. As such, it is proposed [12] that the 'Sinner's Circle' [15] (Fig. 5a) which is commonly used to represent the four main factors that determine domestic laundering performance, namely *mechanical action*, *time*, *temperature* and *detergency*, can be modified so as to apply to dye wash-off, such that, the four main factors involved are *mechanical action*, *time*, *temperature* and *auxiliary* (eg reducing agent, detergent, alkali, etc.) (Fig. 5b). In the context of conventional, multi-stage reactive dye wash-off, as exemplified by the process depicted in Fig. 2, water can be considered to be the most important of the five main factors shown, not simply because water is used in each of the

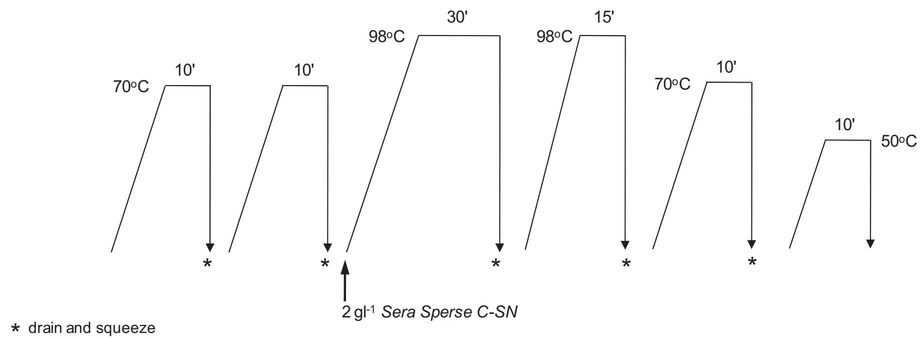

Fig. 2. Conventional wash-off method.

six wash-off stages but, rather, because it is by means of water as a vehicle, that the other contributory factors in wash-off, namely *mechanical action*, *time*, *temperature* and *detergency*, are conveyed. As such, Fig. 5c perhaps reflects the vitally important and all-encompassing role of water in conventional, multi-stage, wash-off processes; of course, the relative contributions of the five factors shown in Fig. 5c (ie *mechanical action*, *time*, *temperature*, *auxiliary* and *water*) will vary, according to dye type, fibre type, liquor ratio, substrate, depth of shade, etc.

Water undertakes manifold activities in traditional, reactive dye wash-off, such as fibre wetting, fibre swelling, dissolution medium, heating medium, rinse medium for removed, vagrant dye, etc. As previously recounted [12], no single medium was identified [16] that could perform all of the many and varied functions undertaken by water in immersion dye wash-off processes; indeed, it was found that a minimum amount of water was necessary to saturate the substrate and enable the crucially important and highly complex processes of fibre wetting and swelling to occur. The term 'interstitial water' was used to describe this minimum amount of water [12], and, in doing so, distinguish fibre wetting and fibre swelling from those processes, such as heating, provision of mechanical action, etc. which are undertaken by 'bulk water' which comprises the vast majority of the water employed in a traditional wash-off stage. As these two 'types' of water are likely to be in a state of constant interchange, there is in essence, little, if any, difference between water that resides within the interstices of the fibrous substrate (ie 'interstitial water') and that which surrounds the water-swollen fibre (ie 'bulk water') and, therefore, each type of water can be assumed to be able to provide the various roles that water undertakes in a wash-off stage (heating, swelling, rinsing, etc.) [12]. Experimental findings [16] revealed that polyamide beads could be used as a replacement of some or all of the 'bulk water' employed in conventional wash-off, this being based upon the nylon fibre's well-known, remarkable susceptibility to 'grey' (ie absorb vagrant dyes) during repeated domestic laundering, as reflected in the substrate's unique substantivity [12,17] towards all dye classes even under aq alkaline conditions and which accrues from the presence of polar groups ($-NH_2$; $-COOH$; $-CONH$; $-COCH_3$) in the polymer, as well as a 'wet' glass transition temperature below the temperatures (30, 40, 60, 95 °C) likely to be encountered in domestic laundering and an ability to both absorb water and swell [12]. The decision to use polyamide in bead form was based on considerations of cost, availability, reproducibility, high surface area and, most importantly, the provision of an appropriate level of physical interaction with a dyed substrate [12]. Hence, in this work, the novel, bead wash-off process comprised three main components namely the reactive dyed cotton, the polyamide beads and a small amount of water that was necessary to swell the dyeings and facilitate both dye removal and its transfer to the beads.

As discussed previously [1], no attempt was made to relate the results obtained to dye structure owing to the paucity of published contemporary reactive dye structures. As such, the three dyes used were chosen, arbitrarily, as being representative examples of contemporary, bifunctional, monochlorotriazinyl reactive dyes. Two depths of shade were used namely, 2% and 5% omf, as these provided typical medium/deep depth dyeings. The results displayed in Tables 1 and 2 for the dyeings prior to wash-off as well as after wash-off using the standard wash-off method were reported in a previous study [1] which used the three bis(aminochlorotriazine) reactive dyes employed herein.

3.2. No wash-off

As reported earlier [1], the fastness, of each of the three dyes used, to repeated wash testing at 60 °C, of the 2% omf dyeings

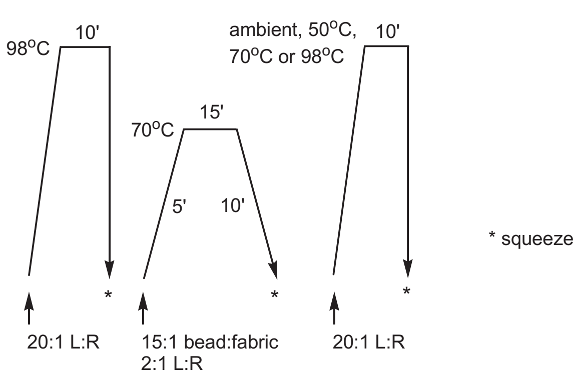

Fig. 3. Water based bead wash-off method.

