Understanding and controlling dye transfer in the laundry process

Lucy Jane Cotton

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The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Domestic dye release and dye transfer is an environmental problem that occurs every time a garment is washed. While it has been previously recognised, insufficient knowledge on types of dyes, mechanisms and wash settings exists to provide a significant decrease of dye transfer from clothes that make up an average consumer wash load. In particular, there is not currently a sustainable solution to reduce dye transfer from textiles.

The research herein explored dye identification through Raman spectroscopy of a validated model wash load, mechanistic understanding of wash parameters, ionic strength and pH on both dye release and dye re-adsorption, and full wash testing to provide less dye transfer. It was found that reactive dyes predominantly make up a consumer wash load, and that high ionic strength and low pH increased the substantivity of the dye for the fibre.

Cold washes and quick washes were beneficial for reducing dye transfer, with the duration of the wash proving to be the most significant factor. Acidified detergent provided benefits for the reduction of dye transfer from this model.

Denim was also investigated as a specialty textile that is a known dye transfer donor. Analytical and supramolecular chemistry were used to understand the staining species. Wash parameters, pH, agitation and presence of detergent were studied for their effects on dye transfer. The staining species from denim was found to be a complex between indigo and cellulose oligomers. It was attracted most to wool fibres and after further investigation, was attracted most to arginine of the molecules tested, with which it formed a hydrogen bonded complex. This suggested compatibility between arginine and the staining species, which is likely anionic. Addition of arginine to wash loads reduced dye transfer from denim, as did acidified detergent.

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1.1. Impact of textiles on the environment

Global fibre production for textiles in 2018 was over 105 million tonnes, of which over 73 million tonnes was synthetic and non-renewable, mainly polyester, nylon, acrylic and olefin fibres.[1] The clothing industry creates carbon emissions of 1.2 billion tonnes a year, which is greater than aviation. The manufacture and consumer care of clothes consumes high levels of water, energy and non-renewable resources.[2] 'Fast fashion' is now a global phenomenon as more people are wearing more clothes for shorter times. Those garments tend to start their lives in factories in South and East Asia, often far from their end users. China is the world's biggest exporter of clothes and currently the US is the world's largest importer of textiles, which in 2018 had a value of US $30 billion.[3] Waste from textiles can be divided into two groups: pre-consumer textile waste and post-consumer textile waste.[3] Pre-consumer textile waste refers to the waste generated during the processing of these textiles; post-consumer textile waste refers to waste generated during consumer use and disposal.

1.1.1. Pre-consumer textile waste

The World Bank, an organisation that funds sustainable solutions for reducing poverty, estimated that between 17-20% of all industrial water pollution comes from the dyeing and chemical finishing of textile fabrics.[4] Dyestuffs may enter waterways from both dye synthesis plants as well as from effluent of industries using dyestuffs, such as the textile industry.[5] 10-15% of total dye used in dyehouses may be found in wastewater, with the proportion of this varying due to dye type, fibre of application and relative degree of dye fixation.[6] These dyes may be recalcitrant: resistant to light, temperature and microbial decomposition.[5] The presence of dyeing effluent in a watercourse is aesthetically undesirable, but has a more serious environmental impact; dyeing effluent has high biochemical oxygen demand (BOD) and consequently algae overpopulate watercourses and block sunlight transmission into water; this, combined with the spectral absorption

of the dye itself, can affect photosynthetic processes of flora in the immediate environment, hence, a reduction in oxygen levels in the water is observed; in severe cases this can result in suffocation of aquatic flora and fauna.[7] In addition, the dyestuffs may be toxic to aquatic organisms due to the presence of subsistent metals and chlorine.[8] Even small amounts of dyes, such as 1 ppm for certain dyestuffs, are capable of causing noticeable discoloration of water and having these negative effects.[9]

1.1.2. Wastewater treatment

It is accepted that in the case of dye effluent, removal of the colour of the dye molecules is sufficient (often achieved by bleaching methods), rather than full removal of the organic compounds.[9] Due to the large variety of synthetic dyes that may be present in wastewater, conventional methods have different effectiveness of degradation of these species, meaning not all are broken down and that some toxic and environmentally damaging degradation products may still be left behind.[10,11] Wastewater contains solid soils which can be suspended within textile effluent, therefore, one of the first processes of treating wastewater is to sieve out the larger solid soils such as fibres, lint and yarns.[12] For smaller soils, flocculation is a technique that is used, whereby small particles are stirred together to slowly form larger, heavier particles which sink and can be collected.

Once the solid soils are removed, the focus remains on the liquid waste which after dyeing processes, usually has a high pH and so, requires neutralisation with multivalent cations. This can be followed by further flocculation and addition of coagulation agents such as aluminium sulfate and ferric chloride to remove any floating particles and decolourise the textile wastewater. Another technique is ozonation, the introduction of ozone into the wastewater which degrades organic compounds by acting as a strong oxidising agent. This technique reduces chemical oxygen demand (COD), colour and toxicity of wastewater. In a similar manner, the Fenton reaction can be employed.[12] Strong oxidising agents are added to wastewater to degrade organic compounds. An acidic solution with Fe^{2+} ions is then added. This reaction can reduce COD of textile wastewater by around 80%.

While these physical and chemical processes perform well to treat wastewater, they can also be expensive and produce toxic intermediates. Therefore, biological methods of wastewater treatment have also been assessed for performance such as the use of enzymes or even whole cells to break down unwanted molecules. Adsorption and sedimentation are two biological methods for removing chemicals from wastewater. Some microorganisms such as *Galactomyces geotrichum*, *Saccharomyces cerevisiae*, and *Trichosporon beigelii*, have also been found to degrade some dye substances in anaerobic conditions. Laccases are multi-copper containing enzymes which can degrade aromatic structures such as anthraquinonoid moieties, although not all reactive dyes. However, high anionic strength may cause deactivation of the enzyme.

1.1.3. Post-consumer textile waste

When considering the impacts of post-consumer textile waste in the environment, the 'use' phase of the life cycle assessment is very important. Laundry has a significant effect on the environmental impact of clothing;[13] analysis undertaken by the Waste and Resources Action Programme (WRAP) in the UK suggests that carbon emissions associated with washing, drying and ironing account for about a third of the lifetime emissions of clothing.[14] Microfibres released when synthetic textiles are washed are a global problem and account for over a third of all plastic reaching the open ocean,[15] which can have a devastating effect on wildlife.[16] However, it is not only microfibres from synthetic textiles that are a problem. Recent research into the composition and abundance of microfibers in seafloor sediments from southern European seas found 6,965 ± 3,669 microfibres m^{-2}, varying in fibre length from 3 to 8 mm, and of these fibres identified nearly 80% were cellulosic, comprising dyed cotton, linen (natural cellulose) and regenerated cellulose (*e.g*. viscose).[17] Acrylic jumpers are also significant (followed by polyester) with over 700,000 individual fibres released from an average 6 kg wash load; washing powder and water temperature were only minor factors in influencing fibre release.[18]

The Department for Environment Food and Rural Affairs (DEFRA) also complied a report in 2009 to investigate cleaning of clothing during the use phase affects the environment.[19] It was found that clothes washing used resources such as water and fossil fuels, produced both solid and hazardous waste such as packaging and detergent waste, emissions of NO_x and SO_x, and water eutrophication and toxicity from detergents. It identified benefits from; line drying clothes instead of tumble drying, low temperature wash settings and high spin settings for drying. The study found that more concentrated detergents, both powders and liquids had lower impacts on the environment when a life cycle assessment was considered.

A 2017 report compiled by WRAP entitled ‘Valuing Our Clothes- the true cost of how we design, use and dispose of clothing in the UK’ highlights core opportunities to save money and resources across clothing life cycle.[14] These opportunities include the reduction of environmental impacts from laundering of clothes, and keeping clothes out of landfill, which has become an increasing concern as consumers adopt trends like ‘fast-fashion’.

In the UK, it is estimated that 350,000 tonnes of clothing are thrown away by consumers and end up in landfill every year.[14] These textiles pose an environmental threat whilst in landfill, such as the release of greenhouse gas methane into the atmosphere during the degradation of some items.[20,21] This degradation can take a relatively long time, between around 6 months and 20 years.[3] Other synthetic textiles such as polyester are resistant to biodegrading and so continue to take up land during disposal. Dyes and other chemicals used in the processing of these textiles can also leach into the soil of landfills and collect in groundwater.[22]

Another implication of ‘fast-fashion’ is increased production of clothing. The need to produce more clothes to satisfy the consumerist trend further exacerbates these environmental issues.[23] For example, the growing of cotton, one of the most dominant fabrics, for new clothing requires vast amounts of water and pesticides which is not sustainable and creates further waste.[24]

In the UK, it is reported that the average item of clothing is in active use for only 3.3 years and that between 2015 and 2016 opportunities to practice

greener disposal behaviours such as donating, selling, recycling or passing on old clothes were down between 3 to 4%.[25] Research has also found that 1 in 10 consumers stated they would cease wearing a garment after a laundry mishap, such as dye transfer, shrinkage or garment damage, rather than attempt to mend or alter it themselves which can further shorten the lifespan of garments.14 It has been estimated that increasing the active use of clothing by as little as 3 months, before disposal, can produce a reduction in carbon, water and waste footprints by 5-10%.[14]

1.1.4. Dye transfer and measurement with ΔE_{2000}

Domestic dye transfer occurs when dye migrates out of a 'donor' textile and redeposits elsewhere onto an 'acceptor' textile during a wash causing discoloration, which in the case of high colour contrast garments, may be the same textile. Dye transfer refers to this phenomenon occurring in an aqueous environment.[26] Transfer can also occur in a dry environment through contact of textiles, this is referred to a 'crocking'. When dye transfer occurs, it deteriorates the appearance of a garment and may make garment donating to charities and textile banks less likely.

