

Sustainable Chemistry Method to Improve the Wash-off Process of Reactive Dyes on Cotton

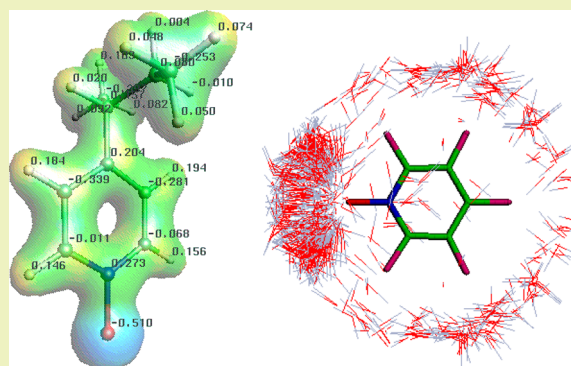
M. Nabeel Amin[†] and Richard S. Blackburn^{*,‡}

[†]School of Textile & Design, University of Management & Technology, C-II, Johar Town, Lahore 54000, Pakistan

[‡]Sustainable Materials Research Group, Centre for Technical Textiles, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, United Kingdom

ABSTRACT: Reactive dyes are extensively used for coloration of cellulosic fibers because of their excellent wash fastness (stability to washing with aqueous detergent solutions), which arises from covalent bond formation between dye and fiber. However, up to 40% of the dyestuff may hydrolyze in the dyeing process; this hydrolyzed dye has affinity for the fiber via hydrogen bonding and van der Waals interactions, but is not covalently bonded and as such exhibits poor wash fastness. Accordingly, these reactive dyeings require a multistep “wash-off” process after dyeing, involving various aqueous rinses and washings, in order for the dyeing to achieve the characteristic very high wash fastness. Wash-off and subsequent effluent treatment can account for up to 50% of the total cost of reactive dyeing and consumes significant amounts of water and energy; from a sustainable chemistry and engineering perspective, consumption of water and energy are arguably the biggest issues in textile dyeing. Existing and developmental dye transfer inhibiting (DTI) polymers were employed to remove unfixed (hydrolyzed) dyes. It was found that the use of DTI in the wash-off of reactive dyes enables a much more efficient, economical and sustainable process to be developed, which significantly reduces operation time, water consumption and energy consumption. Different DTI polymer types varied in their efficacy of dye removal; poly(vinylpyridine-*N*-oxide) polymers were the most effective with respect to the level of hydrolyzed dye removal closely followed by the poly(vinylpyridine betaine) polymers, which were also highly efficient in hydrolyzed dye removal, with poly(vinylpyrrolidone) polymers being the least effective. These differences were attributed to variations in the magnitude and delocalization of positive electrostatic potential of the functional moieties in the polymers and the extent of and propensity for hydrogen bonding with the hydrolyzed reactive dyes.

KEYWORDS: Reactive dyes, Wash-off, Water, Energy, Hydrolyzed dye, Dye transfer inhibiting polymers



INTRODUCTION

Cotton and other cellulose substrates comprise over 40% of world textile consumption. Of all the dyes employed for coloration of cellulosic fibers, reactive dyes find greatest use with over 50% of world consumption.^{1–3} Reactive dyes are desirable because of their excellent wash fastness, which arises from covalent bond formation between dye and fiber through either nucleophilic substitution or Michael addition reactions, depending upon the nature of the reactive group in the dye. Reactive dyeing essentially has two stages. In the first stage, the dye adsorbs onto the cellulosic substrate through hydrogen bonding and van der Waals interactions; dyes are applied from aqueous solutions with electrolyte (sodium sulfate or sodium chloride),⁴ which is needed to overcome the long-range repulsion forces operating between anionic dyes (as a result of water-solubilizing sulfonic acid groups) and the negative ζ -potential acquired by cotton surface in aqueous media.⁵ Moreover, this repulsive force can be exacerbated through the formation of anionic carboxylic acid (COOH) groups in the cotton substrate, formed via oxidation of glucose moieties in

cellulose during processing operations such as bleaching or mercerizing,^{6,7} which owing to their relatively low pK_a values will be ionized at the pH values typically encountered during dye application. Without electrolyte addition, adsorption of dye on the fiber will not occur, and with dyes such as reactive dyes, which are very soluble in water, a high amount of electrolyte is required in the dyeing process, often up to 150 g dm⁻³. Electrolyte also supports dye penetration into the fiber interior (diffusion), which leads to better dye uptake and fixation.^{8,9}

In the second stage, alkali is added to achieve a pH of around 11 in order to generate sufficient cellulosate anions (cell-O⁻) within the substrate for covalent bond formation between dye and fiber (fixation); the neutral species (cell-OH) is not sufficiently nucleophilic for reaction between dye and fiber to occur. However, this alkaline environment produces hydroxyl ions in the aqueous dyeing solution with which the reactive dye

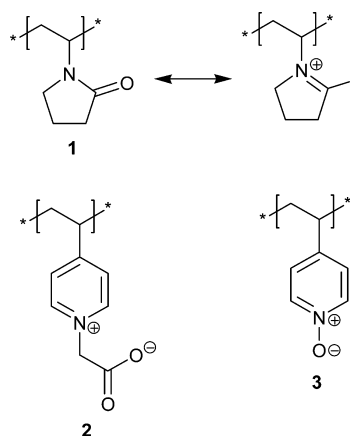
Received: January 15, 2015

Revised: March 4, 2015

Published: March 11, 2015

is able to react, in competition with the cellulosate anions in the fiber, to form hydrolyzed dye. Up to 40% of the dye maybe hydrolyzed in the dyeing process, this hydrolyzed dye has high affinity for the fiber, through hydrogen bonding, van der Waals and ion-dipole forces, but is not covalently bonded.^{5,6,10,11} Accordingly, these reactive dyeings require a multistep “wash-off” process after dyeing, involving various aqueous rinses and washings, in order for the dyeing to achieve the characteristic very high wash fastness. This wash-off and subsequent effluent treatment, to remove the resultant color pollution, can account for up to 50% of the total cost of reactive dyeing.⁸