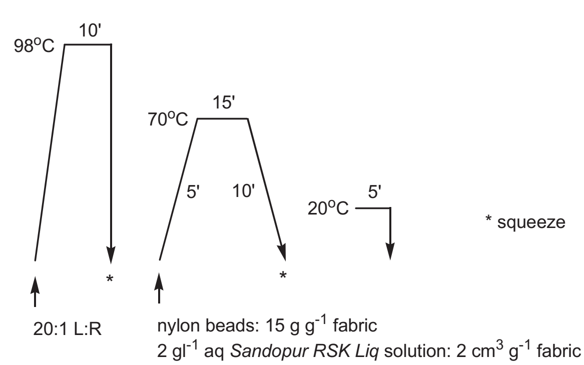

Fig. 4. Wash-off agent based bead wash-off method.

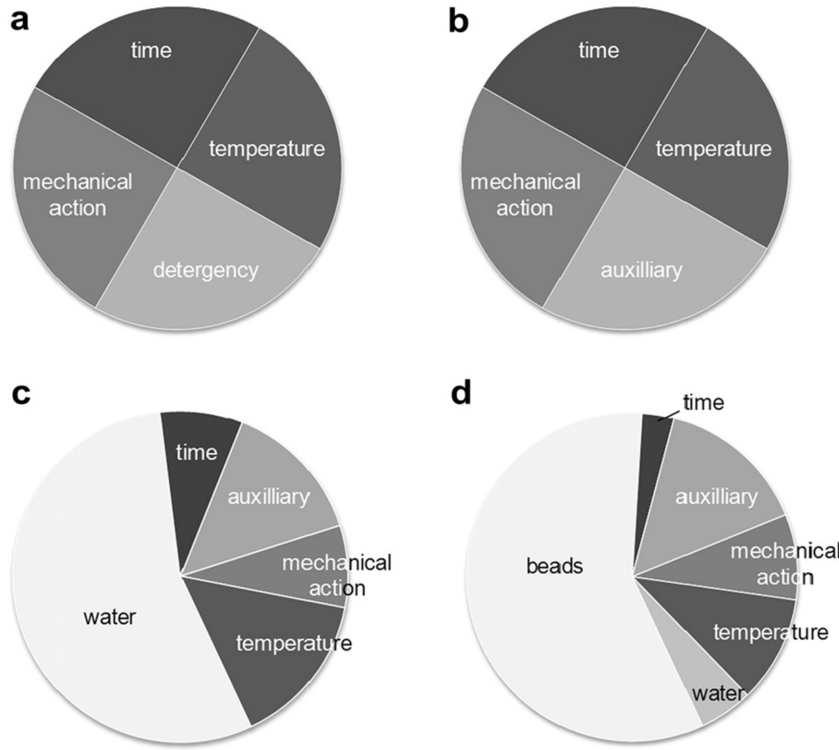

Fig. 5. Variations in the Sinner's Circle.

which had received no wash-off was poor, in terms of both the extent of staining of the adjacent cotton component of the multifibre strip material (Table 1) and the change in shade of the dyeings (Table 2). These findings are due to unfixed dye having been removed from the dyed fabrics during repeated wash testing and transferred to the adjacent cotton component of the multifibre strip material. The extent of this dye removal is reflected in both the corresponding colour strength (K/S values) (Fig. 6) and lightness (L*) values (Table 2), obtained before and after wash testing for the dyeings which had been subjected to five repeated washes. Whilst repeated washing increased the chroma of each of the dyeings, as shown by the respective changes in the a* and b* values as well as increased C* values for the dyeings (Table 2), the very small changes in hue angle (ho) coupled with the unchanged λ_{max} values for the dyeings (Table 2) after five wash fastness tests reveal that repeated washing had no effect upon the hue of the dyeings.

3.3. Standard wash-off

Washing-off the 2% omf dyeings using the dye maker's recommended, five-stage method (Fig. 2) resulted in improved fastness to repeated wash testing, compared to dyeings which had received no wash-off (Tables 1 and 2), insofar as, the degree to which the shade of the dyeings was changed as a result of repeated washing was reduced (Table 2) and the extent of staining of the adjacent cotton fabric (Table 1) was markedly reduced compared to the dyeings which had not been washed-off. The colorimetric data (Table 2) show that, for each of the three dyes used, the standard wash-off method removed unfixed dye from the dyeings, as evidenced by the higher L* values of the standard washed-off samples compared to those of their non-washed off counterparts, as well as the respective colour strength values depicted in Fig. 6. The colorimetric data in Table 2 also show that there was little difference between the colour of the unwashed-off dyeings and those which had been subjected to the standard wash-off, this being reflected in the observation (Table 2) that the λ_{max} values of the two sets of dyeings were unchanged after five wash fastness tests.

3.4. Bead wash-off

3.4.1. Water-based process

Previous studies revealed that the duration of five-stage wash-off processes recommended by the makers of bis(aminochlorotriazine) dyes [1] as well as bis(vinyl sulfone), aminochlorotriazine/vinyl sulfone and bis(aminochlorotriazine/vinyl sulfone) dyes [2] for cotton could be reduced markedly by using a wash-off process that employed three separate treatments with water at 98 °C. This particular three-stage, chemical-free, wash-off process also reduced considerably, both the amounts of water and chemicals used in the recommended wash-off methods, thereby enabling reductions to be achieved in both the COD and BOD_5 environmental indicators [1,2]. The observation [1] that the first 98 °C water rinse stage of the three-stage, chemical-free, wash-off method had been especially effective in removing reactive dye was the reason behind the decision to employ a 98 °C water rinse as the first stage of the new, three-stage, water-based, bead wash-off method employed herein (Fig. 3). A temperature of 70 °C was used in the subsequent bead wash-off stage since this had previously [12] been found to provide adequate levels of both dye removal and adsorption during the relatively short contact time with the polyamide beads (15 min). As a final water rinse stage was deemed necessary to remove all vagrant dye from the dyeing, four temperatures were investigated, namely 21 °C (ambient), 50 °C, 70 °C and 98 °C (Fig. 3). The four different bead wash-off methods are differentiated hereafter as:

- 98 °C/bead/21 °C;
- 98 °C/bead/50 °C;
- 98 °C/bead/70 °C and;
- 98 °C/bead/98 °C.

Table 1
Staining of adjacent materials obtained for 2% omf dyeings.

