UNIVERSITY OF LEEDS

This is a repository copy of *Improved garment longevity and reduced microfibre release* are important sustainability benefits of laundering in colder and quicker washing machine cycles.

White Rose Research Online URL for this paper: http://eprints.whiterose.ac.uk/154480/

Version: Accepted Version

Article:

Cotton, L, Hayward, AS, Lant, NJ et al. (1 more author) (2020) Improved garment longevity and reduced microfibre release are important sustainability benefits of laundering in colder and quicker washing machine cycles. Dyes and Pigments, 177. 108120. ISSN 0143-7208

https://doi.org/10.1016/j.dyepig.2019.108120

© 2019, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/.

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/

1 Improved garment longevity and reduced microfibre release are important

2 sustainability benefits of laundering in colder and quicker washing machine

3 cycles

- 4 Lucy Cotton,^{*a*} Adam S. Hayward,^{*b*} Neil J. Lant,^{*b*} Richard S. Blackburn^{*a*}*
- 5 ^aSchool of Design, University of Leeds, Leeds, LS2 9JT, UK
- 6 ^bProcter & Gamble, Whitley Road, Longbenton, Newcastle-upon-Tyne, NE12 9BZ, UK
- 7 *E-mail: r.s.blackburn@leeds.ac.uk; Tel: +44 113 343 3757

8

9 Abstract

- 10 The global impact of laundering clothing is significant, with high levels of water, energy use, and pollution associated 11 with this consumer care process. In this research, the impacts of washing temperature and washing time on garment colour 12 loss (dye fading), colour transfer (dye staining), and microfibre release were evaluated using retail consumer clothing. 13 Significantly greater colour loss and greater colour transfer were observed for a 40 °C, 85 min wash cycle compared to 14 cold-quick (25 °C; 30 min) cycle. Desorbing dyes were found to mainly be reactive dyes. From fundamental kinetic 15 studies, it was observed that significant increases in both rate of dye desorption and total dye desorption occurred when 16 increasing from 20 °C to 40 °C, but the difference in dye release between 40 °C and 60 °C was not as significant; the 17 same kinetic trends were observed for dye transfer. Microfibre release was significantly greater for the 40 °C, 85 min 18 cycle in comparison with the cold-quick cycle, and this effect continued with further washes. These results mean that 19 reducing time and temperature in laundry could have a significant impact in terms of extended garment longevity and 20 reduced dye and microfibre liberation into the environment, in addition to energy savings. 21 22 Keywords: Dye transfer; Washing; Textiles; Low temperature; Microfibre; Laundry.
- 23

24 **1. Introduction**

25 Global fibre production for textiles in 2017 was over 105 million tonnes, comprising ~53.7 million tonnes of polyester, 26 \sim 25.8m tonnes cotton, \sim 6.7m tonnes regenerated cellulosics (e.g. lyocell, viscose), \sim 5.5m tonnes other plant fibres (e.g. 27 linen, hemp), ~5.7m tonnes polyamide, ~6m tonnes other synthetics, ~1.2m tonnes wool, and ~0.4m tonnes other natural 28 protein fibres [1]; whilst some of this fibre is used in household and industrial textiles, most of these fibres are used in 29 clothing. Manufacturing of textiles and leather creates carbon emissions of 84 million tonnes per year [2], which, together 30 with consumer care of clothing, also consumes high levels of water, energy and non-renewable resources [3,4]. 'Fast 31 fashion' is now a global phenomenon leading to more people wearing more items of clothing fewer times before disposal. 32 Garments tend to start their lives in factories in South and East Asia, often far from their end users. Dyes and other 33 chemicals used in textile dyeing and finishing processes are an environmental problem during manufacturing [5,6]; dyes 34 in watercourses are aesthetically undesirable, but they have a more serious environmental impact, textile dyes in high 35 concentrations in watercourses prevent the reoxygenation capacity of the receiving water and reduce sunlight, thereby 36 upsetting biological processes in aquatic fauna and also the photosynthesis process of aquatic flora [7-9]. In addition, 37 some dyestuffs contain heavy metals (e.g. Cr, Co, Cu) that may be toxic to aquatic organisms [10,11]. In many parts of 38 the world, remediation techniques are employed to adsorb dyes in wastewater onto biomass before the wastewater is 39 released to the watercourse; this biomass with dye adsorbed slowly degrades, but still presents an environmental issue in 40 terms of its disposal [7].