Another extremely important sustainability consideration is the amount of water used in this wash-off process; a process involving over seven separate rinsing stages is not uncommon. High volumes of water and numerous repeated individual wash-off stages are often required to effect a dilution in electrolyte and alkali concentration in the wash-off bath; a wash-off process might include a cold water wash at 25–60 °C, a hot water wash at approximately 60–80 °C, scouring with anionic surfactant at 80–90 °C, followed by subsequent hot and cold water rinses.¹² Electrolyte remains at the end of the dyeing process and, in typical industrial processes, significant amounts are carried over into the wash-off process as the fabric holds at least its own mass of dyeing solution; as a result, the first wash-off stage may contain an electrolyte concentration of up to 15 g dm⁻³. Electrolyte not only increases dye-fiber substantivity, but also can cause dye molecules to aggregate, as a result of which, the hydrolyzed dye molecules become difficult to remove from the fiber. As the electrolyte concentration of the wash-off bath needs to be below 2 g dm⁻³, and ideally below 1 g dm⁻³, in order to achieve effective color removal, the first two stages of the wash-off procedure are mainly employed to reduce electrolyte concentration. Subsequent stages then remove the hydrolyzed dye, and all noncovalently bound dye must be removed to achieve the high level of wash fastness expected. These hot water rinsing and washing stages require high amounts of energy to raise the temperature of large volumes of cold water from ambient temperature to those needed for efficient washing, and the time taken to empty, fill and heat up washing baths considerably lengthens the total process and reduces productivity.



The use of dye transfer inhibitors (DTI) in domestic laundering detergent compositions is well-known. The stain inhibition character of these auxiliaries is effective on both cotton and polyamide fibers in formulations containing nonionic and/or anionic surfactants. Suitable formulations that reduce the problem of dye staining in domestic laundering

have been described¹³ employing cationic and zwitterionic surfactants with a nonionic detergent. Such DTIs include polymers such as poly(vinylpyrrolidone) (1), poly(vinylpyridine betaine)¹⁴ (2), and poly(vinylpyridine-*N*-oxide) (3). These polymers are permanent dipoles and, as such, can hold soils and vagrant dye, which may be washed from fabric during laundering, in solution and prevent their redeposition onto fabric.¹⁵ Currently, such DTIs are used in domestic washing formulations (powder, liquid, tablet) at concentrations between 0.2 and 1.0% on mass of the total formulation.¹⁶

From a sustainable chemistry and engineering perspective, consumption of water and energy are arguably the biggest issues in textile dyeing. In this paper, existing and developmental DTIs are employed to remove unfixed (hydrolyzed) dyes following reactive dyeing of cotton, with the objective of gaining a significant cost saving and sustainability benefit as a result of a dramatically reduced wash-off procedure, which will save water, time, and energy.

EXPERIMENTAL SECTION

Materials. The fabric used was 100% cotton, plain weave, 150 g m⁻². Table 1 shows the DTIs used in this study; all DTIs were