Dye	Number of washes	Wool						Acrylic						Polyester						Nylon 6,6						Cotton						2° acetate					
		a	b	c	d	e	f	a	b	c	d	e	f	a	b	c	d	e	f	a	b	c	d	e	f	a	b	c	d	e	f	a	b	c	d	e	f
Yellow 84	1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	4/5	5	5	1	4/5	4	4	4	4/5	4	4/5	4/5	4/5	4/5	5
	2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	4/5	2	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5
	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3	5	5	5	5	5	5	5	5	5	5	5
	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3/4	5	5	5	5	5	5	5	5	5	5	5
	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5	5	5	5	5	5	5
Red 141	1	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5	5	5	5	5	4/5	5	5	5	5	5	5	5	1	4/5	4	3/4	4	4	3/4	5	4/5	4/5	4/5	4/5
	2	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	2	4/5	4/5	4/5	4/5	4/5	4	5	5	5	4/5	5
	3	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	3	5	4/5	4/5	4/5	4/5	4/5	5	5	5	4/5	5
	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3/4	5	4/5	4/5	4/5	4/5	4/5	5	5	5	5	5
	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5	5	5	5	5	5	5
Navy 171	1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4	4/5	5	5	5	5	5	5	1	4/5	3	3/4	3/4	4/5	5	4/5	4/5	4/5	4/5	5
	2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4	5	5	5	5	5	5	5	2	5	3/4	4	4	5	5	5	5	5	5	5
	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5	5	3/4	5	4	4	4/5	5	5	5	5	5	5	5
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	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	4/5	4/5	5	5	5	5	5	5	5

a = no wash-off; b = standard wash-off; c = 98 °C/bead/21 °C; d = 98 °C/bead/50 °C; e = 98 °C/bead/70 °C; f = 98 °C/bead/98 °C.

The colorimetric data in Table 2 show that each of the four bead wash-off processes generally reduced the depth of shade of the 2% omf dyeings, compared to that of the unwashed-off dyeings, prior to repeated washing, as reflected by the higher L* values of the washed-off samples. Hence, each wash-off process removed unfixed/hydrolysed dye, this also being shown by the corresponding colour strength values (Fig. 6) of the dyeings before wash fastness testing; it is apparent that the four bead wash-off methods varied slightly in their ability to remove surplus dye.

Tables 1 and 2 show the levels of staining and shade change obtained, respectively, for 2% omf dyeings which had been subjected to repeated wash testing at 60 °C, for each of the four, nylon bead wash-off methods used. In the context of the extent of staining of adjacent cotton material, it is apparent that whilst similar levels of fastness were recorded for each of the four temperatures employed in the final water rinse stage (ie 21 °C, 50 °C, 70 °C and 98 °C), a final rinse in water at 98 °C imparted slightly lower staining. Indeed, the extent of staining obtained using the 98°C/bead/98 °C process was similar to that achieved using the standard, five-stage wash-off process. The shade change ratings achieved for the four bead wash-off methods were very similar to those obtained for the standard wash-off process (Table 2). The K/S values shown in Fig. 6 reveal that, for each of the three dyes used, the depth of shade of the dyeings after wash testing, was not too dissimilar to that achieved for the dyeings which had been washed-off using the standard wash-off process. The corresponding colourimetric data in Table 2 reveals that there was very little difference between the colour of the dyeings which had been subjected to each of the four bead wash-off processes and the standard process; this is confirmed by the finding (Table 2) that the λ_{max} values for all sets of dyeings were mostly unchanged after five wash fastness tests.

The results so far obtained indicate that each of the four bead wash-off processes was effective in removing surplus dye from the 2% omf dyeings and imparted levels of fastness that were comparable to those secured using the five-stage, standard wash-off process. As the 98 °C/bead/98 °C wash-off method had produced levels of staining that were very similar to those secured using the standard wash-off method (Table 1), it was decided to determine the effectiveness of the 98 °C/bead/98 °C wash-off in the case of 5% omf dyeings.

Table 3 shows that washing-off the 5% omf dyeings using the dye maker's recommended, six-stage method (Fig. 2) resulted in improved fastness to repeated wash testing, compared to the corresponding dyeings which had not been washed-off. The degree to which the shade of the dyeings was changed as a result of repeated washing was reduced and the extent of staining of the adjacent cotton fabric was markedly reduced compared to the dyeings which had not been washed-off. It is also apparent from Table 3 that the 98 °C/bead/98 °C method imparted levels of staining and shade change that were comparable to those secured using the standard, six-stage, wash-off process. Hence, the results obtained clearly show that the 98 °C/bead/98 °C wash-off process was effective not only in removing surplus dye from the 5% omf dyeings, but also imparted levels of fastness that were comparable to those secured using the six-stage, standard wash-off process.

As mentioned, because reactive dyes on cellulosic fibres require a stringent wash-off to remove hydrolysed dye, together with any non-reacted dye and auxiliaries at the end of dyeing so as to attain the desired level of fastness and correct shade, very high volumes of water are routinely consumed during wash-off. From an effluent viewpoint, the commercial wash-off agents that are commonly used to aid reactive dye wash-off contribute to effluent load; indeed, reactive dyeing wash-off processes and the concomitant treatment of the ensuing effluent can account for ~50% of the total dyeing cost [2]. In this context, as the three-stage, 98 °C/bead/98 °C

Table 2
Colourimetric data for 2% omf dyeings.