41 It is known that laundry has a significant impact on the environmental impact of clothing [4]; analysis undertaken 42 by the Waste and Resources Action Programme (WRAP) in the UK suggests that carbon emissions associated with 43 washing, drying and ironing account for about a third of the lifetime emissions of clothing [12]. Plastic microfibres are 44 released when synthetic textiles are washed; they are a global problem and account for over a third of all plastic reaching 45 the open ocean [13], which can have a devastating effect on wildlife [14]. It has been shown that over 700,000 individual 46 fibres are released from an average 6 kg wash load [15]. However, it is not only microfibres from synthetic textiles that 47 are a problem. Recent research into the composition and abundance of microfibres in seafloor sediments from southern 48 European seas found $6,965 \pm 3,669$ microfibres m⁻², varying in fibre length from 3 to 8 mm, and of these fibres identified 49 nearly 80% were cellulosic, comprising dyed natural cellulosic fibres (e.g. cotton, linen) and regenerated cellulosic fibres 50 (e.g. viscose) [16]. Textiles increasingly make up a large proportion of landfill waste as consumers dispose of faded or 51 discoloured garments; in developed countries, almost three-quarters of discarded clothing ends up in landfill or being 52 burned, with less than 1% being recycled into other garments. Whilst in landfill, some textiles release the greenhouse gas 53 methane into the atmosphere during degradation [17] and most synthetic fibres in landfill are essentially non-degradable. 54 Despite significant research into the effect of dyes and other chemicals in the manufacturing supply chain, little research 55 has been conducted into how consumers contribute to dyestuffs entering waste waterways through domestic laundering 56 of dyed garments. Dye transfer is the term used to describe discoloration that happens when migrant dye from 'donator' 57 textiles in a wash system re-deposits onto 'acceptor' textiles; in some cases, such as textiles with high contrast colouring, 58 the same textile acts as donator and acceptor. While it is known that dye transfer occurs, and indeed which dyes exhibit 59 poor wash fastness, the identification of dyes that bleed in modern consumer textiles is little understood. The use of dye 60 transfer inhibitors (DTIs) in domestic laundering detergent compositions is well-known; cationic and zwitterionic 61 surfactants in formulations containing non-ionic and/or anionic surfactants hold soils and vagrant dye, which may be 62 washed from fabric during laundering, in solution and prevent their redeposition onto fabric [18,19]. Current DTIs still 63 work on the assumption that direct dyes are the most problematic dye species and so have often only targeted them [20]; 64 however, most cellulosic fibres are now dyed with reactive dyes, and hydrolysed, unfixed reactive dyes pose a highly

65 significant issue in terms of desorption and staining. Hydrolysed reactive dyes typically have significantly different 66 geometries in comparison with direct dyes and their interactions with current DTIs are limited; in comparison planar, 67 often larger, direct dyes have a greater extent of interaction with existing DTIs [19]. In previous research, technical fabrics 68 are used or dyebaths are simulated, using known dye standards, but even applying optimal parameters for dye removal to 69 real-life textile effluent yields discrepancies due to the difference between authentic textile effluent and synthetic dye 70 solutions [21-24]. These dye 'standards' used for testing are not representative of dyes currently used on real consumer 71 items, mainly due to lack of knowledge and traceability in the complex, modern, global garment manufacture and supply 72 chain, and there is little justification for why these 'standards' continue to be used in such experiments.

In this research, we develop an analytical model to assess consumer wash loads in order to understand the real effect of laundry on dye desorption and dye re-adsorption (staining) by using real consumer garments. The aim of this research is to understand how cold-quick washing impacts garment longevity, in terms of dye fading and dye transfer, and what is liberated into wastewater during the laundering cycle, in terms of microfibres and types of dyes.

77

78 **2. Methods**

79 2.1. Materials

All garments were purchased from BTC Activewear, UK. Dark retail loads comprised twelve t-shirts D1 to D12 and vibrant retail loads comprised eight t-shirts L1 to L8 (Table 1); all t-shirts were size XL. Undyed (white) tracer fabrics comprised eighteen different t-shirt fabrics W1 to W18 (Table 2) each with dimensions of 5 cm × 5 cm. Each square was tagged onto a 27 cm × 30 cm piece of knitted cotton provided by Warwick Equest, UK. The detergent used in full-scale washing machine tests was a single Ariel Soluble Unit Dose (SUD) 3in1 POD detergent, purchased from Asda, UK. All other chemicals were purchased from Sigma-Aldrich, UK.

87	Table 1: Garments used in laundering experiments.
----	---

Code	Colour	Fabric and construction	Manufacturer
D1	Dyed black	100% cotton, 145 g m ⁻²	Fruit of the Loom
D2	Dyed bottle green	100% cotton, 145 g m ⁻²	Fruit of the Loom
D3	Dyed burgundy	100% cotton, 145 g m ⁻²	Fruit of the Loom
D4	Dyed deep navy	100% cotton, 145 g m ⁻²	Fruit of the Loom
D5	Dyed light graphite	100% cotton, 145 g m ⁻²	Fruit of the Loom
D6	Dyed navy	100% cotton, 145 g m ⁻²	Fruit of the Loom
D7	Dyed purple	100% cotton, 145 g m ⁻²	Fruit of the Loom
D8	Dyed royal blue	100% cotton, 145 g m ⁻²	Fruit of the Loom
D9	Dyed black	100% polyester, 140 g m ⁻²	Fruit of the Loom
D10	Printed in green camouflage	100% ring spun pre-shrunk cotton, 170 g m ⁻²	Anvil
D11	Dyed in grey and red (2-colour)	50% polyester, 25% cotton, 25% rayon, 140 g m ⁻²	Bella Canvas
D12	Dyed in red	100% polyester jersey knit, 153 g m ⁻²	Gildan
L1	Dyed in fuchsia	100% cotton, 145 g m ⁻²	Fruit of the Loom
L2	Dyed in azure	100% cotton, 145 g m ⁻²	Fruit of the Loom
L3	Dyed in Kelly green	100% cotton, 145 g m ⁻²	Fruit of the Loom
L4	Dyed in lime	100% cotton, 145 g m ⁻²	Fruit of the Loom