Dye transfer can be measured and quantified using the parameter 'Delta E'. This parameter measures the difference between two colours in the colour sphere, using the coordinates on the L* (lightness), a* (green-red) and b* (yellow-blue) axes (Figure 1.1).[27] Every colour can be described using co-ordinates on these axes. The currently recommended version from the CIE of colour measurement, based on experimental data is ΔE_{2000}, published in 2001.[27,28] ΔE_{2000} can be calculated using equation 1.1:

$$\Delta E^*_{2000}\sqrt{\left(\frac{\Delta \mathrm{L}'}{k_L S_L}\right)^2 + \left(\frac{\Delta C\prime}{k_C S_C}\right)^2 + \left(\frac{\Delta H\prime}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C\prime}{k_C S_C}\right)\left(\frac{\Delta H\prime}{k_H S_H}\right)} \quad (1.1)$$

Where $\Delta C'$ is the difference in chroma, $\Delta H'$ is the difference in hue, $k_L S_L$ is a lightness weighting function, $k_C S_C$ is a chroma weighting function and $k_H S_H$ is a hue weighting function, and R_T is a rescaling factor of the CIELab a* axis.

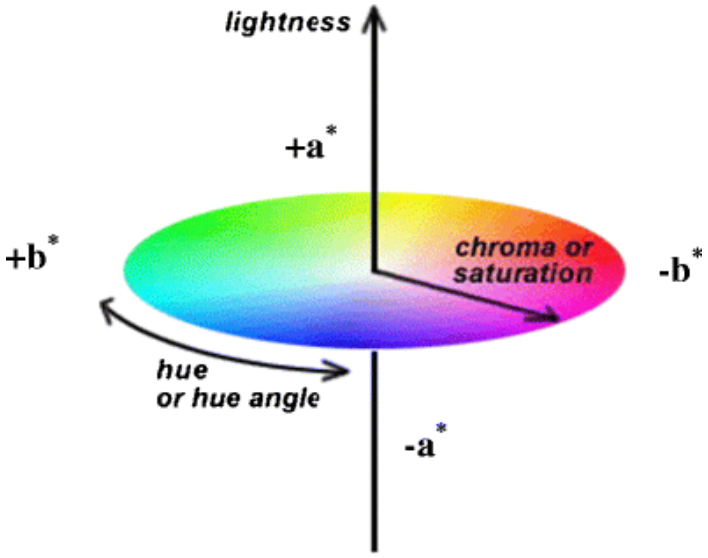


Figure 1.1: CIELAB colour space.[29]

1.2. Detergents and detergent ingredients

In recent years in the UK, there has been a shift away from powder detergents towards liquid tablet detergents. However, powder detergents do continue to sell and make up a significant percentage of overall sales in laundry detergents.[29] This trend is due to consumers being able to reduce the cost per load and with liquid tablets and enjoy their convenience and higher usability. Because of this shift in buying behaviour, manufacturers are concentrating on new innovations and product launches in the liquid tablet detergent area, thus making other detergent types such as bar detergents and handwash detergents unable to compete performance-wise.

It has also been reported that many consumers are not loyal to a laundry brand and instead, choose which products to buy based on affordability.[29] In order to stand out in the competitive market, manufacturers are looking to appeal to consumers in different ways, such as by improving the perfume aspect of their detergent products. Another route that is being taken by manufacturers, is to focus on producing more environmentally friendly detergents. For example, Tesco has launched its ‘Eco Active’ range of products which are formulated from plant-based ingredients and packaged in fully recyclable material.

Another innovation in the ‘green’ detergent field is the product ‘Day2’ from Unilever.[29] This spray aims to clean, soften, freshen and iron clothes and textiles which may not be soiled enough to require laundering. The idea of this product is to reduce the amount of clothing that needs to be washed in a washing machine, thus reducing water and energy consumption.

In 2018, there was still an increase in percentage value growth of laundry aids that protect colours of garments on the previous year, such as Colour catchers (14.7% increase), colour enhancers (8.6% increase) and whiteners (4.6% increase).[29] This suggests that detergents alone are still not sufficient at providing the colour care required by consumers.

Consumers want to spend less time on household chores such as laundry and so choose products which enable quick results.[30] Part of this may include the ability to wash garments of all different colours and fabric types together, in one combined wash. This may bring garments of different colours into contact with each other, increasing the risk of visible dye transfer.

1.2.1. Surface Active Agents

Surface active agents, or surfactants, are amphiphilic molecules comprising of a hydrophilic head group and a hydrophobic long chain tail group (Figure 1.2).[31]

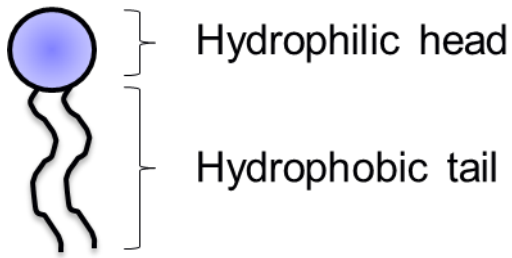


Figure 1.2: Schematic picture representing the head group and tail group of a surfactant molecule.

Surfactants increase wettability of water by lowering surface tension. They can also help loosen and remove soils and emulsify or suspend these soils

in the wash liquor. The amphiphilic nature of these molecules allows for structure sure as bilayers and micelles to be formed in aqueous media as shown in Figure 1.3. The formation of these structures such as micelles allows for encapsulation of soils in the wash liquor, removing them from solution. The hydrophilic head groups may be anionic, cationic, amphoteric or non-ionic in nature. Cationic surfactants typically have a positively charged nitrogen atom in their head group.

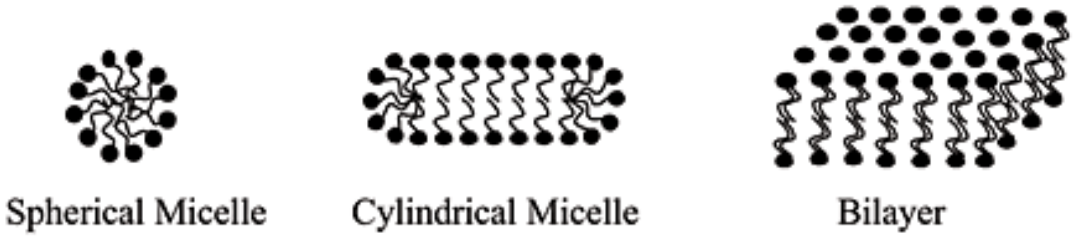


Figure 1.3: Schematics of common structures formed by surfactant molecules in aqueous solution.[32]

1.2.2. Builders

The purposes of a detergent builder include binding to water hardness ions such as calcium and magnesium to soften water which can occur through sequestering or precipitation.[30] Other functions include the dispersal of soluble salts such as calcium carbonate so as to not form larger crystals within the wash liquor, suspend colloidal soils in the wash liquor, to buffer the wash liquor to maintain an alkaline pH, and to improve the performance of surfactants. Inorganic builders include sodium tripolyphosphate. Organic builders include nitrilotriacetic acid (NTA) and ethyldiaminetetraacetic acid (EDTA) (Figure 1.4) which may act as substitutes for traditional inorganic phosphate-containing builders that were environmentally hazardous through eutrophication.[33]

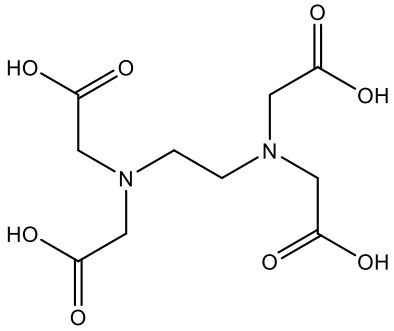


Figure 1.4: Structure of EDTA (M_w: 292.24 g mol^{-1}).

Acrylic acid homopolymers and copolymers have been used as builders to perform the necessary functions.[34] Polycarboxylates have also been utilised as builders particularly in powder processing to improve stability and homogeneity of a detergent slurry while reducing viscosity.

1.2.3. Anti-redeposition agents

Anti-redeposition agents ensure that soils which have been loosened during washing are prevented from redepositing back onto textiles. The most popular anti redeposition agent is the anionic carboxymethylcellulose (CMC) (Figure 1.5), which functions by adsorbing onto soils forming an anionic complex. This CMC-soil complex is repulsed by anionic fibres such as cotton.[31] Other anti-redeposition agents may be non-ionic polymers which adsorb onto soils and prevents redeposition by steric repulsion.

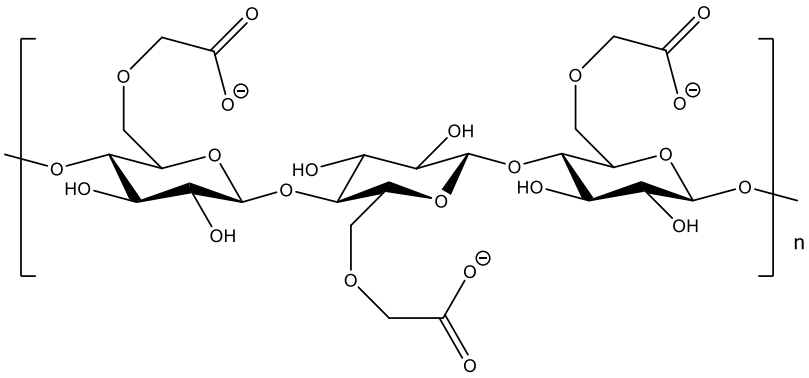


Figure 1.5: Structure of carboxymethylcellulose.

1.2.4. Enzymes

The main kinds of enzymes present are proteases, lipases, amylases and cellulases; the enzymes function to break down components such as proteins, lipids, starches and cellulose respectively.[35] While proteases, lipases and amylases are primarily used to break down soils that may be found on unwashed garments, cellulases are included to maintain the overall fabric care by biopolishing and removing pills that can form on garments.

1.2.5. Bleaching agents

Bleach and bleaching agents are present in detergents to decolourise soils and stains, as well as to preserve the whiteness of garments.[31] In dry, powder detergents, oxygen bleaches will contain an inorganic peroxygen compound such as sodium perborate tetrahydrate or sodium percarbonate. When dissolved, these compounds produce hydrogen peroxide which is the oxidizing agent that breaks up or decolourises soils. Liquid detergents tend to contain hydrogen peroxide without the need for a precursor.

1.2.6. Other ingredients

Perfumes, dyes and opacifiers are added to detergent compositions to provide pleasing aesthetics to the product.[31] Other additives include optical brighteners, which are fluorescent blue-white dyes such as anionic diamino stilbene derivatives.[36] They mask yellowing that may be noticeable on light coloured garments.