Dye	Wash-off method	Number of washes	Change in shade	L*	a*	b*	C*	ho	λ_{max}/nm
Yellow 84	None	0	–	64.5	33.6	73.3	80.6	65.3	440
		5	3/4	69.6	30.4	76.8	82.6	68.4	440
	Standard	0	–	69.9	29.5	77.1	82.6	67.6	440
		5	4	70.5	31.3	74.7	83.5	69.0	440
	98 °C/bead/21 °C	0	–	69.4	33.8	80.6	87.4	67.3	440
		5	4	70.3	32.6	78.5	85.0	67.5	440
	98 °C/bead/50 °C	0	–	69.1	33.3	79.8	86.5	67.4	440
		5	4	69.0	31.4	77.4	83.6	67.9	440
	98 °C/bead/70 °C	0	–	68.8	32.5	79.5	85.8	67.8	440
		5	4	68.7	30.8	76.8	82.7	68.1	440
	98 °C/bead/98 °C	0	–	70.7	29.2	75.7	81.1	68.9	420
		5	4	71.4	29.9	76.8	82.4	68.7	440
Red 141	None	0	–	36.6	54.6	–0.2	54.6	359.7	540
		5	3	40.8	59.6	2.57	59.6	2.5	540
	Standard	0	–	39.9	59.4	1.2	58.4	1.2	540
		5	4	41.0	58.7	1.1	57.4	1.1	540
	98 °C/bead/21 °C	0	–	39.9	58.4	1.2	58.5	1.2	540
		5	4	40.8	59.4	2.1	59.4	2.0	540
	98 °C/bead/50 °C	0	–	41.2	60.1	2.1	60.1	2.1	520
		5	4	41.7	57.7	5.2	57.9	5.1	540
	98 °C/bead/70 °C	0	–	40.6	60.0	1.97	60.0	1.9	540
		5	4	41.1	60.4	2.7	60.5	2.5	540
	98 °C/bead/98 °C	0	–	40.6	59.6	1.5	59.7	1.4	540
		5	4	41.8	59.4	1.3	59.4	1.3	540
Navy 171	None	0	–	26.9	–2.2	–18.7	18.8	263.3	620
		5	3/4	27.7	–2.3	–18.6	18.7	262.9	620
	Standard	0	–	29.0	–2.9	–19.1	19.3	261.1	620
		5	4	28.5	–2.6	–17.7	17.9	261.3	620
	98 °C/bead/21 °C	0	–	27.7	–2.6	–18.9	19.0	262.2	620
		5	4	28.2	–2.5	–18.6	18.8	262.1	620
	98 °C/bead/50 °C	0	–	27.2	–2.1	–19.2	19.3	263.8	620
		5	4	28.1	–2.5	–18.7	18.9	262.5	620
	98 °C/bead/70 °C	0	–	27.9	–2.7	–19.1	19.3	262.0	620
		5	4	28.7	–2.6	–18.6	18.8	261.9	620
	98 °C/bead/98 °C	0	–	27.3	–2.3	–18.4	18.5	262.9	620
		5	4	28.1	–2.6	–18.8	19.0	262.2	620

wash-off process for the 5% omf dyeings used only half of the number of rinse stages of the standard, six-stage wash-off process, the bead wash-off therefore offers potential savings in time; since less water and no detergent was used in the 98 °C/bead/98 °C wash-off then the three-stage bead wash-off reduces considerably, both the amounts of water and chemicals compared to the standard wash-off method, thereby offering potential environmental advantages (eg reductions in COD, BOD_5 and other environmental indicators). An indication of the nature and magnitude of the benefits that could accrue from the use of the 98 °C/bead/98 °C wash-off compared to the recommended wash-off process is provided by comparing the photographs shown in Fig. 7 with those in Fig. 8. Fig. 7 shows the residual wash-off liquors obtained for 5% omf dyeings obtained in the case of the six-stage, standard

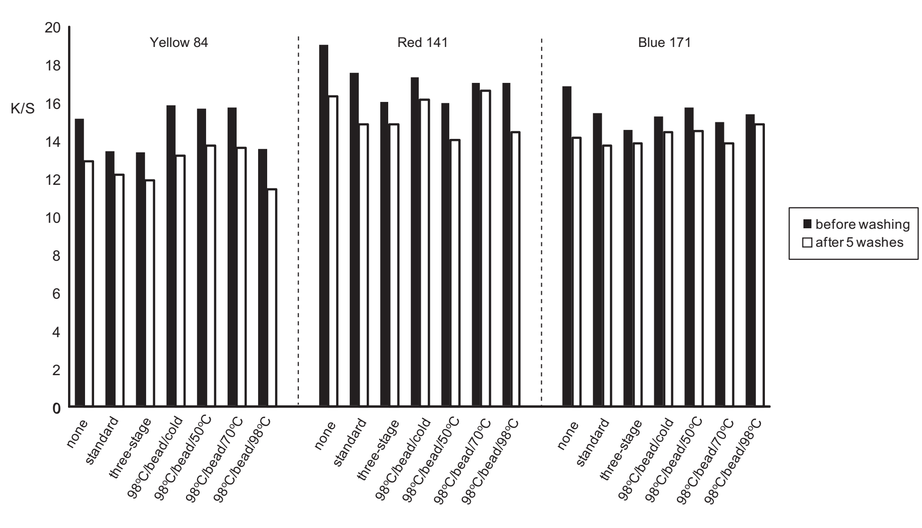


Fig. 6. Colour strength before and after repeated washing.

Table 3
Staining and shade change obtained for 5% omf dyeings.

Dye	Number of washes	Shade change				Wool				Acrylic				Polyester				Nylon 6,6				Cotton				2° acetate			
		a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d
Yellow 84	1	–	–	–	–	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	1/2	4/5	4/5	4	4	4/5	4/5	4/5
	2	–	–	–	–	4/5	4/5	5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	2	4/5	4/5	4/5	5	5	5	5
	3	–	–	–	–	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3	4/5	4/5	4/5	5	5	5	5
	4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3/4	5	5	5	5	5	5	5
	5	3/4	4	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5	5	5
Red 141	1	–	–	–	–	4/5	4/5	4/5	4/5	3/4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	5	1	4	4/5	4	3/4	4/5	4/5	4/5
	2	–	–	–	–	4/5	4/5	4/5	5	4	4/5	4/5	4/5	5	5	5	5	4/5	4/5	4/5	5	2	4	4/5	4/5	4	5	5	5
	3	–	–	–	–	5	4/5	5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	2/3	4/5	4/5	4/5	4/5	5	5	5
	4	–	–	–	–	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	3	4/5	5	4/5	4/5	5	5	5
	5	2/3	3/4	3/4	4	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	3/4	4/5	5	4/5	5	5	5	5
Navy 171	1	–	–	–	–	4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	4/5	4/5	1	3	4/5	4	5	4	4/5	4/5
	2	–	–	–	–	5	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	5	2	3/4	4/5	4/5	5	4/5	4/5	5
	3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	2/3	4	4/5	4/5	5	5	5	5
	4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3/4	4/5	5	4/5	5	5	5	5
	5	3/4	3/4	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	5	5	5	5

a = before wash-off; b = standard wash-off; c = 98 °C/bead/98 °C; d = 98 °C/bead + *Sandopur*/cold.