L5	Dyed in orange	100% cotton, 145 g m ⁻²	Fruit of the Loom
L6	Dyed in red	100% cotton, 145 g m ⁻²	Fruit of the Loom
L7	Dyed in sunflower	100% cotton, 145 g m ⁻²	Fruit of the Loom
L8	Dyed in sky blue	100% cotton, 145 g m ⁻²	Fruit of the Loom

88

89 **Table 2:** Undyed (white) tracer fabrics used in laundering experiments.

Code	Fabric and construction	Manufacturer
W1	100% cotton, 135 g m ⁻²	Fruit of the Loom
W2	100% cotton, 150 g m ⁻²	Anvil
W3	100% cotton, 170 g m ⁻²	Gildan
W4	100% cotton, 145 g m ⁻²	B&C
W5	100% cotton, 140 g m ⁻²	Russell
W6	100% cotton, 175 g m ⁻²	Russell
W7	100% polyester, 169 g m ⁻²	Gildan
W8	50% polyester, 25% cotton, 25% rayon, 159 g m ⁻²	Anvil
W9	100% polyester, 140 g m ⁻²	Fruit of the Loom
W10	65% polyester, 35% cotton, 160 g m ⁻²	Kustom Kit
W11	100% polyester, 160 g m ⁻²	Spiro
W12	100% polyester, 150 g m ⁻²	Xpres
W13	65% polyester, 35% cotton, 155 g m ⁻²	Russell
W14	100% cotton, 220 g m ⁻²	Tee Jays
W15	100% polyester, 140 g m ⁻²	Spiro
W16	95% polyester, 5% Spandex, 160 g m ⁻²	Tee Jays
W17	52% cotton, 48% polyester, 122 g m ⁻²	Bella Canvas
W18	100% polyester, 161 g m ⁻²	Gildan

90

91 **2.2. General Procedures and Instrumentation**

92Raman measurements were carried out using a Renishaw InVia confocal Raman microscope using a HPNIR laser of93wavelengths 532 nm and 785 nm. All spectra were measured between 200 cm⁻¹ and 1900 cm⁻¹. Baseline corrections were94carried out using WiRE software and other processing was carried out using Bio-Rad KnowItAll® Informatics System,95Academic Edition. UV/visible spectrophotometry was carried out using a using a Jenway 6850 UV/Vis96Spectrophotometer at 2 nm intervals; spectral properties and wavelength of maximum absorbance ($\lambda_{max-vis}$) were97evaluated. Colour measurement of fabric samples was conducted using a Gretag Macbeth Colour-Eye 7000A.

98

99 2.3. Model Validation

100 The selection of commercially available coloured t-shirts was assembled to mimic two average UK consumer wash loads,

101 a vibrant coloured load and a dark coloured load. The white tracer fabrics were included to act as acceptors for migrant

102 dye and varied in material composition to account for liberation of different classes of dyes from different fabrics. The

103 different t-shirts (making up each retail load) and the tracer fabrics were washed in a Miele 3622 washing machine using

104 the following programs: "Cold Express" (25 °C; 30 min; 1600 rpm spin cycle); "40 °C Cotton Short" (40 °C; 85 min;

105 1600 rpm spin cycle). For each wash cycle, 1 single Ariel SUD 3in1 pod detergent was added directly into the washing106 drum. For repeated washing the two programs were repeated for a total of 16 cycles.

107 After washing, t-shirts (D1-D12 and L1-L8) and whiteness monitor fabrics (W1-W18) were left to air dry for 24 108 h and then measured according to CIEDE2000 using a Gretag Macbeth Color-Eye[®] 7000A (X-Rite Ltd, Manchester, 109 U.K.) spectrophotometer to determine the colour difference between unwashed and washed fabric. ΔE_{2000} values were 110 calculated using equation 1 [25] for each whiteness monitor using the differences in lightness (*L'*), chroma (*C'*) and hue 111 (*H'*) values between unwashed and washed fabric where k_LS_L is a lightness weighting function, k_CS_C is a chroma weighting 112 function, k_HS_H is a hue weighting function, and R_T is a rescaling factor. Whiteness loss of two ΔE_{2000} units is very 113 noticeable to the eye.

114
$$\Delta E_{2000}^* \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right) \left(\frac{\Delta H'}{k_H S_H}\right)}$$
(1)

115

116 **2.4.** Dye liberation from individual items in model load

Five swatches, each measuring 5 cm × 5 cm, were taken from each of the 12 t-shirts in the dark model load (60 samples, total mass = 23 g) and placed into a Copley Scientific tergotometer pot with 300 mL city (Newcastle-upon-Tyne, UK) tap water and stirred at 40 °C at 150 rpm for 90 min. Samples of the liquor were collected and measured by UV-Vis spectroscopy.