1.3. Previous technologies for domestic dye transfer inhibition

1.3.1. Laccase enzymes

Laccases are multi-copper enzymes, which can perform one electron oxidation of both aromatic and non-aromatic substrates.[37,38] By using molecular oxygen as the final electron acceptor, the only by-product

released is water and so, this is an environmentally friendly method of dye de-coloration. It has been found that laccases can be employed to break down aromatic structures in dyes, destroying the chromophore and thus discolouring the dye.[11] Lignin peroxidase enzymes have been previously investigated for the degradation of synthetic dyes, but laccases are preferred alternatives due to their ability to successfully degrade aromatic dyestuffs in more favourable conditions. It has been found that laccases are more suitable as they are able to more rapidly degrade anthraquinonoid dyes, in comparison with indigoid and azo dyes.[3,39] Laccases may have potential as additives to detergents to target domestic dye transfer.[40] However, as laccases have been used to bleach textiles such as denim before, the concentration of these enzymes in a detergent system needs to be carefully controlled as unwanted dye fading of textiles and garments is possible.[37]

1.3.2. Solid state adsorption

Solid state adsorption has been investigated as a means for collecting fugitive dyestuffs predominantly in industrial wastewater treatment plants. Many investigated adsorbents include waste products from food and agriculture industries, and activated carbon, which is efficient at adsorbing acid dyes that can be difficult to remove with cheaper materials.[41,42] However there has also been some research into the development of domestic products that consumers can employ in their wash to reduce dye transfer. One such product is a nonwoven anionic- colour-catcher fabric which is added to washing machine drum along with the garments to be washed.[43] This fabric is coated with cationic dye-sequestering agents that in theory should attract any anionic dye in the wash liquor and remove it from solution. While this idea is simple to employ, it has not fully eliminated the problem of dye transfer. One reason for this may be because the dye type that the colour-catcher was designed to adsorb is anionic dyes. It is not currently known if these dyes are still significantly used on modern garments and if so, how many of these garments make up an average UK wash load. The cationic nature of the colour catcher means it will not adsorb cationic dyes such as basic dyes which are used to colour acrylic fibres. While these

fabrics may adsorb anionic dyes, in an average wash load, the comparative surface area of a colour catcher sheet is lower than the garments in the wash. Therefore, migrant dye particles may never come into contact with the colour catcher sheet before they re-adsorb onto an acceptor garment in the wash. The non-woven colour-catcher is only a single use item and so is disposed of after each wash. For these reasons, colour-catcher nonwovens do not provide a broad enough nor sustainable reduction in dye transfer.

1.3.3. Bleaching agents

Bleaching agents have also been investigated for their ability to reduce dye transfer, by bleaching the migrant dye in the wash liquor before it redeposits.[44] This mechanism requires the migrant dye to be bleached as soon as it has left the donor textile before it reaches an acceptor textile. Some detergents contain bleaching agent catalysts to increase the speed at which a bleaching agent can perform. These catalysts need to be stable enough to maintain the bleaching effect while dye is slowly released from garments throughout a wash. However, there have been issues with these catalysts such as the 1,4,7-trimethyl-1,4,7-triazocyclonoane manganese complex (Mn-TMTACN) (Figure 1.6) that caused serious deterioration to clothing and lead to product recall.[45]

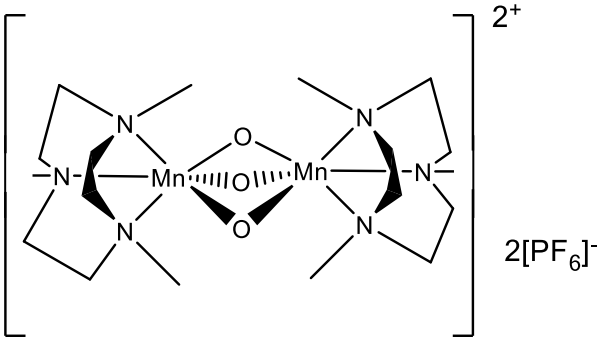


Figure 1.6: Structure of Mn-TMTACN bleaching agent catalyst (M_w: 589.30 g mol^{-1}).

1.3.4. Surfactant encapsulation

Dye molecules have previously been found to have an affinity for surfactants in aqueous environments. Cationic and zwitterionic surfactants above their critical micelle concentration, in formulations containing non-ionic and/or anionic surfactants hold soils and vagrant dye within micelles in solution (Figure 1.7) and so, prevent their redeposition onto fabric.[46] However, below their critical micelle formulations, in sub-micellar regions, 1:1 ratio of surfactant to dye complexes can form and this can actually increase the dye's deposition onto cotton.[47] In fact, this technique has often used to gain uniform, level dyeing on cellulosics.[48] Therefore controlled concentrations of surfactants are required to ensure that dye transfer isn't exacerbated by increased dye desorption onto acceptor fabrics.

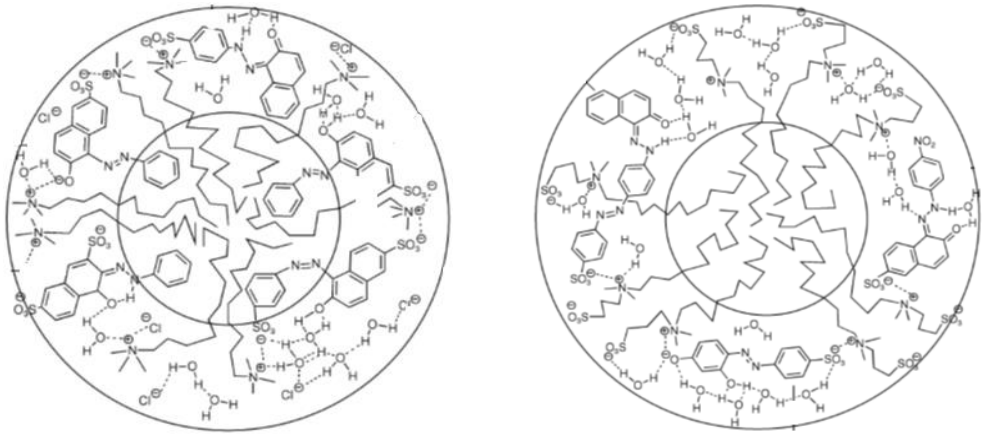


Figure 1.7: Azo dyes encapsulated in cationic micelle (left), and zwitterionic micelle (right).[47]

1.3.5. Dye transfer inhibitor polymers

Water-soluble polymers such as polyvinylpyrrolidone (PVP) (Figure 1.8) act as specialty polymers called dye transfer inhibitors (DTIs) which can be added to detergents during manufacture.[49] PVP and its derivatives are polymers designed to complex with dyestuff that has migrated from textiles, and hold them in solution thus preventing redeposition onto other textiles.[50] The driving force for the complexation between DTI polymers and dyes comes from both supramolecular interactions, such as electrostatic interactions, as well as entropic gain from the desolvated polymer.[51]

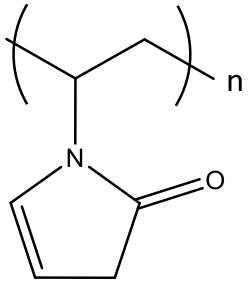


Figure 1.8: Polyvinylpyrrolidone structure.

Original DTI polymers were designed to work on direct dyes and were noted to have limited efficiency against dye transfer from other dye classes.[34] There can be interactions between these non-ionic polymers and anionic surfactants, which are normally present in detergent formulations, which cause the polymers to be incorporated inside surfactant micelles, and reducing their performance. However, if the surfactant system is instead made up of equal ratios of anionic and non-ionic surfactants, this issue is reduced.

1.4. Previous literature targeting of dyes

While it is known that dye transfer occurs, and indeed which dyes exhibit poor wash fastness, the identification of dyes that bleed in modern consumer textiles is little understood. The assumptions made about the problematic dyes have dominated and directed previous research. Current DTIs still work on the assumption that direct dyes are the most problematic dye species and so have often only targeted them,[52] however, most cellulosic fibres are now dyed with reactive dyes and hydrolysed, unfixed reactive dyes pose a highly significant issue in terms of desorption and staining.

In previous research of industrial dyebaths, technical fabrics are used or dyebaths are simulated, using known dye standards, but even applying optimal parameters for simulated dye removal to real-life textile effluent yields insufficient results due to the difference between authentic textile effluent and synthetic dye solutions.[53,54,55,56] The implication of this is that the

chosen dyes in these investigations do not sufficiently represent dyes used on real consumer items, mainly due to lack of knowledge and traceability in the complex, modern, global garment manufacture and supply chain.

Several times in the literature, it is mentioned that azo dyes (synthetic dyes which contain an –N=N– bond) are the largest and therefore 'most important' class of dyes to target when wanting to decolorize textile effluent. However the literature then goes on to discuss methods of decolourization of dyes such as Methyl Orange and Methyl Red (C.I. Acid Red 2).[57,58,59,60] These dyes, typically used as pH indicators instead of as textile colourants, are significantly smaller molecules than more commonly used textiles azo dyes, such as reactive dyes. This difference in chemical size may mean that techniques to discolour Methyl Red may be sterically hindered by larger dyes such as C.I. Reactive Red 195 (Figure 1.9).

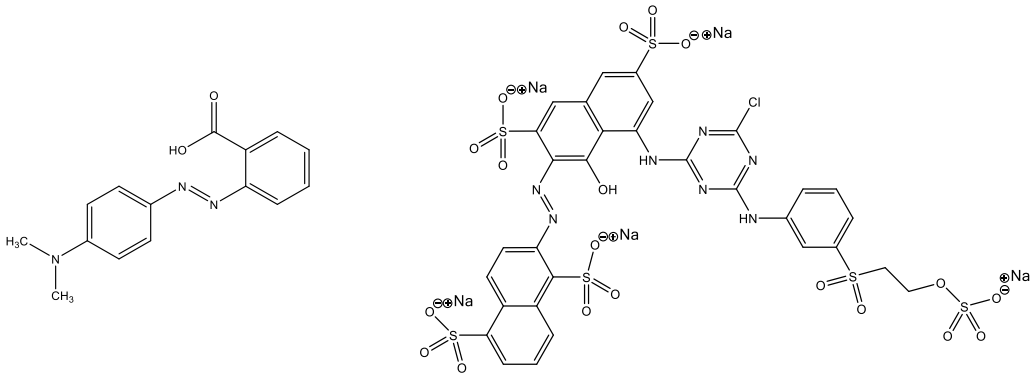


Figure 1.9: Structure of C.I. Acid Red 2 (left, M_w: 269.30 g mol^{-1}) and C.I. Reactive Red 195 (right M_w: 1136.32 g mol^{-1}).