wash-off process whilst Fig. 8 shows the corresponding residual liquors secured for the three-stage, 98 °C/bead/98 °C wash-off process. It is evident that for both wash-off methods, the initial 98 °C water rinse removed by far the greatest amount of dye; indeed, it is well known that the first rinse stage in a conventional wash-off process for reactive dyes removes not only unfixed/hydrolysed dye but also reduces the often very high electrolyte concentration within the substrate. Often, much more dye is removed during the first stage of wash-off than during any of the other rinse stages, this being attributable to the greater driving force for dye desorption, namely the dye concentration gradient between the dyed fibre and the rinse medium (water in this case). In the case of the 5% omf dyeings which had been subjected to the six-stage, recommended wash-off process (Fig. 7) dye removal continued during the second rinse stage, but lower amounts of dye were abstracted, presumably because of a lower driving force for dye desorption; during this stage of the conventional wash-off process, the electrolyte level in the substrate can be expected to have been further lowered, this being essential for the expeditious removal of unfixed reactive dye during subsequent wash-off stages. Whilst treatment at high temperature in the presence of the wash-off agent (*Sera Sperse CS-N*) during the third wash-off stage removed further sizeable amounts of dye (Fig. 7), the three subsequent water rinses removed lower quantities of dye, culminating in an almost colourless residual dye liquor in the case of the final, sixth, wash-bath (Fig. 7). Interestingly, in the case of the 98 °C/bead/98 °C wash-off process (Fig. 8), the colour of the final rinse stage was similar to that achieved for the fourth rinse stage of the

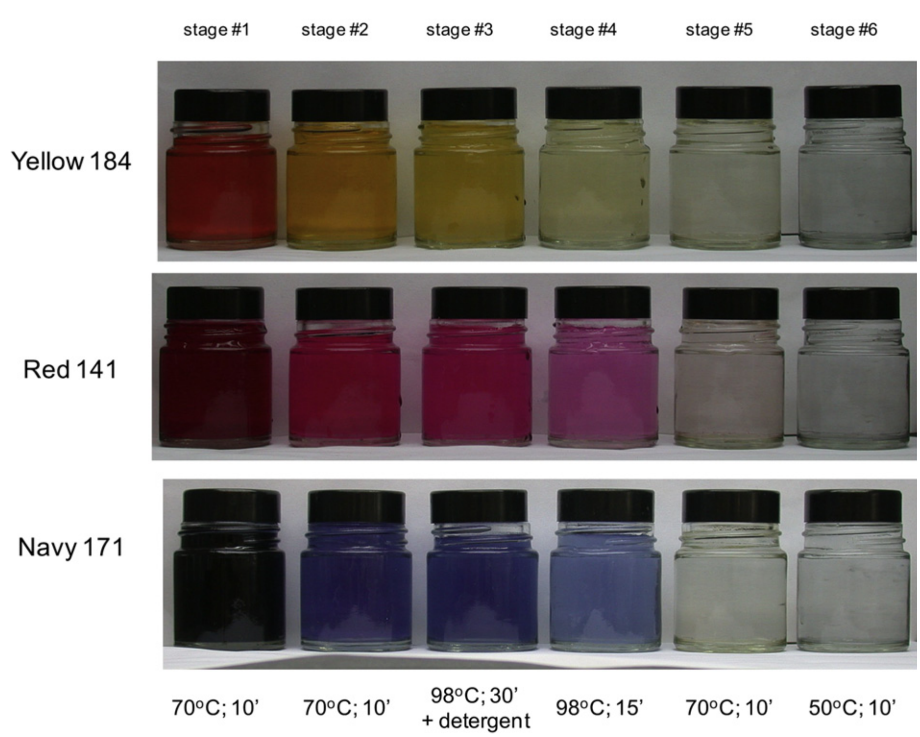


Fig. 7. Residual wash-off liquors obtained for 5% omf dyeings washed-off using the standard wash-off process.

Fig. 8. Residual wash-off liquors obtained for 5% omf dyeings washed-off using 98 °C/bead/98 °C process.

standard method (Fig. 7), indicating that the amount of dye removed by and adsorbed by the polyamide beads (stage #2 in Fig. 8) corresponds to that removed by the second and third stages of the standard wash-off process (Fig. 7). Fig. 8 reveals that not all vagrant dye had been removed by the 98 °C/bead/98 °C wash-off process insofar as the residual wash-off liquor obtained for the final (#3) rinse stage was slightly coloured whereas the liquor obtained for the final (#6) stage of the standard wash-off process (Fig. 7) was virtually colourless. This finding is of interest, as the staining and shade change results obtained for the 5% omf dyeings (Table 3) show that there was no difference in fastness observed for the dyeings which had been washed-off using the two wash-off methods, which implies that the amounts of vagrant dye which remained in the cotton at the end of the 98 °C/bead/98 °C process had no effect on the level of fastness achieved after five washes. This raises the question as to whether it is necessary to remove virtually all traces of vagrant dye from the reactive dyeings by means of wash-off, as achieved using the recommended, standard, six-stage process (Fig. 7) or, instead, whether it is acceptable to remove only a large proportion of such vagrant dye, as achieved in the case of the 98 °C/bead/98 °C wash-off process (Fig. 8). To this end, a modified bead wash-off process was devised, as discussed below.

3.4.2. *Wash-off agent process*

As conventional reactive dye wash-off processes commonly use surfactant-based proprietary wash-off agents to expedite dye removal, it was decided to modify the water-based, 98 °C/bead/98 °C wash-off process (Fig. 3) thus far recounted by the inclusion of the anionic wash-off agent, *Sandopur RSK Liq.* in the bead stage (#2) of wash-off (Fig. 4); accordingly, the final, 98 °C water rinse used in the 98 °C/bead/98 °C wash-off process was replaced with a cold water rinse, after promising preliminary results had been obtained.