Table 1. DTIs Used to Remove Hydrolyzed Reactive Dye

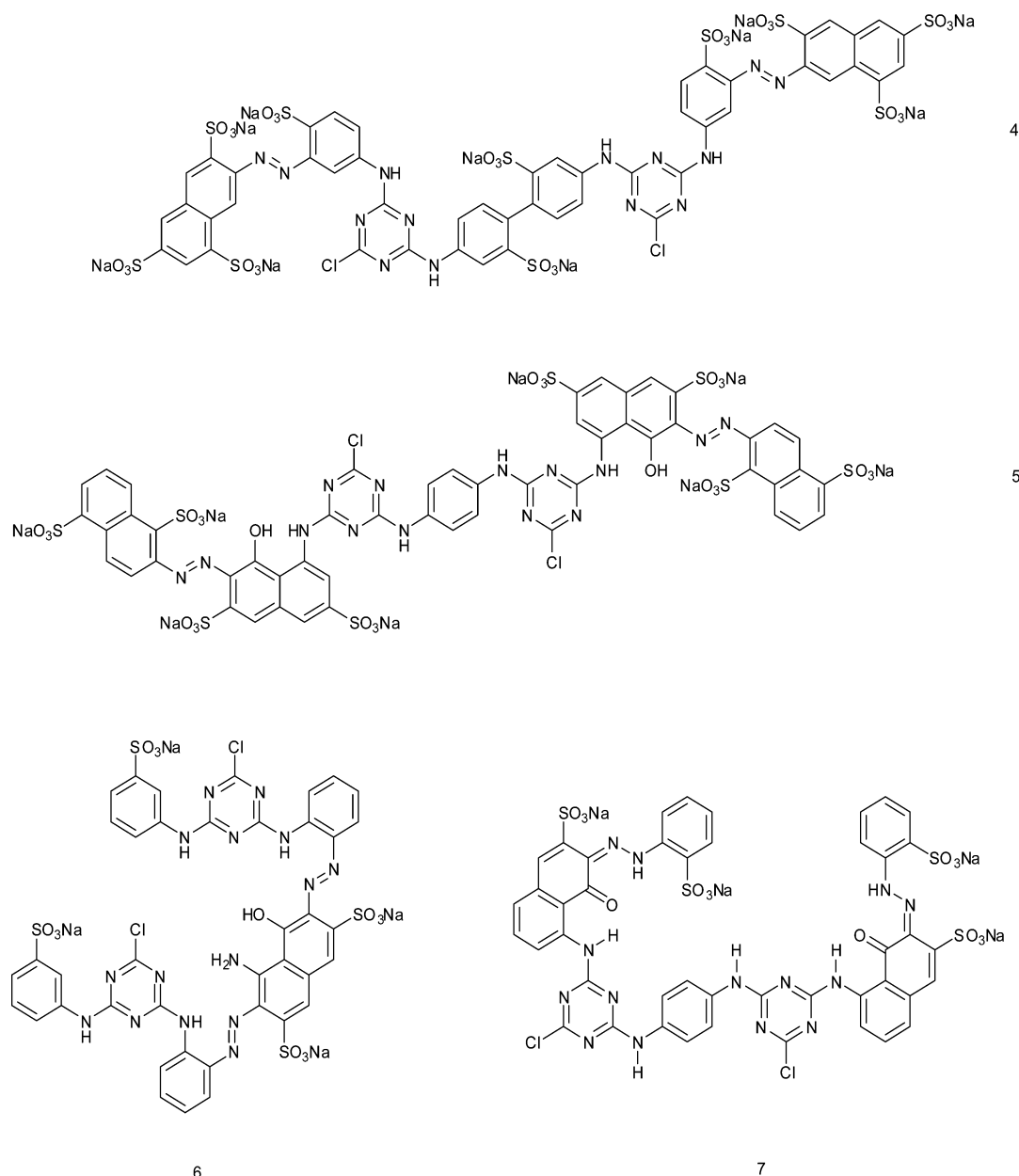
commercial name	chemical type	M_r (g mol ⁻¹)	form supplied
PVP	1	10 000	solid powder
PVP K-15 ^a	1	6000–15 000	solid powder
PVP K-30 ^a	1	40 000–80 000	solid powder
PVP K-90 ^a	1	900 000–1 500 000	solid powder
PVP K-120 ^a	1	2 000 000–3 000 000	solid powder
Chromabond S-100	2	35 000	40% (w/w) aqueous solution
Chromabond S-403E	3	30 000	40% (w/w) aqueous solution
PVNO Classic	3	25 000–28 000	40% (w/w) aqueous solution
PVNO Europe	3	11 000–15 000	40% (w/w) aqueous solution

^aThe average relative molecular mass may range from 6000 to 3 000 000 g mol⁻¹ as distributed by the grades in terms of Fikentscher K-values.¹⁷

supplied by Uniqema, except the two poly(vinylpyridine-*N*-oxide) polymers and the 10 000 M_r poly(vinylpyrrolidone) (PVP) polymer, which were supplied by Reilly Industries, Inc., USA. All DTIs are water-soluble, and the DTI–dye complex formed in these experiments remains in aqueous solution and does not precipitate. A commercial sample of Sandozin NIE was obtained from Clariant, which was included to evaluate the effect of a simple nonionic surfactant (that may be used in standard wash-off processes) under the novel wash-off method used for the DTIs.

The dyes used were all known to be problematic with respect to removal of hydrolyzed dye, hence, requiring extensive wash-off treatments. Commercial samples of the Procion H-E dyes C.I. Reactive Yellow 84 (4), C.I. Reactive Red 141 (5), and C.I. Reactive Blue 171 (6) were kindly supplied by DyStar. Uniqema supplied a sample of 100% cotton, plain weave, 150 g m⁻², dyed on an industrial-scale with C.I. Reactive Red 120 (7), this was given no wash-off treatment or rinsing prior to supply. Although the applied dye species would be those shown in 4–7, in terms of the dye species that would be removed during the wash-off process, it would be expected that the structure would be the hydrolyzed form (all –Cl substituted with –OH). All other general chemicals were obtained from Aldrich.

Dyeing. Cotton samples were dyed in sealed stainless steel dye pots of 300 cm³ capacity, housed in a laboratory-scale Roaches Pyrotec



2000 dyeing machine, according to the dye manufacturer's recommended method.¹⁸ Woven cotton fabric (5 g), the reactive dye (3% on mass of fiber), and anhydrous sodium sulfate (90 g dm⁻³) were added to distilled water with a total solution: fiber ratio of 10:1 and the temperature held at 50 °C for 20 min. The temperature was then raised at a rate of 1.5 °C min⁻¹ to 80 °C and held for 30 min. Sodium carbonate (20 g dm⁻³) was added to achieve a pH of 10.5 for nucleophilic substitution reaction with the dye and held at 80 °C for a further 60 min. The fiber was removed from the dyeing solution, retaining 200% of its mass of the dyeing solution, this was adopted to mimic dyeing conditions of industrial processes.

Wash-off. Dyed cotton samples were washed-off using the standard wash-off procedure (Figure 1; a six-stage process according to the dye manufacturer's recommended method¹⁸) using sealed stainless steel dyepots of 300 cm³ capacity, housed in a laboratory-scale Roaches Pyrotec 2000 dyeing machine. Throughout the wash-off process shown in Figure 1 (and Figure 2) "dyed fabric" is material that is dyed and unrinsed, and wet with twice its weight of original dyebath or preceding wash-off bath; in the case of the dyed and unrinsed C.I. Reactive Red 120, this was the "dyed fabric" used.