Other literature produced synthetic textile wastewater using dyes such as erythrosine, which is a food colouring and is also a smaller molecule than most reactive dyes.[61] Because of this, the proposed method of decolourization may not be effective for garment dye transfer. Therefore, the validity of this research is reliant on the correct dye classes being targeted. Moreover, many technologies which have been developed in previous literature refer to wastewater treatment plant applications and may not be practical to scale down to a domestic washing solution.[62]

1.5. Fibre composition for apparel

1.5.1. Natural fibres: cellulose, wool and silk

Natural fibres may be subcategorised as being either cellulose based, such as cotton and flax, or proteinaceous such as wool and silk. Cotton is the most dominant of the cellulosic fibres with around 25 million tonnes produced in 2016.[3] It is composed almost entirely of pure cellulose (Figure 1.11), as well as small amounts of water, lignin and pectin.[63,64] Cotton fibres have a multi-layered cell wall structure consisting of (from outmost to innermost): the cuticle, primary wall, winding layer, secondary wall and lumen (Figure 1.10).[3]

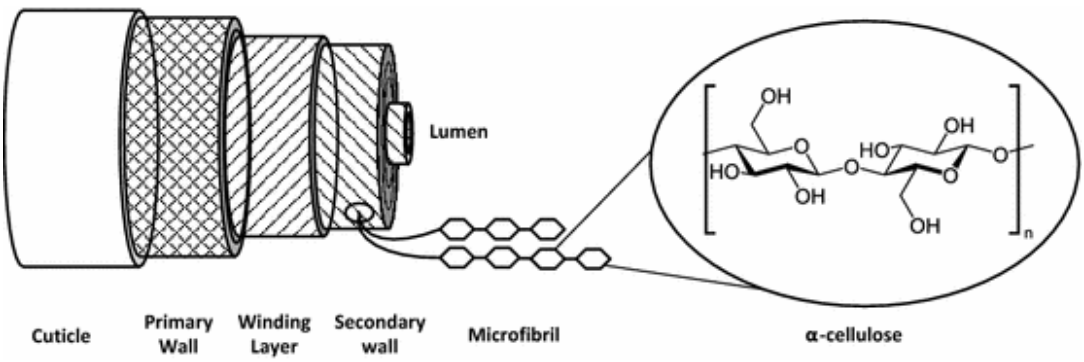


Figure 1.10: Structure of cotton fibre.[3]

Natural cellulosic fibres tend to have shared characteristics including: high moisture absorption, swelling in water, high resistance to degradation in alkaline solutions and low resilience.[65] Growing cotton requires high amounts of water, pesticides, insecticides and fertilizers which have negative impacts on the environment.

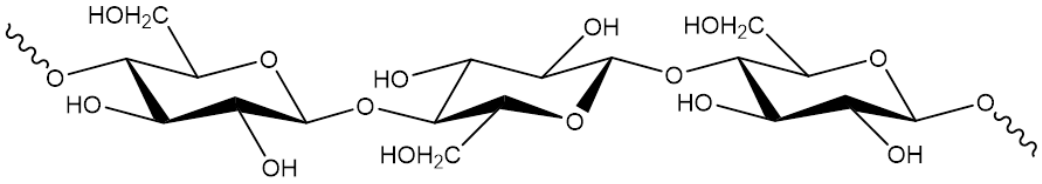


Figure 1.11: Cellulose is a polymer of D-glucose monomers, linked together by β-1,4-glycosidic bonds.

The cotton fibre contains both crystalline and amorphous regions. In the crystalline regions, the cellulose polymer chains are highly organised and so can interact with neighbouring chains through hydrogen bonding and Van der Waals interactions. The amorphous region contains disordered polymer chains without correct geometry for intermolecular bonding to occur between chains. Because of this, amorphous cellulose regions are more easily hydrolysed by cellulase enzymes.

Natural proteinaceous fibres share characteristics such as: good resilience, highly hygroscopic and hydrophilic, alteration of mechanical properties when water is absorbs, harmed by alkalis, chlorine bleach and perspiration, and not readily flammable.[65] Wool grows in the hair follicles of an animal and has distinctive overlapping surface cells known as scales.[65] The sub-microscopic structure is composed of an outer cuticle, a cortex and a medulla. Wool from sheep is the most commonly used for textiles as it is the most abundant. The chemical structure is composed of amino acids which are joined together with a dipeptide bond to form a keratin polymer.[66] The different amino acids that can make up the keratin polymer have unique functional side groups which have different chemical properties. Polar amino acids in the polymer account for hydrophilicity of the fibre, whereas sulfur-containing amino acids like cysteine make the fibre susceptible to degradation from moths and beetles. The size of the amino acid side groups can affect how closely the polymer chains pack together.[65] Wool fibres are around 25-30% crystalline and 75-80% amorphous. Therefore, a range of colourants and chemicals can be used on wool to alter its appearance and properties. Disulfide bonds, covalent bonds that occur between two sulfur atoms found in amino acids such as cysteine, can form between polymer chains, increasing fibre

strength (Figure 1.12). Ionic bonds can also form between amino acids such as aspartic acid and arginine.

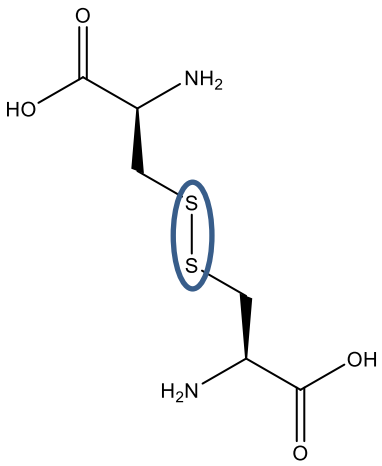


Figure 1.12: Disulfide bond (circled) between two cysteine molecules.

Silk is produced by the larvae of certain insects such as spiders and silkworms, the latter of which is typically used in industry. Silk strands are taken directly from a cocoon and an outer coating of sericin is dissolved away so that the fibres may be used.[65] Silk is composed of amino acids that form a polypeptide called fibroin. Approximately 86% of fibroin is made of the three amino acids glycine, alanine and serine (Figure 1.13). Because the side chains of these amino acids are small, the fibroin polymers may pack together closely, forming hydrogen bonds and so, around 70-75% of silk fibre is estimated to be crystalline which increases the strength of the fibre. Silk can absorb water due to being both hygroscopic and hydrophilic.

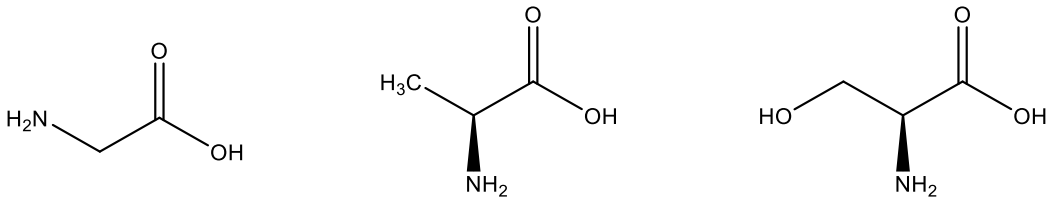


Figure 1.13: Structure of amino acids (from left to right) glycine (M_w: 75.07 g mol^{-1}), L-alanine (M_w: 89.09 g mol^{-1}) and L-serine (M_w: 105.09 g mol^{-1}).

1.5.2. Synthetic fibres: acrylic, cellulose diacetate, nylon and polyester

During 2007 to 2010, demand for synthetic fibres rose from 55.5% to 60.1% as it has been reported that cotton blended with synthetic fibre has higher customer preference.[65] Synthetic fibres are produced by combining small, organic molecules with water and air. Typical properties of synthetic fibres include: lowest moisture regain and softening temperatures (in comparison to natural fibre counterparts), highly oleophilic, high electrical resistivity which can cause static build-up, resistance to moths, mildew and fungi, and toughness.

Acrylic fibres are long chain polymers that must contain at least 85% by weight acrylonitrile units.[65] In an acrylic homopolymer, acrylonitrile is the monomer (Figure 1.14). The carbon-carbon double bond of acrylonitrile is broken, and further acrylonitrile molecules add on end-to-end in a chain-growth polymerisation. In copolymers other monomers such as acrylic acid and vinylpyrrolidone may be used. Purposes of the co-monomers may be to increase solubility of the polymer, by using anionic molecules, or to increase sites that can be dyed such as halogenated molecules. Some acrylics may be graft polymers which increases receptivity to dyeing due to the more open and less crystalline structure compared to other acrylics. However, acrylics are less crystalline than other synthetic fibres and bonding between polymer chains is weak.

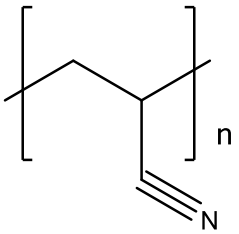


Figure 1.14: Structure of poly(acrylonitrile).

Acetate, diacetate and triacetate fibres are made from cellulose fibres, where a certain proportion of hydroxyl groups have been acetylated (Figure 1.15).[65] The acetylation makes the fibres hydrophobic, and due to the

random placement and bulkiness of the acetyl groups, the fibre does not crystallize and hydrogen bonding does not easily occur between polymer chains.

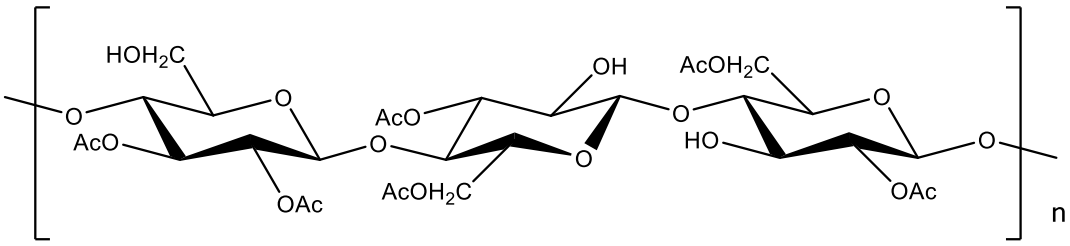


Figure 1.15: Structure of secondary cellulose acetate.