Table 3 shows that when 5% omf dyeings were washed-off using the 98 °C/bead + *Sandopur*/cold rinse process depicted in Fig. 4, the levels of staining obtained for the first two or so wash tests were greater than those recorded for the 98 °C/bead/98 °C wash-off process, whereas at the end of five repeated wash tests at 60 °C, the levels of staining obtained were the same as those achieved using the 98 °C/bead/98 °C method. This finding implies that the use of the bead + *Sandopur*/cold rinse stages of the 98 °C/bead + *Sandopur*/cold rinse wash-off were less effective in removing vagrant dye from the dyeings during wash-off than were the bead/98 °C stages of the 98 °C/bead/98 °C wash-off process. This is confirmed by the finding (Table 3) that the *Sandopur* based bead wash-off process imparted lower shade changes to the dyeings. The observation (Table 3) that identical levels of staining were achieved after five repeated washes using both the 98 °C/bead/98 °C process and the 98 °C/bead + *Sandopur*/cold rinse process can be attributed to vagrant dye having been removed from the dyeings during wash testing. The results in Table 3 reveal that for each of the three dyes used, the 98 °C/bead + *Sandopur*/cold rinse process imparted similar levels of wash fastness as the standard, six-stage wash-off process.

The colour of the corresponding residual wash-off liquors and beads obtained for the 98 °C/bead + *Sandopur*/cold rinse process are shown in Fig. 9. When these are compared to those obtained using the water-based, 98 °C/bead/98 °C method (Fig. 8), it is

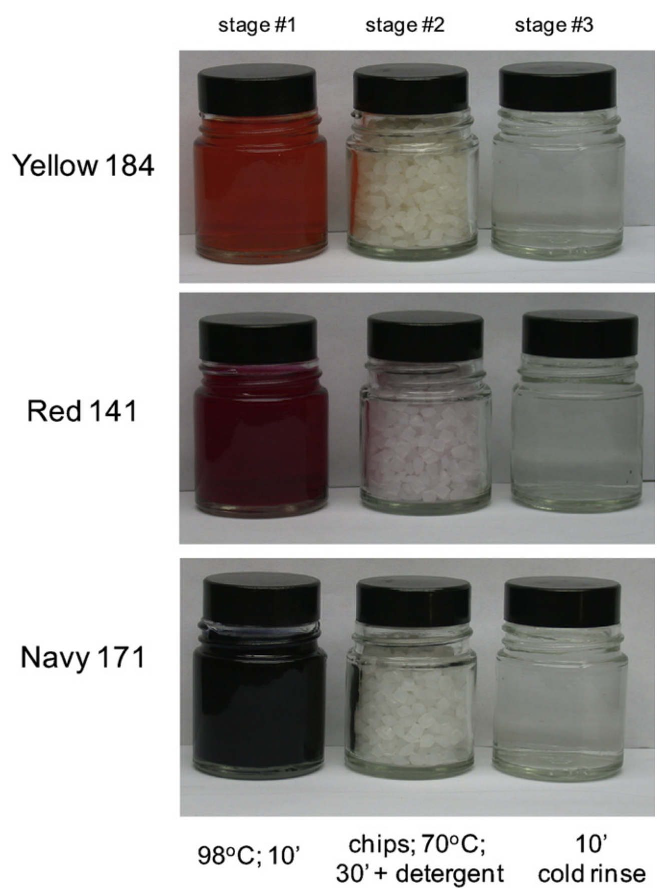


Fig. 9. Residual wash-off liquors obtained for 5% omf dyeings washed-off using 98 °C/bead + *Sandopur*/cold rinse process.

apparent that whilst similar levels of dye removal were achieved after the first (98 °C) water rinse stage, the liquors obtained from the final cold rinse stage (Fig. 9) were colourless compared to the coloured liquors of the final 98 °C water rinse stage in the case of the 98 °C/bead/98 °C wash-off process (Fig. 8). In addition, the beads were less coloured in the case of the 98 °C/bead + *Sandopur*/cold rinse process (cf Figs. 8 and 9) owing to the lower extent of dye removal achieved, as evidenced by the lower shade change ratings for the 98 °C/bead + *Sandopur*/cold rinse process (Table 3) (Fig. 9).

Hence, the results obtained show that the 98 °C/bead + *Sandopur*/cold rinse process imparted levels of wash fastness that were comparable to those secured using both the 98 °C/bead/98 °C bead method and the six-stage, standard wash-off process, even though the surfactant-based bead wash-off process was less effective in removing vagrant dye from the 5% omf dyeings. Thus, in the context of the question raised earlier, as to whether it is necessary to remove virtually all traces of vagrant dye from the reactive dyeings by means of wash-off, as achieved using the recommended, standard, six-stage process (Fig. 7) or, instead, whether it is acceptable to remove only a large proportion of such vagrant dye, as achieved in the case of the 98 °C/bead/98 °C wash-off process (Fig. 8), it seems clear, in view of the findings obtained for the 98 °C/bead + *Sandopur*/cold rinse process that, in terms of repeated wash fastness, it is not necessary to remove all traces of vagrant dye during reactive dye wash-off. This particular conclusion, which is based on the results presented herein, indicate that the single wash test methodology that is currently adopted in wash testing (eg ISO CO5) does not provide a satisfactorily realistic representation of repeated washing, as undertaken during domestic laundering and, therefore, that some repeated wash testing methodology should be adopted.

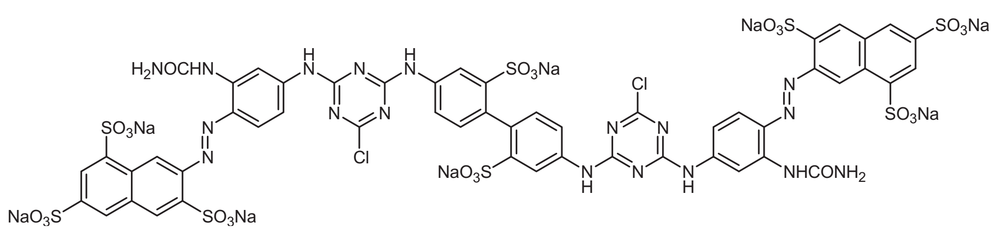
3.5. Energy and water usage considerations