121

122 **2.5. Desorption kinetics measurements**

123 Three swatches, each measuring $5 \text{ cm} \times 5 \text{ cm}$, were taken from each of the 12 t-shirts in the dark model load (36 samples, 124 total mass = 14 g) and placed into a Copley Scientific tergotometer pot with 500 mL city (Newcastle-upon-Tyne, UK) 125 tap water and stirred at a predetermined temperature (20 °C, 40 °C, 60 °C) at 150 rpm. At 6-minute intervals, 3 mL 126 aliquots of the wash liquor were removed, and 3 mL of water (pre-heated to the temperature of the experiment) added to 127 restore the experiment volume and repeated until 60 minutes had elapsed in total. Aliquots were measured by UV-Vis 128 spectroscopy and mean absorbance (A) values at 548 nm ($\lambda_{max-vis}$ of wash liquor) at $\lambda_{max-vis}$ were recorded against time (t) 129 for each temperature. The precise composition of the dye mixture evolved from the model wash load was not known, 130 however, to allow for a quantitative comparison of dye desorbed and adsorbed, properties of C. I. Reactive Black 5 were 131 used as it was observed from Raman studies that this dye was released in significant quantities; whilst this does not 132 represent an absolute quantification of moles of dye released, it allows for quantitative comparison between conditions. 133 Concentration (c) was calculated from A values based on the Beer-Lambert law ($A = \varepsilon cl$) using the molar extinction

- 134 coefficient (ε) for C. I. Reactive Black 5 in water (45.5 dm³ mmol⁻¹ cm⁻¹) [26], based on a pathlength (l) of 1 cm.
- 135

136 **2.6.** Adsorption kinetics measurements

137 Dye wash liquor was prepared from washing one of each t-shirt in the dark model load in a Kenmore 600 Series washing 138 machine filled with 45 L of city (Newcastle-upon-Tyne, UK) water on the Supersetting for 18 minutes, with a water 139 temperature of 25 °C. This wash liquor from the model retail load was used as a source of dye for kinetic adsorption 140 experiments involving adsorption of dyes in that wash liquor onto a white swatch of 100% cotton fabric. 500 mL of wash 141 liquor was added to a Copley Scientific tergotometer pot and brought to a predetermined temperature (20 °C, 40 °C, 60 142 °C). One 5 cm × 5 cm square of white, 100% cotton tracer fabric (470 ± 14 mg) was added and the wash liquor stirred at 150 rpm. At 6-minute intervals, 3 mL aliquots of liquor wash collected and 3 mL of fresh wash liquor (pre-heated to the

temperature of the experiment) added to restore the experiment volume, and repeated until 60 minutes had elapsed in

- total. Aliquots were measured by UV-Vis spectroscopy and mean A at 548 nm ($\lambda_{max-vis}$ of wash liquor) were recorded
- against time (*t*) for each temperature; *c* was calculated as described above in 2.6.
- 147

148 **2.7. Microfibre release experiments**

- 149 Microfibres were collected and quantified using a similar method to Napper & Thompson [14]. Washing machines were 150 thoroughly cleaned prior to testing and confirmed to release no fibres by running a cycle without any garments inside. 151 Water was collected from the drain hose of the washing machine for the complete wash and rinsing process. After each 152 wash, any fibres remaining in the machine were washed out and collected by running an additional 'washout' cycle with 153 no detergent after the fabrics were removed. All water from the test run and washout cycle was then filtered through 20 154 um CellMicroSieve® (BioDesign Inc.), washed with clean tap water, fibres re-suspended in clean tap water and then 155 filtered onto pre-weighed Whatman No 541 filter paper using a Buchner funnel under vacuum before drying overnight at 156 50 °C. The mass of collected fibres was then calculated, considering the percentage loss in filter paper weight on drying, 157 measured by taking the average % loss of 10 similar papers. Microfibre release data are presented as mg of released fibre 158 per kg initial dry fabric load mass.
- 159

160 **3. Results**

161 **3.1.** Impact of washing temperature and time on dye fading and dye transfer on full scale

162 Two parameters that consumers can easily change in their washes are the length of time of a wash and the temperature of 163 a wash. Therefore, these combined parameters were examined in full scale, consumer relevant tests using washing 164 machines and detergent. Considering the effect of colour loss after repeated laundering, Figure 1 shows the colour change 165 (ΔE_{2000}) between unwashed t-shirts and the same t-shirt after 16 wash cycles, and it is observed that there is significantly 166 greater colour loss observed for the 40 °C Cotton Short (85 min) cycle in comparison with the Cold Express (30 min) 167 cycle. These observations provide evidence that in a 'real' situation increases in washing time and washing temperature 168 increase colour loss over repeated laundering.



Figure 1: Colour loss (expressed by mean ΔE_{2000}) for a selection of fabric samples from both vibrant and dark colours

loads after 16 wash cycles, washed on 40 °C Cotton Short and Cold Express programs. Error bars show ± standard deviation of 3 repetitions.