In comparison, dyed cotton samples were washed-off in a novel three-stage process using sealed stainless steel dyepots of 300 cm³

capacity, housed in a laboratory-scale Roaches Pyrotec 2000 dyeing machine. In the first stage, dyed woven cotton fabric (5 g) was added to distilled water with a total solution: fiber ratio of 10:1 and the temperature held at 20 °C for 10 min. The bath was then dropped. In the second stage, the samples from the first stage and the DTI polymer (1 g dm⁻³ active solids) were added to distilled water with a total solution: fiber ratio of 10:1 and the temperature held at 40 °C for 10 min. In the third stage, the samples from the second stage were added to distilled water with a total solution: fiber ratio of 10:1 and the temperature held at 20 °C for 10 min (Figure 2). For comparison to industrial processes, where high electrolyte content carry-over is often observed, the wash-off process detailed above was repeated including anhydrous sodium sulfate (20 g dm⁻³) at the second stage.

Color Measurement. Spectral reflectance factors (taken between 400 and 700 nm wavelengths in 20 nm increments) of the samples were measured using a Datacolor Spectraflash SF600 reflectance spectrophotometer (Datacolor International Ltd., UK) interfaced to a computer. Each fabric sample was folded twice to give a total of four layers. Four different areas of each sample were measured and the average color value was automatically calculated and saved by the computer.

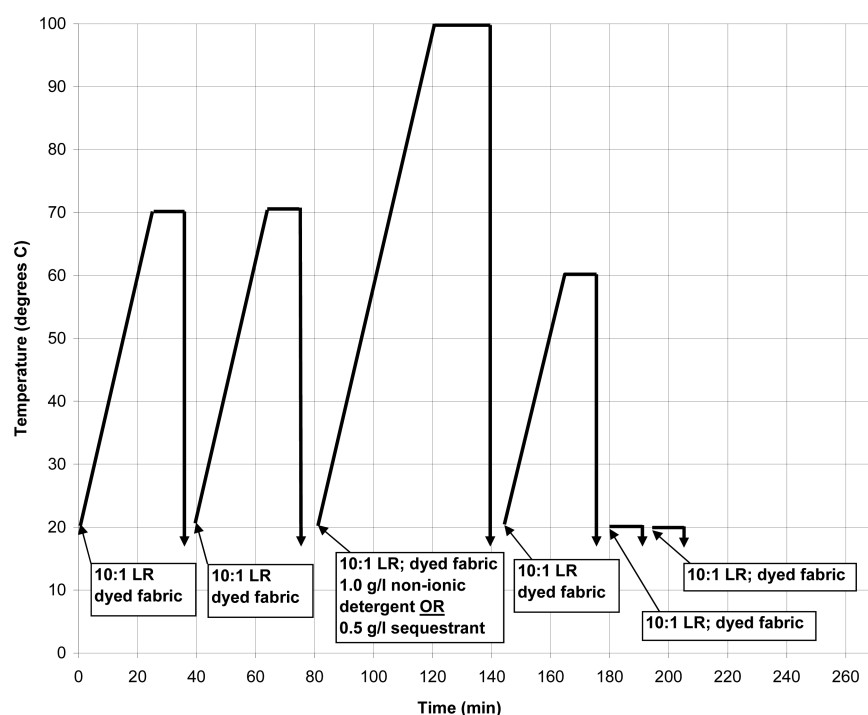


Figure 1. Standard Procion H-E wash-off procedure.¹⁸

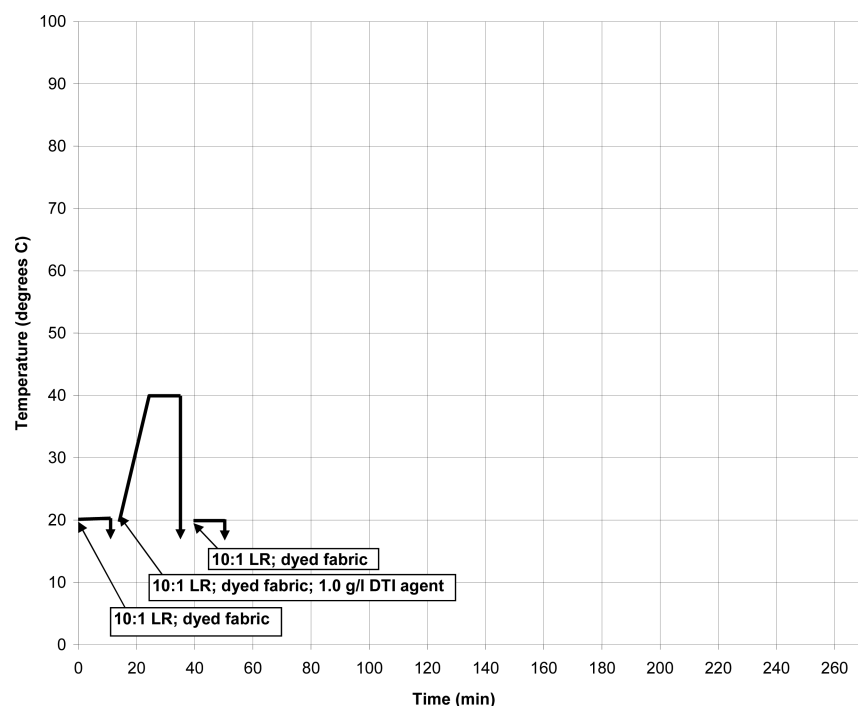


Figure 2. DTI wash-off procedure.