From an energy viewpoint, as the two, bead wash-off processes used here each comprise three stages compared to either the five (in the case of 2% omf dyeings) or six (for 5% omf dyeings) stages of the recommended, standard wash-off processes, it follows that the bead wash-off methods should offer potential energy savings. To get a very approximate idea of the magnitude of the amount of energy used in the different wash-off processes, Eq (1) was employed to calculate the amount of heat required (Q; kJ) to raise the temperature of m kg of water from 21 °C (T_1) to the final temperature (T_2; 50, 70 or 98 °C) of the particular stage of the wash-off, where c_w is the specific heat capacity of water at 21 °C (4.18 kJ kg^{-1} K^{-1}) and Eq (2) was used to calculate the heat involved in raising the temperature of n kg of nylon beads from 21 °C (T_1) to T_2 (50, 70 or 98 °C), where c_n is the specific heat capacity of nylon 6 at 20 °C (1.67 kJ kg^{-1} K^{-1} [18]):

$$Q = m \cdot c_w (T_2 - T_1) \quad (1)$$

$$Q = n \cdot c_n (T_2 - T_1) \quad (2)$$

In using Eqs 1 and 2, no attempts were made to take into account the effects of the various chemicals, substrate, etc upon specific heat capacity, nor the amount of heat required to maintain



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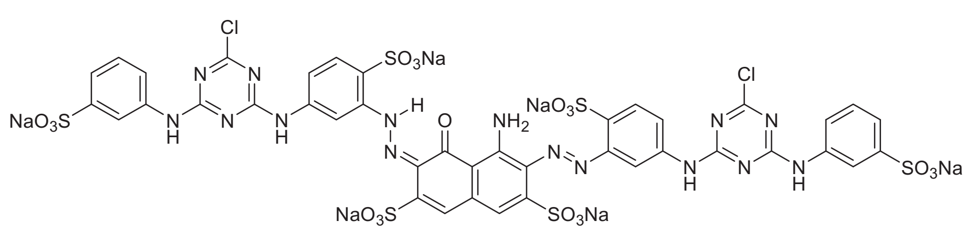

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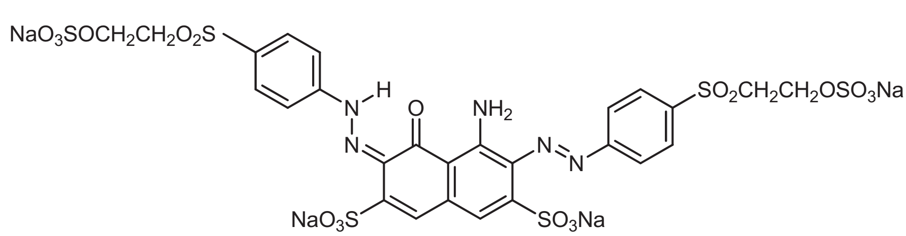

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the heated wash-off liquor and beads at the final temperature. As Table 4 shows, in the case of the 2% omf dyeings, a large amount of energy (1058 kJ) would in total be consumed in heating the water that would be used in the five stages of the standard wash-off process, since each stage involved the use of a 10:1 liquor ratio. However, less heat energy (808 kJ) would in total be consumed in washing-off the 2% omf dyeings using the 98 °C/bead/98 °C wash-off process not only because three, rather than five stages were involved but, more importantly, because the bead stage used only a 2:1 water:fibre ratio rather than a 10:1 liquor ratio and, therefore, a smaller mass of water required heating. Nevertheless, although less water was used in the bead stage, the beads themselves required heating and, as Table 4 shows, a 15:1 bead:fibre ratio was employed in the bead stage of the 98 °C/bead/98 °C process. This 15:1 bead:fibre ratio is clearly greater than the 10:1 water:fibre ratio used in the standard wash-off stages; indeed, according to the assumptions upon which the calculations were made (ie a 100 g fibre sample), then the respective masses of water and beads which require heating are 1 kg of water, in the case of a 10:1 water:fibre ratio and 1.5 kg beads in the case of a 15:1 bead:fibre ratio. However, because nylon has a much lower specific heat capacity than water (1.67 kJ kg^{-1} K^{-1} compared to 4.18 kJ kg^{-1} K^{-1}) then much less energy is needed to heat the larger mass (1.5 kg) of nylon beads than the 1 kg of water, which explains why, for the bead stage of wash-off, heating 1.5 kg of beads from 21 to 70 °C requires some 123 kJ whereas to raise only 1.0 kg of water over the same temperature range requires 205 kJ (Table 4).

In the case of the 5% omf dyeings, Table 4 reveals that whilst the total heat energy consumption for the six-stage standard wash-off process was, not surprisingly, the highest of the four wash-off methods studied (1380 kJ), that of the 98 °C/bead + *Sandopur*/cold rinse process was by far the lowest (486 kJ), owing not only to the use of both the 2:1 water:fibre ratio and 15:1 bead:fibre ratio for the bead stage but, most significantly, because of the zero heat energy input required for the final room temperature rinse stage.

From the perspective of water usage, if 1 kg of cotton which had been dyed using 2% omf dye were washed-off using the standard wash-off method (Fig. 2), the five wash-off stages required would necessitate the use of 50 kg of water (employing a 10:1 L:R) whilst the six-stage wash-off process required for the 5% omf dyeing would consume 60 kg of water (Fig. 2). In contrast, Figs. 3 and 4 reveal that only 22 kg of water would be consumed using each of the two bead wash-off processes, regardless of the depth of shade applied. A measure of the practical savings in water that could accrue from using bead wash-off can be gained when it is considered that in 2000 [19], 4 $\times$ 10^9 kg of cotton was dyed using 8 $\times$ 10^7 kg of reactive dye by immersion (exhaust) methods, which, during wash-off, would consume 200 $\times$ 10^9 kg or 240 $\times$ 10^9 kg of water, if either a five-stage or a six-stage wash-off process, respectively, were used compared to 88 $\times$ 10^9 kg of water if either of the two bead wash-off processes were used, resulting in a water saving of ~55–60%.