Figure 2. Raman spectra showing identification of (a) C. I. Reactive Black 5 (1) on cotton (standard), (b) navy cotton t-shirt, (c) deep navy cotton t-shirt, (d) C. I. Disperse Red 356 (2) on polyester, and (e) red polyester t-shirt.

Comparison of the UV-vis spectra of wash liquors of each t-shirt demonstrated that, generally, cotton fabrics liberate significantly more dye than polyester fabrics. The low release of dye from polyester is due to the high T_g of the

- 182 fibre, and associated inaccessibility of dye to wash water, combined with the hydrophobicity of disperse reducing their 183 ability to be released into an aqueous environment [27]. The exception is the black polyester fabric (D9), which does 184 liberate a significant colour, suggesting a higher level of dye loading on the fabric. $\lambda_{max-vis}$ for the combined model wash 185 solution was 548 nm. Figure 2 shows examples of Raman spectra of the t-shirts making up the retail dark load; these were 186 compared to spectra of known dyes on fabric; Raman spectroscopy is a sensitive technique that can measure the light 187 scattered from a dye in a fabric [28]. Certain functional groups have characteristic spectral features (similar to FT-IR), 188 hence, dyes in the model load can either be fully identified through matching spectra with dye library standards, or specific 189 functional groups can be identified. The presence of water-soluble functional groups, such as -SO₃, ruled out certain dye 190 types such as vat dyes, which generally do not have such functional groups [29].
- 191 As Shown in Figure 2a-c, peaks at 489 cm⁻¹ are attributed to an SO₂ group, and peaks at 1189 cm⁻¹ and 1213 cm⁻¹ 192 ¹ are attributed to the sulfatoethylsulfone (–OSO₂O–) group, as determined from peak tables and spectra of known dyes; 193 these functional groups are typically found in certain classes of reactive dyes [30]. Further assignment of phenyl/naphthyl 194 ring (1592 cm⁻¹) and aromatic primary amine (1287 cm⁻¹) functions, alongside general comparison of Raman spectra, 195 enabled confirmation of the presence of C. I. Reactive Black 5 (1) on the navy cotton t-shirt and deep navy cotton t-shirt 196 (Figure 2a). As Shown in Figure 2d-e, peaks at 883 cm⁻¹ are attributed to a C–O–C group, and peaks at 1150 cm⁻¹ are 197 attributed to an aromatic ring/C-O-C moiety. Further assignment of aromatic ring (1539 cm⁻¹ and 1001 cm⁻¹) and 198 CH₂/CH₃ (1427 cm⁻¹) functions, alongside general comparison of Raman spectra, enabled confirmation of the presence 199 of C. I. Disperse Red 356 (2) on the red polyester t-shirt (Figure 2d).
- 200 Considering the effect of colour transfer over repeated laundering, it was observed that for most white receiver 201 fabrics, significantly greater colour transfer to the tracer fabrics was observed for the 40 °C Cotton Short (85 min) cycle 202 in comparison with the Cold Express (30 min) cycle. These observations provide evidence that, in a 'real' situation, 203 increases in washing time and washing temperature increase dye transfer.
- 204

205 **3.2.** Kinetic experiments on dye desorption and re-adsorption

In a real laundry scenario, as described above in 3.1, dye desorption and dye re-adsorption occur simultaneously during washing. However, it is useful to separate these two phenomena to understand the system more completely; dye transfer is a two-part process, vagrant dye must be initially released from dyed fabric in order to be subsequently transferred to receiver fabric. In order to gain better understanding of these two processes kinetic desorption and re-adsorption experiments were carried out separately on a small scale; any understanding gained may offer insights into how to reduce one or both phenomena in practice.

Figure 3 shows the concentration of dye released/desorbed (q) with increasing t for each temperature, and it is observed for all temperatures that there is a steady increase in dye desorption over 60 min. It is also evident that as temperature increases greater dye desorption occurs as evidenced by a higher concentration of dye in the water phase; it is additionally noted that the difference in dye released between 20 °C and 40 °C is significantly greater in comparison with than the difference between 40 °C and 60 °C.





221

Figure 3. Mean q_t values of wash liquor dye desorption from dark model wash load over time at 20 °C (blue), 40 °C (green) and 60 °C (red). Error bars show ± standard deviation of three repetitions.

The data from dye desorption experiments were fitted to a pseudo-second order kinetic model [31], as described in equation 2:

(2)
$$\frac{\partial q_t}{\partial t} = k(q_e - q_t)^2$$

where q_t and q_e are the concentrations of dissolved sorbate adsorbed at a given time (*t*) and at equilibrium, respectively (mol g⁻¹). The term k_2 is the rate constant of the pseudo-second order equation (g mol⁻¹ min⁻¹). For the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of equation 2 becomes equation 3:

228
$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$
 (3)