Nylon is formed from polyamide chains which can pack closely together to form hydrogen bonds and so, the fibre is highly crystalline (between 65-85%) and strong.[65] The fibres are named by the monomers that are used to produce them. Nylon-6 is produced from only one monomer, ε-caprolactam which requires a ring opening step before polymerisation. Nylon-6,6 is made from two different monomers, hexamethylene diamine and adipic acid (Figure 1.16). These monomers polymerise by forming an amide bond which has a by-product of water. The fibre is hydrophilic due to the polar amide bond, though longer nylons such as nylon-12 will have some regions of hydrophobicity.

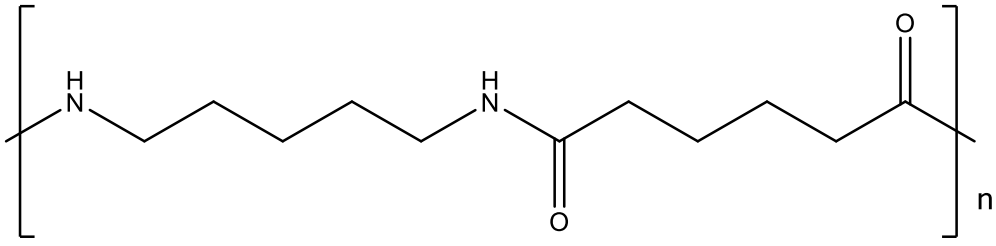


Figure 1.16: Repeat unit of nylon-6,6.

Polyesters are synthesised using a condensation polymerisation between an alcohol and a carboxylic acid, forming an ester bond.[65] One of the most

dominant polyesters is polyethylene terephthalate (PET) (Figure 1.17) which is synthesised from ethylene glycol and terephthalic acid. Polyesters are usually hydrophobic in nature and don't readily form hydrogen bonds due to the low polarity of the polymer. There can be close associations of the polymer chains through induced dipole-dipole interactions from delocalised electrons above and below the aromatic rings.

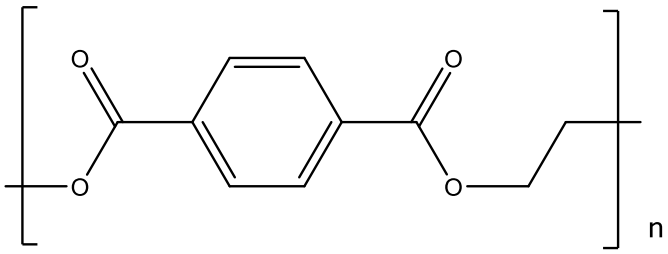


Figure 1.17: Structure of poly(ethylene terephthalate).

1.6. Dye classes

1.6.1. Direct dyes

Direct dyes are named so because they can be directly adsorbed onto a cellulosic fibre in an aqueous medium with electrolyte.[67] The dyes are usually planar and possess water-soluble groups, typically sulfonates or sulfonic acids. An example of a direct dye, C.I. Direct Blue 71, is shown in Figure 1.18. Direct dyes tend to provide bright colours. The wash fastness of direct dyes is poor due to the water solubility of the molecules. This can be reduced by a post-dyeing application of a cationic fixing agent such as poly(diallyldimethylammonium) (Figure 1.19).

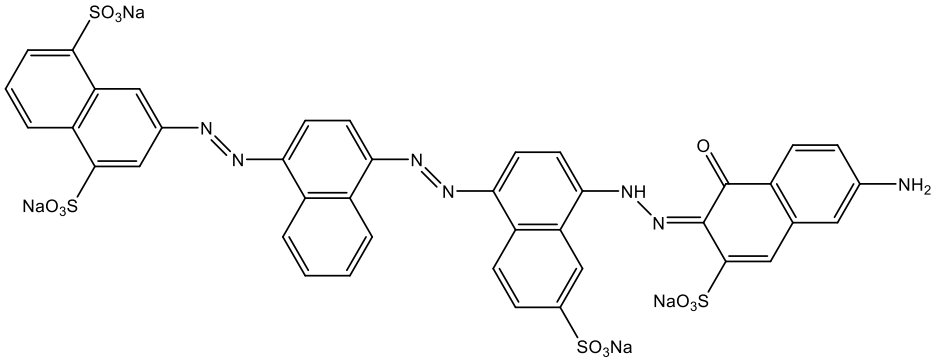


Figure 1.18: Structure of C.I. Direct Blue 71 (M_w 992.8 g mol^{-1}).

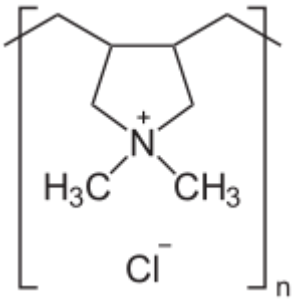


Figure 1.19: Structure of poly(diallyldimethylammonium).

1.6.2. Sulphur dyes

Typically used for the dyeing of cellulosics, sulphur dyes require weak reducing agents such as sodium sulfide to become soluble in water.[68] Once reduced in a heated aqueous solution, sulphur dyes exhibit substantivity for cellulosics and then become fixed onto the fibre during oxidation. These dyes are known for producing darker and more muted colours of textiles, such as greens, browns, blacks and blues. Sulphur dyes are defined by starting materials, consisting of mono- or poly-aromatics and the method of incorporating sulfur, the sulfurization technique, being used. Figure 1.20 shows the starting material of C.I. Sulphur Violet 5. Sulfurization techniques include, sulfur baking, where a starting material is heated with sulfur at around 250-300 °C, and polysulfide melting in which a suspension of starting materials and sulfur is stirred below 180°C until sulfurization is complete.

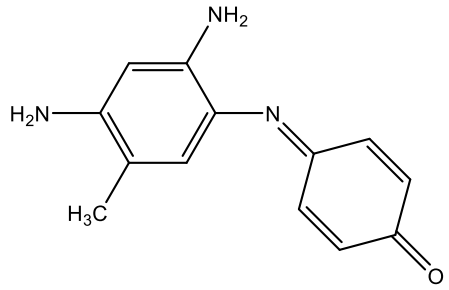


Figure 1.20: Structure of component of C.I. Sulphur Violet 5 (M_w: 226 26 $gmol^{-1}$).

1.6.3. Reactive dyes

Reactive dyes form strong covalent bonds with cotton resulting is strong wash fastness. The two main types of reactive dye are vinyl sulfone dyes, which undergo nucleophilic addition onto the cotton substrate, and halogeno-heterocyclic dyes which instead undergo nucleophilic substitution.[69] Reactive dyes require an alkaline pH and electrolyte to overcome charge repulsion with cotton in an aqueous dye bath. There can be hydrolysis of the reactive dye, whereby the dye reacts with water molecules instead of the intended cotton hydroxyl groups. This reduces the fixation of the reactive dye. An example of a reactive dye is shown in Figure 1.21.

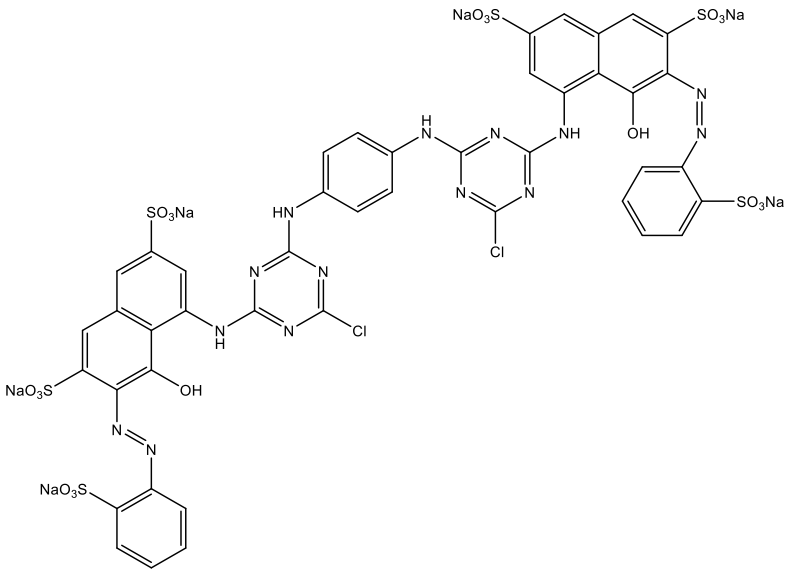


Figure 1.21: Chemical structure of dye C.I. Reactive Red 120 (M_w 1338.1 g mol^{-1}).

1.6.4. Vat dyes

Similar to sulphur dyes, vat dyes are not water soluble and require strong reducing agents to initiate the dyeing process onto cellulosic materials soluble.[68] Vat dyes typically have at least two carbonyl groups which can be reduced in alkaline conditions. This reduction alters the chromophore of the dye and thus is referred to as the leuco form of the dye. The water-soluble leuco dye can be absorbed by the cellulosic and is then oxidised back to the coloured parent for of the dye, thus mechanically trapping the dye within the fibres.[69] Indigo, a common vat dye, is shown in Figure 1.22.

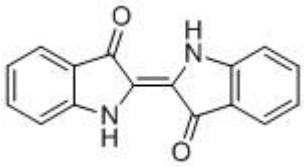


Figure 1.22: Chemical structure of dye indigo (C.I. Vat Blue 1) (M_w: 262.27 g mol^{-1}).

1.6.5. Disperse Dyes

Disperse dyes are insoluble non-ionic and are used to colour hydrophobic fibres, predominantly polyester (PET) however they may also be used on nylon, cellulose acetate and acrylic.[69] An example of a disperse dye is shown in Figure 1.23. These dyes may be loaded into pressurised machines to allow for diffusion of the dye into the substrate fibre. A reduction clear is often required afterwards to remove any unfixed dye that may cause staining if not removed.