CIELAB values (under illuminant D65 using the 10° standard observer) were automatically calculated. The color difference ΔE_{ab}^* was calculated from CIELAB coordinates $L^*a^*b^*$ using eq 1:

$$\Delta E_{ab}^* = \sqrt{[(L_r^* - L_t^*)^2 + (a_r^* - a_t^*)^2 + (b_r^* - b_t^*)^2]} \quad (1)$$

in which the subscripts r and t refer to the reference and test samples, respectively.

Wash Fastness Testing. Samples were subjected to the ISO 105:C06/C2S wash test (60 °C) using SDC multifibre fabric as adjacent.¹⁹ The samples were washed five times using the same piece

of multifibre strip for each washing. After the washed samples were visually assessed using gray-scales according to the ISO 105:A03 test protocol¹⁹ to determine the degree of cross staining. The gray-scale ranges from 5 for no stain on the adjacent fibers down to 1 for severe staining, with half points in between. A gray-scale stain rating of 3 is suggested in the majority of standard performance specifications published by ASTM as a pass/fail borderline,²⁰ although many retailers set a higher standard at a gray-scale rating of 4.

Energy Consumption. The amount of energy consumed by the wash-off processes to heat water was calculated by eq 2, where Q is the heat added, c is the specific heat (water = 4.1868 J g⁻¹), m is mass, and

ΔT is change in temperature. The total energy consumption for the whole wash-off process was calculated by addition of energy consumption for each stage.

$$Q = cm\Delta T \quad (2)$$

Computational Chemistry. The geometry of the methyl capped DTI polymer repeat units (1–3) was optimized using a density functional theory (DFT) method (B88PW91/DZVP) and the charge distribution calculated by using point charge fitting (PCF) charges and produce plots of the electrostatic potential plotted onto a total electron density isosurface (0.09). Blue is used to represent the strongest negative electrostatic potential on the molecule and red the strongest positive electrostatic potential. The other colors are the values in between, green is neutral. In each case the oxygen atoms are negatively charged. The interaction orientation of these repeat units with functional groups that are usually observed on dye molecules were investigated by using ISOSTAR. Plots were constructed of the interaction of any OH group in the Cambridge Scientific Database (CSD) with the pyridine-*N*-oxide and pyrrolidone groups.

RESULTS AND DISCUSSION

Table 2 shows the color difference (ΔE_{ab}^*) between dyeings that had received the standard Procion H-E wash-off procedure

Table 2. Color Difference (ΔE_{ab}^*) between Dyeings That Had Received the Standard Procion H-E Wash-off Procedure (Reference) and the Modified DTI Wash-off Process (No Na_2SO_4 Added)

DTI	C.I. Reactive Red 120	C.I. Reactive Yellow 84	C.I. Reactive Red 141	C.I. Reactive Blue 171
none	2.7	2.8	3.2	1.9
Sandozin NIE	2.3	2.1	1.9	1.8
PVP	1.6	1.2	1.3	1.3
PVP K-15	1.0	1.1	1.2	1.0
PVP K-30	1.4	1.5	1.3	1.2
PVP K-90	0.7	1.0	1.2	1.1
PVP K-120	1.3	1.2	1.4	1.3
Chromabond S-100	1.5	1.1	1.2	1.0
Chromabond S-403E	1.4	0.9	0.8	0.8
PVNO Classic	0.5	0.3	0.5	0.2
PVNO Europe	0.5	0.1	0.4	0.3

(Figure 1) and the modified DTI wash-off process. It is evident from the data that ΔE_{ab}^* in all cases where a DTI was applied was relatively low, suggesting that the wash-off procedures did

not detrimentally effect the final expected visual appearance of the dyeings ($\Delta E_{ab}^* \approx 2.3$ corresponds to a just noticeable difference²¹). Higher ΔE_{ab}^* values are observed where no DTI or nonionic detergent alone were used in the modified wash-off process, which may suggest that these two processes do not sufficiently remove hydrolyzed dye from the fabric that may result in an observable color difference in comparison with the standard Procion H-E wash-off process.

Table 3 shows the gray-scale ratings for the staining of the cotton portion of the adjacent multifibre as a result of the fastness tests; staining to other fiber types was not observed in any case. The standard Procion H-E wash-off procedure (Figure 1) would be expected to give resultant washed-off dyeings that achieved a gray-scale rating of 5, as a result of complete removal of any hydrolyzed dye with only covalently bound dye remaining. From the data, it is evident that without the use of a DTI (none) the developed shortened, lower energy and water consumption wash-off procedure (Figure 2) is insufficient to affect the high gray-scale rating required.

The use of a nonionic detergent (Sandozin NIE) does secure an improved wash-off, but it is still significantly below the standard required. The staining rating is generally worse when sodium sulfate is present, this is expected, as the high level of electrolyte present in the wash-off bath causes aggregation of dye molecules and pushes the [dye in fiber $\leftrightarrow$ dye in solution] equilibrium toward the dye remaining in the fiber, hence an insufficient level of hydrolyzed dye removal was observed. Electrolyte may also reduce the detergency of Sandozin NIE by precipitation. When the DTIs are employed in the developed wash-off procedure, it is clearly evident that, in most cases, they enable the removal of comparatively high levels of hydrolyzed dye removal, which is reflected in higher gray-scale ratings subsequent to wash fastness testing.