229 A plot of t/q_t against t that produces a straight line, confirms the model, where dye desorbed at equilibrium $(q_e) = 1/s$ lope, 230 and the pseudo-second order rate constant $(k_2) = \text{slope}^2/\text{intercept}$. Figure 4 shows high correlation $(R^2 > 0.98)$ of the data 231 with the pseudo-second order model at each temperature. q_e values for dye desorbed at equilibrium obtained herein are 232 theoretical and calculated from the slope of the kinetic data over the 60-minute desorption experiment; q_e values are not 233 measured experimentally as the system does not reach equilibrium by 60 min. From the data in Figure 4 it is clear that q_e 234 increases with T, indicating greater total desorption of dye at higher temperatures in agreement with the qualitative data 235 in Figure 3. It is also clear that k_2 decreases with T, indicating a higher rate of desorption of dye at higher temperatures, 236 where the data also suggests a significant difference between the rate of dye desorption comparing 20 °C and 40 °C, 237 which is likely to be due to the increased thermal energy in the system, which is also in agreement with the observations 238 of the full scale study and the benefits of cold-quick cycles. However, the difference in the rate dye desorption between 239 40 °C and 60 °C is not as significant, suggesting that above 40 °C, similar levels of dye are desorbed over the period 240 examined.



T (°C)	R ²	<i>q</i> ℯ (µmol g⁻	<i>k</i> ₂ (g µmol⁻¹
		1)	min⁻¹)
20	0.989	0.025	6.05
40	0.991	0.044	2.77
60	0.989	0.053	2.26

Figure 4. Plot of t/q_t vs. t confirming a pseudo-second order reaction for dye desorption at 20 °C (blue), 40 °C (green) and 60 °C (red). Inset table shows accompanying data from kinetic model.

Figure 5 shows q_t values over time for dye adsorbed onto the acceptor fabric swatches with increasing t for each temperature. It is observed that q_t increases over time and plateaus for all temperatures and as temperature increases greater re-adsorption of dye occurs as evidenced by a higher concentration of dye on the receiver fabric.

248

244



249

252

Figure 5. Mean q_t values over time as dye is removed from wash liquor solution by adsorption onto acceptor fabric swatch at 20 °C (blue), 40 °C (green) and 60 °C (red). Error bars show ± standard deviation of 3 repetitions.

253 The data from re-adsorption experiments were also fitted to a pseudo-second order kinetic model. Figure 6 shows 254 high correlation ($R^2 > 0.99$) of the data with the pseudo-second order model at each temperature. Again, q_e values for dye 255 desorbed at equilibrium obtained herein are theoretical and calculated from the slope of the kinetic data over the 60-256 minute desorption experiment; q_e values are not measured experimentally even though the system does appear to reach 257 equilibrium over 60 min. From the data in Figure 6 it is clear that q_e increases with T, indicating greater total re-adsorption 258 of dye at higher temperatures in agreement with the qualitative data in Figure 5. It is also clear that k_2 decreases with T, 259 indicating a higher rate of re-adsorption of dye at higher temperatures, where the data also suggests a significant difference 260 between the rate of dye desorption comparing 20 °C and 40 °C. However, as in the case for dye desorption, the difference 261 in the rate dye desorption between 40 °C and 60 °C is not as significant, suggesting that above 40 °C, similar levels of

262 dye are desorbed over the period examined.

In this nil-detergent system, once a temperature of 40 °C is reached, time is more influential for dye release than temperature is. The majority of dye re-adsorption occurs within the first six minutes of the wash; thereafter, q_t levels out, suggesting an equilibrium is achieved between desorption and re-adsorption. At 60 °C, q_t still increases slightly after 60 minutes, suggesting that temperature and time can have a combined effect, with an increase in both parameters producing an increased adsorption.



T (°C)	R^2	<i>q</i> ℯ (µmol g⁻	k₂ (g µmol⁻¹ min⁻
		1)	1)
20	0.995	1.424	6.47
40	0.996	1.593	1.03
60	0.996	1.918	0.17

Figure 6. Plot of t/q_t vs. t confirming a pseudo-second order reaction for dye adsorption at 20 °C (blue), 40 °C (green) and 60 °C (red). Inset table shows accompanying data from kinetic model.

270

271 **3.3.** Impact of washing temperature and time on release of microfibres

272 The effect of washing temperature and time on release of microfibres for model loads (Figure 7) shows that the combined 273 total of microfibres released from all fabrics was significantly greater for the 40 °C Cotton Short (85 min) cycle in 274 comparison with the Cold Express (30 min) cycle. This is compelling evidence that in a 'real' situation that higher 275 temperature and longer wash time increase the mass of microfibres released during washing. Higher temperatures cause 276 more rapid swelling in water of cellulosics fibres, approximately twice the rate at 60 °C compared to 20 °C [32], which 277 may contribute to microfibre generation and release in combination with the mechanical action of the washing machine. 278 What is also evidenced is that on the eighth and sixteenth wash that significant numbers of microfibres are still being 279 released from the fabrics, suggesting that there is a consistent mechanism of microfibre generation and release throughout 280 the life of the fabrics.

In this work we have not quantified the released microfibres in terms the extent to which individual fibre types or fabric constructions release microfibres – what is reported is total microfibre release. Neither have we measured individual fibre properties. However, these investigations are of significant interest and is the subject of ongoing research in this area by the authors and in recent publications by others [15,33,34].