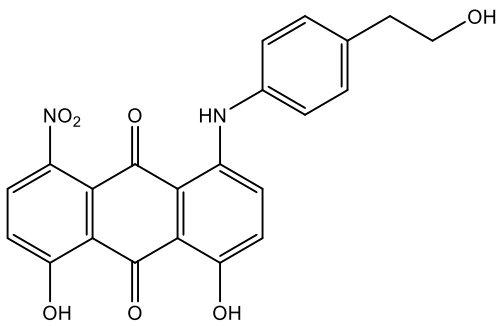


Figure 1.23: Structure of C.I. Disperse Blue 27 (M_w: 420.40 g mol^{-1}).

1.6.6. Acid dyes

Acid dyes are applied to fibres such as wool, nylon and silk from a dyebath using acidic or neutral conditions.[70] The acid dye group contains some individual dye classes such as azo dyes, anthraquinone dyes, and chrome dyes. Most acid dyes contain at least one $–SO_3Na$ group which can provide both water solubility and bonding capabilities to cationic fibres. An example acid dye is shown in Figure 1.24. These dyes can produce bright colours. Acid dyes may also be metal-complex dyes, similar to mordant dyes however acid dyes have the metal already incorporated into the dye structure and so, a mordanting step is not required.[69] Examples of such dyes include C.I. Acid Red 183 and C.I. Acid Black 60.

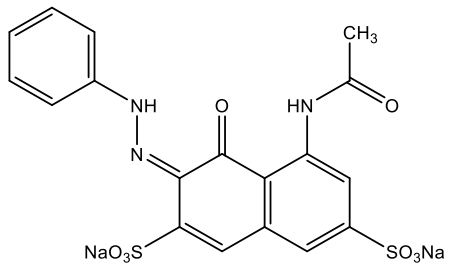


Figure 1.24: Chemical structure of dye C.I. Acid Red 1 (M_w: 509.40 g mol^{-1}).

1.6.7. Basic dyes

Basic dyes can be used to colour nylon and acrylic fibres.[69] These dyes are water soluble and become cationic in aqueous media, becoming electrostatically attracted to negatively charged fibres. The cationic charge of a basic dye may be localised to an ammonium ion, for example as with C.I. Basic Blue 22, or the charge may be delocalised over the dye, such as with C.I. Basic Violet 2 (Figure 1.25).

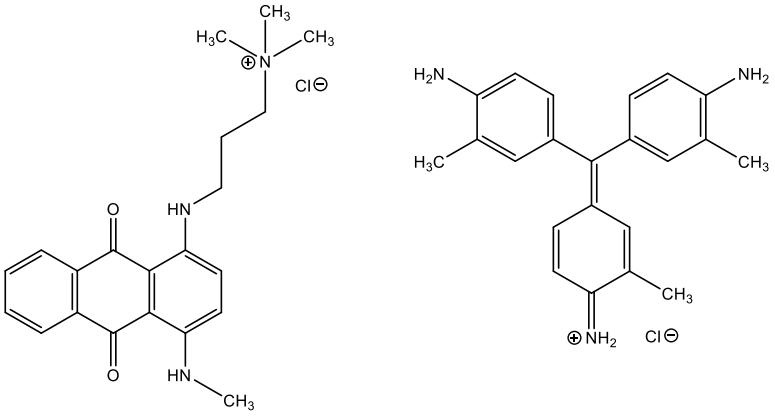


Figure 1.25: Structures of C.I. Basic Blue 22 (left, M_w: 387.90 g mol^{-1}) and C.I. Basic Violet 2 (right, M_w: 365.90 g mol^{-1}).

As there can be such strong electrostatic interaction between cationic dyes and negatively charged fibres, migrating of basic dyes in a dye bath can be poor. For this reason, retarding agents are included in the dyeing process which compete for the dyeing sites with the dye.[71] These compounds are typically quaternized long-chain amines which become cationic in the dye bath. This reduces the surface concentration of the dye on the fibre allowing for a slower rate of dyeing and more migration.

1.7. Purpose of the Research

Every time a garment is laundered, small amounts of dyestuffs are released into the wash liquor. These dyestuffs end up in wastewater streams where they have potentially environmentally damaging and toxic consequences as discussed earlier in this chapter. They also transfer onto garments within the wash, causing discoloration, which may accelerate the end-of-life point of a garment that may subsequently end up in landfill, releasing greenhouse gas emissions as it degrades. While there have been many previous studies investigating dye transfer and discharge into the environment during the manufacturing of textiles, there have only been a handful of academic studies that have investigated dye transfer during the use phase of clothes. It has been suggested that the level of dye transfer is higher when an anionic surfactant is present in a wash compared to a non-ionic surfactant.[72]

However, this research was limited to investigation of dye transfer from only direct dyes with the dye being in powdered form rather than as part of a dyed fabric. Another study did investigate dye transfer from reactive dyes, as well as direct dyes, on fabric. It was found that cationic fixing agents in conjunction with detergent may reduce colour loss caused by washing.[73] There has also been previous research into dye fading that was carried out using realistic laundry methods including a wash simulator and a washing machine.[74] The research showed that bleach within detergents did contribute to colour fading of dyed fabrics, and that this occurred to a higher extend in a washing machine, compared to the wash simulator, This could have implications for method development of a wash simulation. However, what is common between all of this previous research is that there doesn't seem to be any validation for why certain dyes that were investigated were chosen. There is no evidence presented which suggests that any of these tested dyestuffs are actually present in consumer products. In the UK, 97% of households contain washing machines and so, domestic clothes washing is likely to contribute in significant amounts to the overall dyestuffs released into the environment.[75] Therefore, it is important to understand more about the dyestuffs that are present on domestic clothes.

This research aims to identify dye classes that contribute most to domestic dye transfer, through employing analytical techniques and novel model development and validation. The specific objectives of this research are:

- To develop a method to validate a model wash load
- To employ this method to select a model wash load that is representative of current UK consumer wash loads
- To analyse dye species within this validated wash load
- To analyse dye transfer from this wash load
- To analyse dye transfer from Denim, a popular textile across the UK
- To understand parameters that contribute to dye transfer from both the model wash load and denim, and to access whether manipulation of these parameters may reduce dye transfer
- To employ green chemistry to reduce dye transfer from both the model wash load and denim.

This research has implications for both the detergent industry, as well as consumers. Recommendations for reduced dye release and transfer span detergent design and development to optimising wash settings in existing washing machines.

Chapter 2- Development and characterisation of model wash load

2.1. Introduction

Current Dye Transfer Inhibitors (DTIs) still work on the assumption that direct dyes are the most problematic dye species and so have often only targeted them, however, most cellulosic fibres are now dyed with reactive dyes and hydrolysed, unfixed reactive dyes pose a highly significant issue in terms of desorption and staining.[52] In previous research, technical fabrics are used or dyebaths are simulated, using known dye standards, and assumed problematic dyes. However, the outcomes from this research have not always been successful when transferred to 'real' consumer wash loads.[53,76,77,78] This is because there is such little information about which dyes are present in modern clothing and so often, research is focussing on dyes that are not relevant.

The purpose of this chapter was to understand the real effect of laundry on dye desorption and dye re-adsorption (staining) in a consumer-relevant system. A model wash load was developed to represent consumer wash loads and validated against real consumer garments. The validated wash load was then analysed to elucidate dyestuffs that were present on these fabrics.

2.2. Experimental

2.2.1. Materials and solvents

A dark model wash load and a bright model wash load were initially suggested by Procter & Gamble based on what was observed to be present in real consumer wash loads that were sent to the P&G Newcastle Innovation Centre. The dark model wash load comprised the following 11 t-shirts (Table 2.1):

Table 2.1: Dark model wash load details.

T-shirt Colour	T-shirt fabric	Retailer
Black	100% Cotton	Fruit of the Loom
Bottle Green	100% Cotton	Fruit of the Loom
Burgundy	100% Cotton	Fruit of the Loom
Deep Navy	100% Cotton	Fruit of the Loom
Light Graphite	100% Cotton	Fruit of the Loom
Navy	100% Cotton	Fruit of the Loom
Purple	100% Cotton	Fruit of the Loom
Royal Blue	100% Cotton	Fruit of the Loom
Black	100% Polyester	Fruit of the Loom
Grey and Red	50% Polyester, 25% Rayon, 25% Cotton	Bella Canvas
Red	100% Polyester Jersey	Gildan

The bright model wash load comprised the following 11 t-shirts (Table 2.2):

Table 2.2: Bright model wash load details

T-shirt colour	T-shirt fabric	Retailer
Fushia	100% Cotton	Fruit of the Loom
Azure	100% Cotton	Fruit of the Loom
Kelly Green	100% Cotton	Fruit of the Loom
Lime	100% Cotton	Fruit of the Loom
Orange	100% Cotton	Fruit of the Loom
Red	100% Cotton	Fruit of the Loom
Sunflower	100% Cotton	Fruit of the Loom
Sky Blue	100% Cotton	Fruit of the Loom
Sunflower and Kelly Green	100% Cotton	Fruit of the Loom
Aeriel	100% Cotton pre-shrunk jersey knit	Colortone
Rainbow	100% Cotton pre-shrunk jersey knit	Colortone

All t-shirts were size XL and were cut into 5 cm x 5 cm squares.

A selection of undyed, white acceptor fabrics were used in accordance with standard practice at Procter & Gamble dye transfer procedures. They were comprised of the following (Table 2.3):

Table 2.3: Acceptor fabric details.

Acceptor number	Acceptor fabric	Retailer
1	100% Cotton	Fruit of the Loom
2	100% Cotton	Anvil
3	100% Cotton	Gildan
4	100% Cotton	B & C
5	100% Cotton	Russell
6	100% Cotton	Russell
7	100% Polyester	Gildan
8	50% Polyester, 25% cotton, 25% rayon	Anvil
9	100% Polyester	Fruit of the Loom
10	65% Polyester, 35% Cotton	Kustom Kit
11	100% Polyester	Spiro
12	100% Polyester	Xpres
13	65% Polyester, 35% Cotton	Russell
14	100% Cotton	Tee Jays
15	100% Polyester	Spiro
16	95% Polyester, 5% Spandex	Tee Jays
17	52% cotton, 48% polyester	Bella Canvas
18	100% polyester	Gildan

Each acceptor fabric was first washed on a 40°C Cotton Short wash and air dried, according to P&G procedure, to remove any light soils that may have occurred during transportation. L*, a* and b* values of the undyed acceptor fabrics were measured after this wash. Each fabric was cut into a 5 cm x 5 cm square. One of each different acceptor fabric number (Table 2.3) was tagged onto a 27 cm × 30 cm piece of knitted 100% cotton provided by Warwick Equest, in accordance with Procter & Gamble standard practice.