From the data, it is observed that the different DTI polymer types varied in their efficacy of dye removal in the following order: 3 > 2 > 1. Poly(vinylpyridine-*N*-oxide) polymers were the most effective with respect to the level of hydrolyzed dye removal closely followed by the poly(vinylpyridine betaine) polymers which were also highly efficient in hydrolyzed dye removal. Although poly(vinylpyrrolidone) polymers did affect improvement in the wash-off of the hydrolyzed dye, their efficacy was notably inferior to type 2 and 3 DTIs. It is also observed that the lowest ΔE_{ab}^* occurred when type 3 DTIs were used in the wash-off process, suggesting these polymers remove

Table 3. Gray-Scale Ratings for Staining to Adjacent Cotton

DTI	C.I. Reactive Red 120		C.I. Reactive Yellow 84		C.I. Reactive Red 141		C.I. Reactive Blue 171	
	20 g dm ⁻³ Na ₂ SO ₄	no Na ₂ SO ₄	20 g dm ⁻³ Na ₂ SO ₄	no Na ₂ SO ₄	20 g dm ⁻³ Na ₂ SO ₄	no Na ₂ SO ₄	20 g dm ⁻³ Na ₂ SO ₄	no Na ₂ SO ₄
none	2/3	3	2	3	2	3	2/3	3
Sandozin NIE	3/4	4	3/4	4	3	4	3/4	4
PVP	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5
PVP K-15	4/5	5	4	4/5	4/5	4/5	4/5	4/5
PVP K-30	4/5	4/5	4/5	4/5	3/4	4	4	4
PVP K-90	4/5	4/5	4/5	4/5	4	4	4	4
PVP K-120	5	5	4/5	4/5	4	4/5	4	4/5
Chromabond S-100	5	5	5	4/5	4/5	4/5	4/5	4/5
Chromabond S-403E	5	5	5	5	5	5	5	5
PVNO Classic	5	5	5	5	5	5	5	5
PVNO Europe	5	5	5	5	4/5	5	5	5
standard wash-off (Figure 1)	5	5	5	5	5	5	5	5

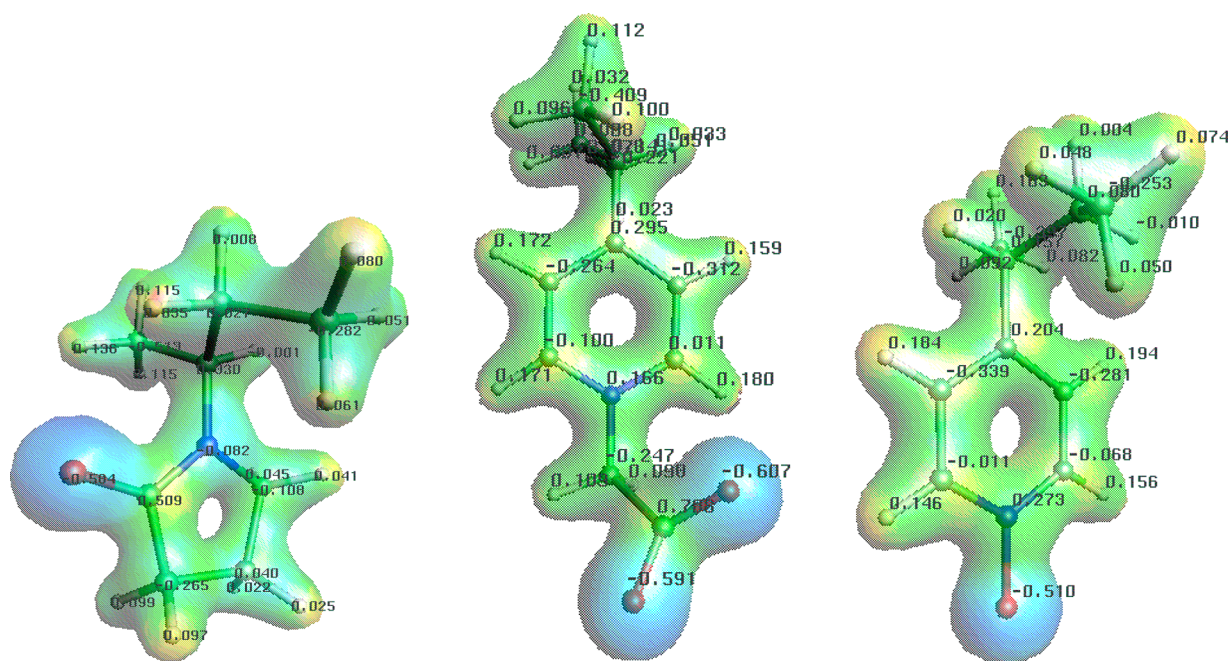


Figure 3. PCF charges plotted onto a total electron density isosurface for DTI polymer repeat units; poly(vinylpyrrolidone) (left), poly(vinylpyridine betaine) (center), poly(vinylpyridine-N-oxide) (right).