Figure 7. Microfibres released (mg of released fibre per kg initial dry fabric load mass) after 1, 8 and 16 wash cycles for
 garment retail loads washed on Cold Express and 40 °C Cotton Short programs: (a) vibrant colours load; (b) dark colours
 load.

290

286

291 **4. Discussion**

Laundering of clothing has a large contribution to the energy expenditure of a clothing product, hence, reducing time and temperature is desirable. Washing clothing at 30 °C rather than 40 °C saves approximately 40% of the energy used per load, and washing at 20 °C instead of 40 °C saves approximately 66% of the energy used per load [35], hence the findings herein have significance in terms of potential energy savings and associated carbon emissions. It is clear from this research that lower temperature, reduced time (cold-quick) laundry also has significant sustainability benefits in terms of reduced colour loss, dye transfer and microfibre release. Significantly greater colour loss and greater colour transfer were observed for a 40 °C, 85 min wash cycle compared to cold-quick (25 °C; 30 min) cycle.

299 Desorbing dyes were found to mainly be reactive dyes. From fundamental kinetic studies, it was observed that 300 significant increases in both rate of dye desorption and total dye desorption occurred when increasing from 20 °C to 40 301 °C, but the difference in dye release between 40 °C and 60 °C was not as significant; the same kinetic trends were observed 302 for dye transfer. Microfibre release was significantly greater for the 40 °C, 85 min cycle in comparison with the cold-303 quick cycle, and this effect continued with further washes. These results mean that reducing time and temperature in 304 laundry could have a significant impact in terms of extended garment longevity and reduced dye and microfibre liberation 305 into the environment, in addition to energy savings. Colour change (and associated dye release into wastewater) and 306 microfibre generation contribute to both pollution of water and more frequent disposal of clothing by the consumer 307 (leading to increased landfill waste). Sustainability benefits from reducing wash time and temperature could be significant 308 in terms of reducing pollution and carbon footprint of clothing in use. The challenge for the detergent industry is to enable 309 the same high standards of cleaning to be achieved in these emerging colder quicker conditions compared to conventional 310 warm and long cycles. This is likely to require further advances in technology such as enzymes.

311

312 Acknowledgements and Funding Information

The authors thank Procter & Gamble and The Engineering and Physical Sciences Research Council (EPSRC) for the provision of an Industrial CASE studentship to LC to allow her to conduct her PhD studies. This research was supported

- 315 by Procter & Gamble and EPSRC through Industrial CASE studentship Voucher 15220142.

316				
317	Author contributions			
318	All	All authors have given approval to the final version of the manuscript.		
319				
320	Dec	laration of competing interest		
321	All	authors have no conflict of interest.		
322				
323	Ref	erences		
324	1.	Textile Exchange, Preferred Fiber & Materials Market Report 2018, https://store.textileexchange.org/wp-		
325		content/uploads/woocommerce_uploads/2019/04/2018-Preferred-Fiber-Materials-Market-Report.pdf (accessed		
326		20 th November 2019).		
327	2.	J. Mowbray, S. Glover, Busting Myths, Ecotextile News, 94 (2019) 11-14.		
328	3.	S. Ceurstemont, Green is the new black: Redesigning clothes to save the planet, New Sci., 3166 (2018) 36-40.		
329	4.	R.S. Blackburn, J.D. Payne, Life cycle analysis of cotton towels: impact of domestic laundering and		
330		recommendations for extending periods between washing, Green Chem., 6 (2004) 59-61.		
331	5.	R.S. Blackburn, S.M. Burkinshaw, A Greener Approach to Cotton Dyeings with Excellent Wash Fastness, Green		
332		Chem., 4 (2002) 47-52.		
333	6.	X. Li, J. Song, J. Guo, Z. Wang, Q. Feng, Landfill leachate treatment using electrocoagulation, Procedia Environ.		
334		Sci., 10 (2011) 1159-1164.		
335	7.	R.S. Blackburn, Natural Polysaccharides and Their Interactions with Dye Molecules: Applications in Effluent		
336		Treatment, Environ. Sci. Technol., 38 (2004) 4905-4909.		
337	8.	C. Zaharia, D. Suteu, A. Muresan, R. Muresan, A. Popescu, Textile wastewater treatment by homogenous oxidation		
338		with hydrogen peroxide. Environ. Eng. Manag. J. 8 (2009) 1359-1369.		
339	9.	C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, A critical review on textile wastewater		
340		treatments: Possible approaches, J. Environ. Manage., 182 (2016) 351-366.		
341	10.	R. Padhi, Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation, Int. J. Environ. Sci., 3		
342		(2012) 940-955.		
343	11.	M. Zarkogianni, I. Eleftheriadis, N. Nikolaidis, E. Tsasaroni, Synthesis, characterization and application of anionic		
344		metal complex azo dyes as potential substitutes for Cr-complex dyes, Text. Res. J. 84 (2014) 2036-2044.		
345	12.	WRAP, Valuing our clothes: the evidence base,		
346		www.wrap.org.uk/sites/files/wrap/VoC%20FINAL%20online%202012%2007%2011.pdf, 2012 (accessed 3rd		
347		April 2019).		
348	13.	J. Boucher, D. Friot, Primary Microplastics in the Oceans: A Global Evaluation of Sources, International Union for		
349		Conservation of Nature: Gland, Switzerland, 2017.		
350	14.	C.M. Rochman, M.A. Browne, B.S. Halpern, B.T. Hentschel, E. Hoh, H.K. Karapanagioti, L.M. Rios-Mendoza, H.		
351		Takada, S. Teh, R.C. Thompson, Policy: Classify plastic waste as hazardous, Nature, 494 (2013) 170-171.		
352	15.	I.E. Napper, R.C. Thompson, Release of synthetic microplastic fibers from domestic washing machines: Effects of		
353		fabric type and washing conditions, Marine Pollution Bull., 112 (2016) 39-45.		
354	16.	A. Sanchez-Vidal, R.C. Thompson, M.Canals, W.P. de Haan, The imprint of microfibres in southern European deep		
355		seas, PLoS ONE, 13 (2018) e0207033.		
356	17.	A.K. Jha, C. Sharma, N. Singh, R. Ramesh, R. Purvaja, P.K. Gupta, Greenhouse gas emissions from municipal solid		
357		waste management in Indian mega-cities: A case study of Chennai landfill sites, Chemosphere, 71 (2008) 750-758.		