Consumer loads were provided to Procter & Gamble from the general public in Newcastle, UK. Liquid detergents used were Ariel Original liquid detergent and Persil Colour gel liquid detergent. All other chemicals were purchased from Sigma-Aldrich.

2.2.2. General Procedures and Instrumentation

Raman measurements were carried out on model wash load fabrics to provide data on dyes present on these fabrics, by comparison to a Raman spectroscopy library of known dyes on fabrics. A Renishaw InVia confocal Raman microscope using a HPNIR laser of wavelengths 532 nm and 785 nm was used to perform these measurements. All spectra were measured between 200 cm^{-1} and 1900 cm^{-1}. Baseline corrections were carried out using WiRE software and other processing was carried out using Bio-Rad KnowItAll® Informatics System, Academic Edition. UV/visible spectrophotometry was carried out using a using a Jenway 6850 UV/Vis Spectrophotometer at 2 nm intervals. Spectral properties and wavelength of maximum absorbance ($\lambda_{max\text{-}vis}$) were evaluated. Colour measurement of fabric samples was conducted using a Gretag Macbeth Colour-Eye 7000A.

2.2.2.1. Model Validation

The 11 different whole t-shirts making up the dark model wash load and the acceptor fabrics tagged onto the cotton fabric were washed in a Miele 3622 washing machine using the following programmes (Table 2.4):

Table 2.4: Washing machine cycles used.

Programme Name	Total cycle length (hours)	Spin cycle (rpm)
40°C Cotton Short	1.25	1600
40°C Express	0.5	1600
Cold Express	0.5	1600
40°C Automatic	1.18	1200
Cold Automatic	1.15	1200

40°C Cotton short is the control wash cycle used at Procter & Gamble to represent an average consumer wash. This was performed to provide initial data about the wash load that could represent a real domestic wash.

The Express washes and the Automatic washes were selected to provide data on how both temperature and time as independent variables separately affected the level of dye transfer. It was not possible to alter the rpm of the spin cycles to be the same for these washes, however the spin takes place after the wash water has been removed and so it is expected that limited dye transfer takes place during this portion of the cycle.

Detergents used were as following: 70 mL directly into each washing drum of Ariel Original Liquid detergent. After the full wash cycle, acceptor fabrics were left to air dry for 24 h and then CIELab colour measured. ΔE_{2000} was calculated using equation 1.1 for each acceptor fabric and the comparison unwashed acceptor fabrics.

2.2.2.2. Dye liberation from individual items in model load

In order to gain absorbance information about the dark wash load as a whole, a benchtop experiment was conducted to liberate dye from swatches of the items in the wash load. Five of each colour t-shirt swatches (5 cm × 5 cm) were 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.

2.2.2.3. Desorption measurements

Benchtop desorption measurements were conducted to collect kinetic data from the model wash load. Three 5 cm × 5 cm swatches of the 11 coloured t-shirts (33 swatches , total mass = 14 g) were added to 500 mL city water in a Copley Scientific tergotometer pot at a predetermined temperature (20 °C, 40 °C, 60 °C) and stirred at 150 rpm. Ionic strength was altered using NaCl; pH was altered using HCl and NaOH. For non-temperature variable measurements, water was used at 40 °C. At 6 min intervals, 3 mL aliquots of the wash liquor were removed, and 3 mL of water added to restore the wash volume; aliquots were measured by UV/vis spectroscopy. Average absorbance (A) values at $\lambda_{max\text{-}vis}$ were recorded against time (t).

2.2.2.4. Adsorption measurements

A sample of wash liquor from the model wash load in water was prepared for dye adsorption studies. A top-loading washing machine was used to extract dyestuffs from the model wash load into water as these kinds of washing machines typically have higher agitation levels that front-loading washing machines, allowing for maximum dyestuffs to enter the wash liquor. This is beneficial as the initial absorbance of the wash liquor will be higher and it is easier to observe any changes in the absorbance value. Dye wash liquor was prepared from washing one of each t-shirt in the dark retail load in a Kenmore 600 Series washing machine filled with 45 L of city water on the Supersetting for 18 minutes, with a water temperature of 25°C, a pre-existing method for operating this machine. 500 mL of this wash liquor was added to a Copley Scientific tergotometer pot and brought to a predetermined temperature (20 °C, 40 °C, 60 °C) with one 5 cm × 5 cm square of white, 100% cotton acceptor fabric (470 ± 14 mg). Ionic strength was altered using NaCl. pH was altered using HCl and NaOH. For non-temperature variable measurements, wash liquor was used at 40 °C. The wash liquor was stirred at 150 rpm. At 6 minute intervals, 3 mL aliquots of liquor wash collected and

replaced with 3 mL of fresh wash liquor. These aliquots were then measured for Ultraviolet- visible trace using a Jenway 6850 UV/Vis Spectrophotometer and the absorbance is plotted over time. Average *A* values at $\lambda_{max\text{-}vis}$ were recorded against *t*.

2.3. Results and Discussion

2.3.1. Model Development

Two model wash loads were proposed to accurately represent an average consumer wash load. A 'bright load' was made up of t-shirts in orange, pink, lime green, sky blue and yellow colours, while a 'dark load' was made up of navy, black, bottle green, burgundy and purple colours. These two wash loads were measured for level of discoloration, as measured by ΔE_{2000}, of white acceptor materials and compared to a sample of consumer wash loads (Figure 2.1).

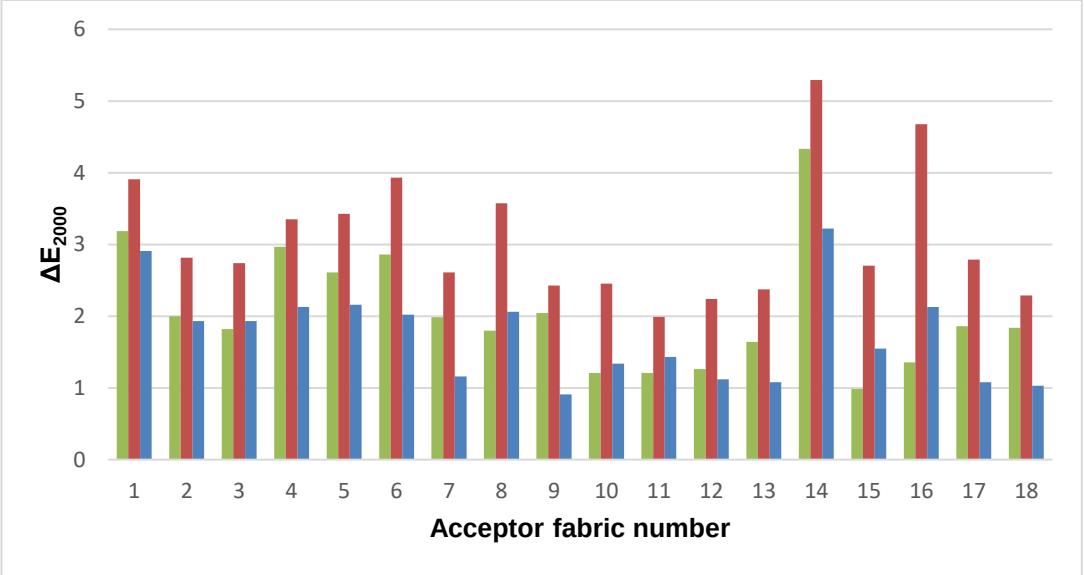


Figure 2.1: Dye transfer values from different initial wash loads on different white acceptor fabrics (Table 2.3). 'Bright load' is green (Table 2.2), 'Dark load' is red (Table 2.1) and average consumer loads are blue.

Initial wash tests suggested that the level of discoloration of acceptor materials from the consumer wash loads was more closely represented

using the bright wash load. However, level of discoloration alone does not fully validate the model. The hue of discoloration was also investigated to ensure that the dyestuffs that cause discoloration from a model accurately represented the consumer wash loads. L*, a* and b* values were compared as seen in Figure 2.2, Figure 2.3 and Figure 2.4 respectively.

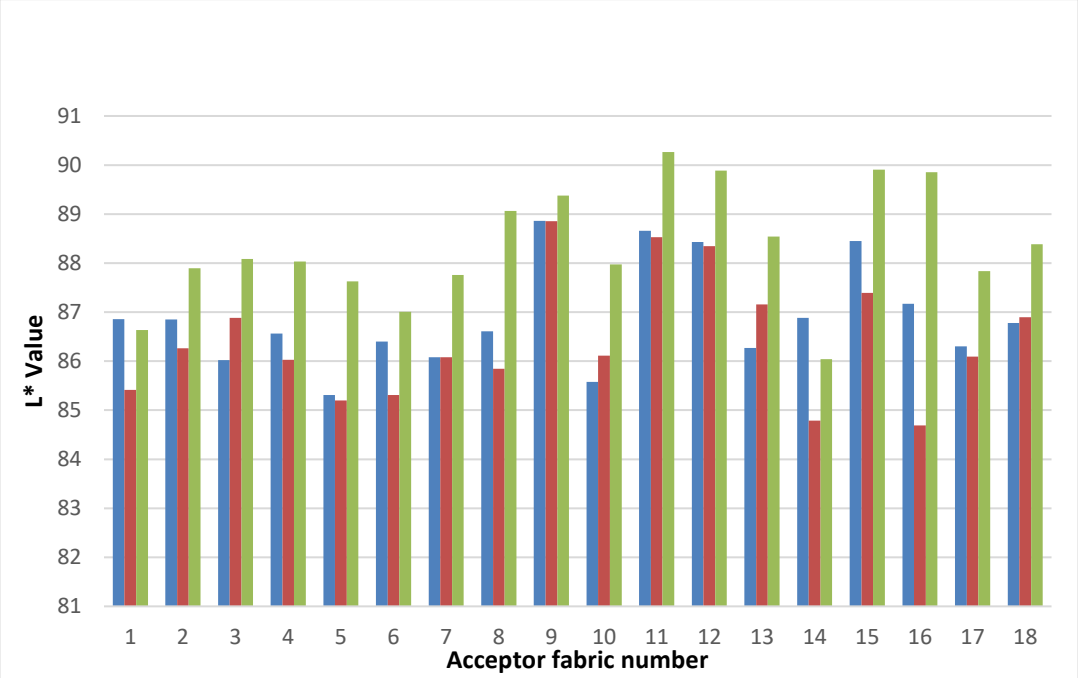


Figure 2.2: Comparison of L* values of acceptor fabrics (Table 2.3) washed with consumer wash loads (blue), 'dark wash load' (red) (Table 2.1) and 'bright wash load' (green) (Table 2.2).