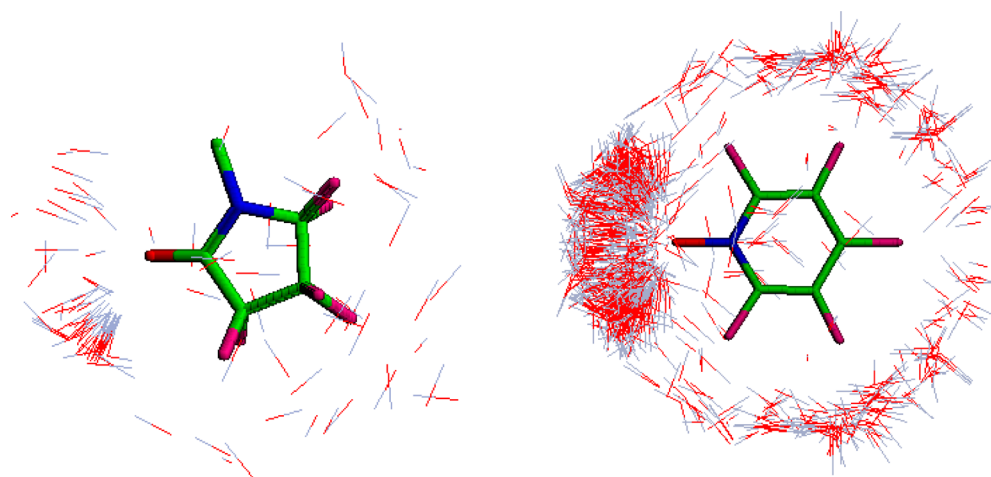


Figure 4. Interaction of pyrrolidone (left) and pyridine-N-oxide (right) with any OH group in the CSD. H atoms on the repeat units have been colored purple and H atoms on the OH group are gray.

similar levels of hydrolyzed dye in comparison with the standard Procion H-E wash-off procedure.

It would be expected that the mode of interaction of these polymeric systems with dye molecules would be affected by the distribution of charge around the repeat unit. From the PCF plots on the electron density isosurface (Figure 3), it is observed that the aromatic DTI polymers (2 and 3) have greater delocalization of positive electrostatic potential in comparison with the aliphatic DTI polymers (1). For poly(vinylpyridine betaine) and poly(vinylpyridine-N-oxide) polymers, the positive electrostatic potential extends around the H atoms of the aromatic ring and that potential on the isosurface is 3.1 times the order of magnitude (average PCF 0.171) in comparison with the aliphatic poly(vinylpyrrolidone) polymers (average PCF 0.055). Additionally, with type 2 and 3 DTI polymers, positive electrostatic potential is relatively equally delocalized around the four H atoms, whereas with type

1 DTI polymers most positive electrostatic potential is concentrated on the two H atoms of C3 on the pyrrolidone ring. As such, the stronger overall electrostatic potential of poly(vinylpyridine betaine) and poly(vinylpyridine-N-oxide) polymers and the uniform delocalization of that potential would explain why such DTI polymers secure superior removal and association with anionic hydrolyzed reactive dye molecules in comparison with poly(vinylpyrrolidone) polymers.

This superior performance is further evidenced and explained through ISOSTAR predictions of interactions of hydroxyl groups with pyrrolidone and pyridine-N-oxide groups (Figure 4). There are a significantly higher number of records relevant to the pyridine-N-oxide group as compared to the pyrrolidone unit, which would indicate that the interaction of OH groups, and subsequent hydrogen bonding, of hydrolyzed reactive dyes with type 3 DTI polymers would be significantly greater and more extensive than type 1 DTI polymers.

The experimental results indicated that type 3 DTI polymers were marginally superior in their performance in comparison with type 2 DTI polymers. Although their positive electrostatic potentials and the delocalization of those potentials are relatively similar, the reason for the superior performance of polymers based on vinylpyridine-*N*-oxide may be related to conformation and accessibility of hydrolyzed reactive dye molecules to the polymers. Poly(vinylpyridine-*N*-oxide) is very planar, insofar as the active moiety extends in one axis from the vinyl polymer backbone, whereas poly(vinylpyridine betaine) extends in two axes from the backbone as the carboxyl group extends out of plane. This could lead to some steric effects that could compromise the effectiveness of the type 2 DTI polymers.

The use of DTIs in the wash-off of reactive dyes on cotton enables a much more efficient process to be developed. Table 4

Table 4. Comparison of Different Wash-off Procedures

procedure	time (min)	water (dm ³ kg ⁻¹) ^a	energy (Q) (MJ kg ⁻¹) ^a
recommended wash-off	205	60	9.21
DTI wash-off	50	30	0.84

^aPer kg fabric processed.

provides a breakdown analysis of the time, water consumption, and energy consumption for the developed DTI procedure in comparison with the standard recommended wash-off procedure. It is evident that the DTI process operation time is <25% that of the standard, the total water consumption is halved, it consumes 9% of the energy of the recommended wash-off process.

It could be argued that the use of these DTIs would provide additional chemical hazard in the effluent, but these types of polymers are already extensively used in domestic laundering. Considering a 1 kg reactive dyed cotton garment that may have a life of 100 washes, based on an average 3 kg washing load²² using 108 g of washing powder per load²³ and with a DTI concentration of 1%,¹⁶ such a garment would consume 36 g of DTI in its life after production. Using the concentrations specified in this work, the same 1 kg garment would consume 10 g of DTI in the new wash-off process, an additional 27% over its full life cycle. However, the DTI would replace the same mass of detergent in the standard wash-off process, so the total mass of chemicals is equal. Additionally, through further development it may be possible to reduce the concentration of DTI polymer required to enable efficient hydrolyzed reactive dye wash-off. Nevertheless, the additional DTI chemicals are far outweighed from a sustainability perspective by the saving made in terms of water and energy and economically in terms of time and energy costs, making this novel wash-off system a much greener alternative.

The application of the DTI wash-off process might affect the treatability of the effluent: if the same amount of dye is present in a smaller volume of effluent, the effluent color would be more intense, and hence less acceptable, but this may make the treatment of the effluent more efficient, particularly if sorption treatment techniques are applied.²⁴ However, the DTI process may result in a higher electrolyte content (total dissolved solids) due to the lower volume of water used in the wash-off process, and this would need to be considered in effluent treatment.