- 358 18. J. Oakes, S. Dixon, Adsorption of dyes to cotton and inhibition by polymers, Color. Technol., 119 (2003) 140-149.
- M.N. Amin, R.S. Blackburn, Sustainable chemistry method to improve the wash-off process of reactive dyes on
 cotton, ACS Sustain. Chem. Eng., 3 (2015) 725-732.
- 361 20. J. Oakes, S. Dixon, Adsorption of dyes to cotton and inhibition by surfactants, polymers and surfactant-polymer
 362 mixtures, Color. Technol., 119 (2003) 315-323.
- 363 21. S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as
 364 semiconductor catalyst, J. Hazard. Mat., 112 (2004) 269-278.
- B.Y. Gao, Q.Y. Yue, Y. Wang, W.Z. Zhou, Color removal from dye-containing wastewater by magnesium chloride,
 J. Environ. Manage., 82 (2007) 167-172.
- 367 23. N. Dafale, N. Nageswara Rao, S.U. Meshram, S.R. Water, Decolorization of azo dyes and simulated dye bath
 368 wastewater using acclimatized microbial consortium Biostimulation and halo tolerance, Bioresour. Technol., 99
 369 (2008) 2552-2558.
- R. Rathinamoorthya, N. Ayswarriya, R. Kadambari, R. Sreelatha, K.G. Janani, Optimization of dye transfer
 inhibition properties of polyvinylpyrrolidone for reactive dye on cotton fabric, Indian J. Fibre Text., 41 (2016) 432439.
- 373 25. G. Sharma, W. Wu, E.N. Dalal, The CIEDE2000 colour-difference formula: Implementation notes, supplementary
 374 test data, and mathematical observations, Color Res. Appl., 30 (2005) 21-30.
- S.-H. Chang, K.-S. Wang, H.-H. Liang, H.-Y. Chen, H.-C. Li, T.-H. Peng, Y.-C. Su, C.-Y. Chang, Treatment of
 Reactive Black 5 by combined electrocoagulation–granular activated carbon adsorption-microwave regeneration
 process, J. Hazard. Mat., 175 (2010) 850-857.
- 378 27. S.M. Burkinshaw, Physico-Chemical Aspects of Textile Coloration, Society of Dyers and Colourists: Bradford, UK,
 379 2016.
- 380 28. J. Was-Gubala, W. Machnowski, Application of Raman spectroscopy for differentiation among cotton and viscose
 381 fibers dyed with several dye classes, Spectrosc. Lett., 47 (2014) 527-535.
- 382 29. G. Hallas, Chemistry of anthraquinonoid, polycyclic and miscellaneous colorants. In Colorants and auxiliaries, J.
 383 Shore (Ed.), Society of Dyers and Colourists: Bradford, UK, 1990.
- 384 30. C.V. Stead, Chemistry of reactive dyes. In Colorants and auxiliaries, J. Shore (Ed.), Society of Dyers and Colourists:
 385 Bradford, UK, 1990.
- 386 31. Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451-465.
- 387 32. G.I. Mantanis, R.A. Young, R.M. Rowell, Swelling of compressed cellulose fiber webs in organic liquids, Cellulose,
 388 2 (1995) 1-22.
- 389 33. F. De Falco, E. Di Pace, M. Cocca, M. Avella, The contribution of washing processes of synthetic clothes to
 microplastic pollution, Sci. Rep. 9 (2019) 6633.
- 34. L. Yang, F. Qiao, K. Lei, H. Li, Y. Kang, S. Cui, L. An, Microfiber release from different fabrics during washing,
 Environ. Pollut. 249 (2019) 136-143.
- 393 35. Energy Savings Trust, Save energy in your home, www.energysavingtrust.org.uk, 2019 (accessed 9th August 2019).
 394