3.6. Bead re-use

As mentioned, Figs. 8 and 9 show that in the case of the 5% omf dyeings, sizeable amounts of vagrant dye that were removed during both the 98 °C/bead/98 °C and the 98 °C/bead + *Sandopur*/cold rinse processes had been adsorbed by the beads. As such, the 98 °C/bead/98 °C wash-off process generated just two coloured rinse liquors compared to the six coloured liquors that ensued from the standard wash-off process (Fig. 7) and, as the 98 °C/bead + *Sandopur*/cold rinse process resulted in a final rinse liquor that was colourless, this particular three-stage wash-off generated just one coloured rinse liquor compared to the six coloured liquors obtained from the standard wash-off process. Hence, both of the bead wash-off methods appear to offer lower effluent loads than the standard wash-off process.

Of course, the argument in favour of using the bead wash-off processes depends on what happens to the coloured beads which contain adsorbed, residual dye. It follows that if it were possible to re-use the coloured bead material in subsequent wash-off processes, this would offer potentially highly attractive cost and environmental benefits. In this context, it was found [20] that when the nylon beads were used 100 times to wash-off (at 70 °C) cotton which had been dyed using 3% omf C.I. Reactive Black 5 (**3**), the beads were able to remove dye from the 100 dyeings without any deterioration in the fastness of the dyeings to the ISO CO6/C2S (60 °C) wash test. In addition, the colour strength of the beads increased gradually with increasing use in the 100 wash-off cycles, this being attributed to the transfer of dye, which had been removed from the dyeings, to the beads during wash-off. As the vagrant dye had not penetrated to the interior of the beads after 100 wash-off processes, it was concluded that the beads could continue to absorb vagrant dye even after 100 wash-off cycles [20]. Indeed, the patented *Xeros* clothes washing system [11], which can save up to 90% of water usage compared to conventional laundry systems, employs beads that can be used up to five hundred times before being recycled [21].

In terms of the energy considerations discussed above, even assuming that the beads can be used for only 100 wash-off cycles, the amount of heat energy that could be saved by employing the bead wash-off rather than the standard wash-off, equates to 250 MJ per kg of fibre and 894 MJ per kg of fibre, in the cases of the 2% omf and 5% omf dyeings, respectively, over 100 cycles. Expressed in more commonly used units of energy measurement, these two

Table 4
Amount of heat energy required for the different wash-off processes.

Wash-off stage	2% omf dyeing						5% omf dyeing					
	Standard wash-off			98 °C/bead/98 °C			Standard wash-off			98 °C/bead + *Sandopur*/cold		
	Temp./°C	Liquor/bead ratio[a]	Q/kJ	Temp./°C	liquor/bead ratio[a]	Q/kJ	Temp./°C	Liquor/bead ratio[a]	Q/kJ	Temp./°C	Liquor/bead ratio[a]	Q/kJ
1	70	10:1	205	98	10:1	322	70	10:1	205	98	10:1	322
2	70	10:1	205	70	2:1	41	70	10:1	205	70	2:1	41
					15:1	123					15:1	123
3	98	10:1	322	98	10:1	322	98	10:1	322	21	10:1	0
4	70	10:1	205	–	–	–	98	10:1	322	–	–	–
5	50	10:1	121	–	–	–	70	10:1	205	–	–	–
6	–	–	–	–	–	–	50	10:1	121	–	–	–
			1058			808			1380			486

[a] The calculation assumed a 100 g fibre mass resulting in 1 kg of water in the case of a 10:1 L:R and 200 g water in the case of a 2:1 L:R as well as 1.5 kg beads in the case of a 15:1 bead:fibre ratio.

values correspond to savings of 69.4 kW h and 248.3 kW h, per kg of fibre washed-off, respectively.

4. Conclusions

In the case of the 2% omf dyeings of the three dyes used, each of the four, water-based, bead wash-off methods used (ie 98 °C/bead/21 °C; 50 °C; 70 °C; 98 °C), whilst similar levels of fastness were recorded for each of the four temperatures employed in the final water rinse stage (ie 21 °C, 50 °C, 70 °C and 98 °C), a final rinse in water at 98 °C imparted slightly lower levels of staining, which were similar to those achieved using the standard, five-stage wash-off. The shade change ratings achieved for the four, water-based, bead wash-off methods were very similar to those obtained for the standard process and, for each of the three dyes used, the depth of shade of the dyeings after wash testing was not too dissimilar to that achieved for the dyeings which had been washed-off using the standard process. There was very little difference between the colour of the dyeings which had been subjected to the four, water-based, bead wash-off processes and the standard process.

For the 5% omf dyeings, the 98 °C/bead/98 °C wash-off process imparted levels of staining and shade change that were comparable to those secured using the recommended, six-stage, standard wash-off process. The 98 °C/bead + *Sandopur*/cold rinse wash-off process imparted levels of wash fastness that were comparable to those secured using both the 98 °C/bead/98 °C bead method and the six-stage, standard wash-off process, even though the surfactant-based wash-off process was less effective in removing vagrant dye from the 5% omf dyeings. As the beads adsorbed a sizeable amount of vagrant dye, bead wash-off generated either one (98 °C/bead + *Sandopur*/cold rinse) or two (98 °C/bead/98 °C) coloured rinse liquors compared to the six coloured liquors that ensued from the standard wash-off process, thereby constituting a lower effluent load.

Calculations indicated that less heat energy would be consumed in washing-off both 2% and 5% omf dyeings using both bead wash-off processes than either of the two standard wash-off methods not only because three, rather than five stages were involved but, more importantly, because the bead stage used only a 2:1 water:fibre ratio rather than the 10:1 liquor ratio employed in the standard wash-off method and the much lower specific heat capacity of nylon than water meant that much less heat was required to heat the large mass of nylon beads.

The results presented show that it was possible to reduce the number of wash-off stages employed and, at the same time, replace a large proportion of the water consumed during wash-off, through the use of the nylon beads; in addition, the *Sandopur* bead wash-off method necessitated the use of only two hot treatments (70 °C and 98 °C) compared to the five or six hot treatments employed in the two standard wash-off processes. Mechanistically, the novel bead wash-off process mimics that of conventional wash-off and can be described in terms of a modified Sinner's Circle such as that depicted in Fig. 5d which, when compared to that of a conventional wash-off process (Fig. 5c) seeks to describe the reduced contributions in time, mechanical action and temperature that accrue from the lower number of wash-off stages, reduced water usage and fewer hot water stages employed in the bead wash-off process.

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