The use of DTIs in the wash-off of reactive dyes on cotton enables a much more efficient, economical, and sustainable process to be developed, which significantly reduces operation time, water consumption, and energy consumption. When the DTIs are employed in the developed wash-off procedure, they enable comparatively high levels of hydrolyzed dye removal through formation of a complex with the anionic dye molecules. Different DTI polymer types varied in their efficacy of dye removal; poly(vinylpyridine-*N*-oxide) polymers were the most effective with respect to the level of hydrolyzed dye removal closely followed by the poly(vinylpyridine betaine) polymers, which were also highly efficient in hydrolyzed dye removal, with poly(vinylpyrrolidone) polymers being the least effective. These differences were attributed to variations in the magnitude and delocalization of positive electrostatic potential of the functional moieties in the polymers and the extent of and propensity for hydrogen bonding with the hydrolyzed reactive dyes.

AUTHOR INFORMATION

Corresponding Author

*R. S. Blackburn. Tel: +44 (0)113 343 3757. Fax: +44 (0)113 343 3704. E-mail: r.s.blackburn@leeds.ac.uk

Author Contributions

The paper was written through contributions of all authors. All authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Uniqema, The University of Leeds and The Overseas Research Students Awards Scheme (ORS) for the provision of scholarships.

REFERENCES

- (1) Blackburn, R. S.; Burkinshaw, S. M. A greener approach to cotton dyeings with excellent wash fastness. *Green Chem.* **2002**, *4*, 47–52.
- (2) Blackburn, R. S.; Burkinshaw, S. M. A greener approach to cotton dyeings. Part 2: Application of 1:2 metal complex acid dyes. *Green Chem.* **2002**, *4*, 261–265.
- (3) Holme, I. Digital Ink Jet Printing of Textiles. *Text. Mag.* **2004**, *31*, 11–16.
- (4) Gordon, S.; Hsieh, Y. L. *Cotton: Science and Technology*; Woodhead Publishing Ltd.: Cambridge, U. K., 2007.
- (5) Broadbent, A. D. *Basic Principles of Textile Coloration*; Society of Dyers and Colourists: Bradford, U. K., 2001; Chapter 16.
- (6) Nevell, T. P. In *The Dyeing of Cellulosic Fibres*; Preston, C., Ed.; Dyers' Company Publications Trust: Bradford, U. K., 1986.
- (7) Blackburn, R. S.; Harvey, A.; Kettle, L. L.; Payne, J. D.; Russell, S. J. Sorption of poly(hexamethyleneguanide) on cellulose: Mechanism of binding and molecular recognition. *Langmuir* **2006**, *22*, 5636–5644.
- (8) Khatri, A.; White, M.; Padhye, R.; Momin, N. H. The use of reflectance measurements in the determination of diffusion of reactive dyes into cellulosic fiber. *Color Res. Appl.* **2014**, *39*, 63–69.
- (9) Khatri, Z.; Ahmed, F.; Jhatial, A.; Abro, M.; Mayakrishnan, G.; Kim, I. S. Cold pad-batch dyeing of cellulose nanofibers with reactive dyes. *Cellulose* **2014**, *21*, 3089–3095.
- (10) Shore, J. In *Cellulosics Dyeing*; Shore, J., Ed.; Society of Dyers & Colourists: Bradford, U. K., 1995.
- (11) Fox, M. R.; Summer, H. H. In *The Dyeing of Cellulosic Fibres*; Preston, C., Ed.; Dyers' Company Publications Trust: Bradford, U. K., 1986.
- (12) Aspland, J. R. *Textile Dyeing and Coloration*; American Association of Textile Chemists and Colorists: Raleigh, NC, 1997; Chapter 8.

- (13) Bishop, D. P.; Nelson, R. T. Detergent compositions. U.S. Patent US 4261869 A, April 14, 1981.
- (14) Shih, J. S.; Srinivas B.; Hornby J. C. Containing surfactants; prevent dye transfer. U.S. Patent US 5776879 A, July 7, 1998.
- (15) Donoghue, S. J.; Schamp K. M. A. Detergent additives comprising dye transfer inhibitors, and process for making them. U.S. Patent US 5849684 A, December 15, 1998.
- (16) Oakes, J. Department of Colour Chemistry, University of Leeds, Leeds, U. K. Personal communication.
- (17) Fikentscher, H.; Mark, H. The viscosity of lyophilic colloids. *Kolloid Zeitschrift* **1929**, 49, 135–148.
- (18) Procion, H.-E. Pattern card, DyStar UK Limited: Halifax, U. K.
- (19) *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th ed., Amendment No. 1; Society of Dyers and Colourists: Bradford, U. K., 1992.
- (20) *Standard Guide for Evaluating Color Transfer or Color Loss of Dyed Fabrics in Laundering (Not Suitable for Detergent or Washing Machine Rankings)*; ASTM D5548-13; ASTM International: West Conshohocken, PA, 2013.
- (21) Gaurav, S. *Digital Color Imaging Handbook*; CRC Press: New York, 2003.
- (22) Collins, M.; Aumônier, S. *Streamlined Life Cycle Assessment of Two Marks & Spencer plc Apparel Products*; Final Report; Marks & Spencer plc: London, 2002.
- (23) Blackburn, R. S. Natural polysaccharides and their interactions with dye molecules: Applications in effluent treatment. *Environ. Sci. Technol.* **2004**, 38, 4905–4909.