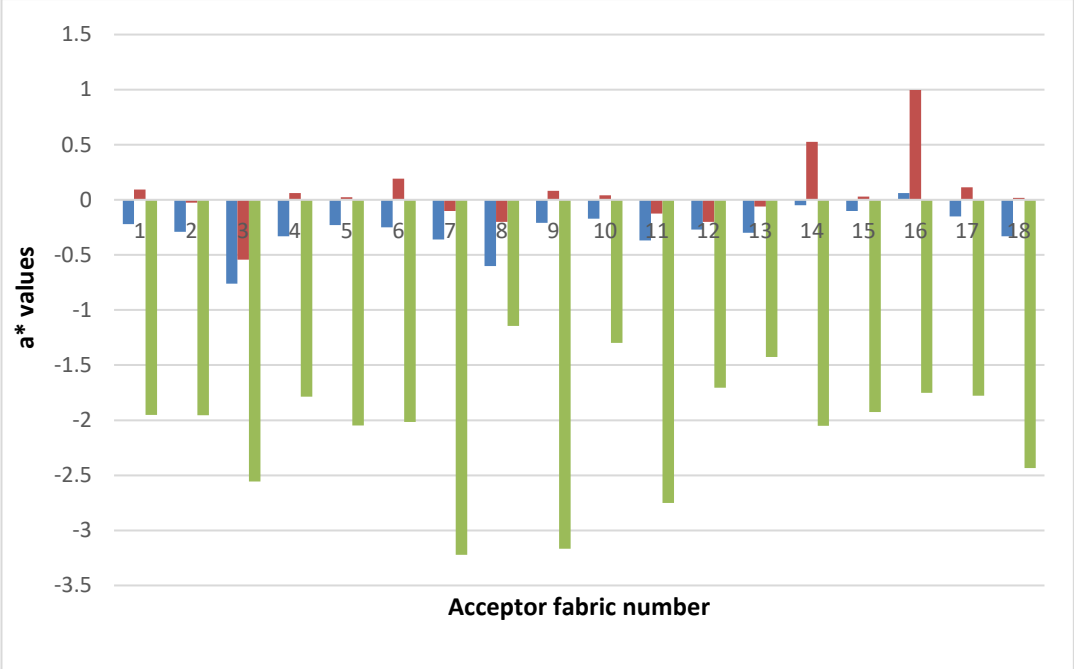


Figure 2.3: Comparison of a* values of acceptor fabrics (Table 2.3) washed with consumer wash loads (blue), 'dark wash loads' (red) (Table 2.1) and 'bright wash loads' (green) (Table 2.2).

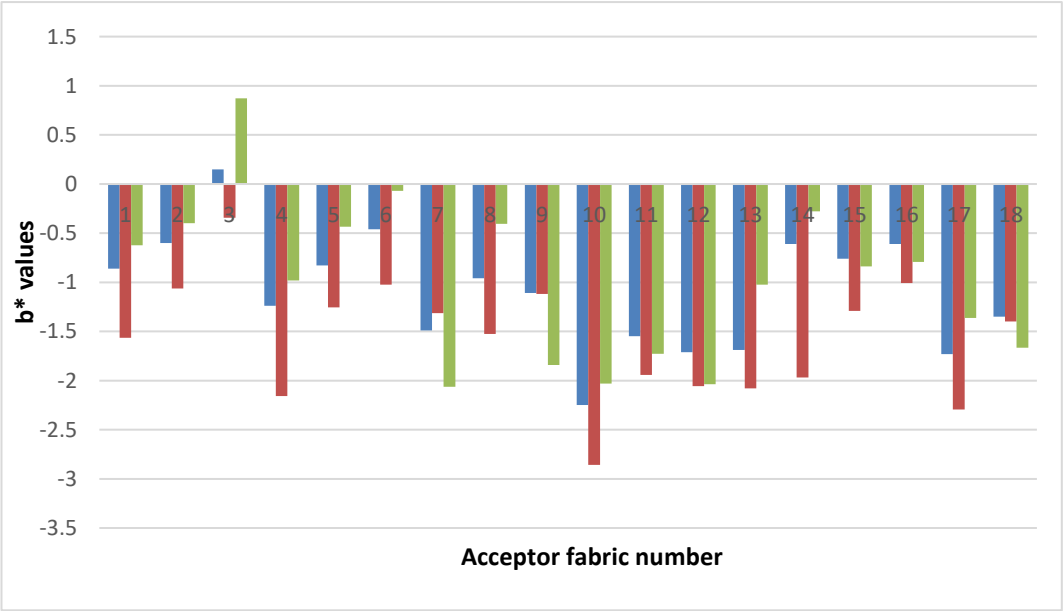


Figure 2.4: Comparison of b* values of acceptor fabrics (Table 2.3) washed with consumer wash loads (blue), 'dark wash load' (red) (Table 2.1) and 'bright wash load' (green) (Table 2.2).

As can be seen in the L*, a* and b* comparisons, it was actually the dark model load that better represented the colours that are released from

consumer wash load. Therefore, it was concluded that the dark model load performs well as a representative model for the consumer load, and hence, dyes used on garments in the dark model wash load may accurately represent the dyes used on garments in the average consumer load. Other replicas of the dark model load were also washed and compared with consumer data, to ensure consistent results between different versions of the same model and that the outcomes were repeatable (Figure 2.5).

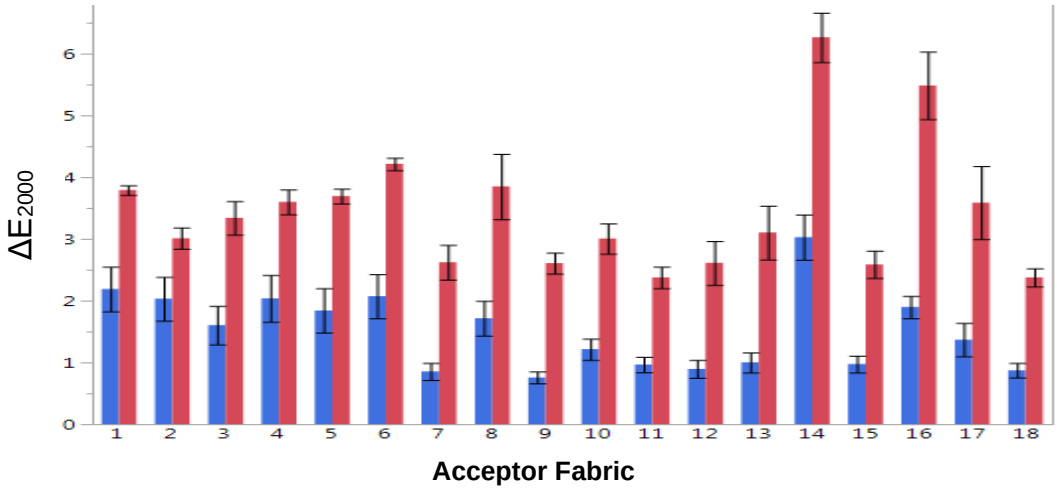


Figure 2.5: Average ΔE_{2000} values of white acceptor materials 1-18 (Table 2.3) from consumer wash loads (blue) and dark wash load (red) (Table 2.1). Error bars show ± standard deviation of three repetitions.

Comparison of the consumer loads and dark model load (Figure 2.5) suggests that, while the model load produces higher ΔE_{2000} values for each acceptor fabric, the level of discoloration of each acceptor fabric is equivalent to the consumer loads. The difference in the extent of ΔE_{2000} values is due to the age of the products washed; after successive washes, the model load gave discoloration values of a more similar magnitude to the consumer wash loads. Mean discoloration from different wash conditions is also proportional between the two wash loads (Figure 2.6).

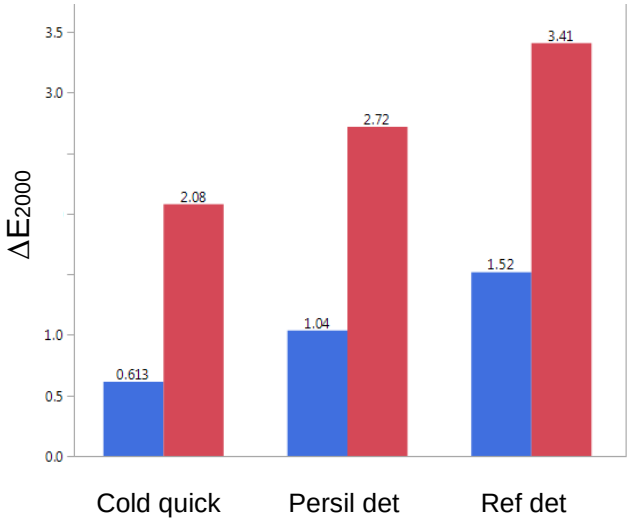


Figure 2.6: Average ΔE_{2000} values of acceptor fabrics (Table 2.3) in different wash conditions after washes with consumer wash load (blue) and model wash load (red) (Table 2.1).

2.3.2. Characterisation of dyes in model load

Comparison of the UV/vis spectra of wash liquors of each t-shirt after stirring in 40 °C water (Figure 2.7) demonstrates that, generally, cotton fabrics liberated significantly more dye than polyester fabrics. This was expected as polyesters are predominantly dyed with hydrophobic disperse dyes, which would not be expected to be readily released into an aqueous environment. The exception is the black polyester fabric, which did liberate a substantial amount colour, suggesting a higher level of dye loading on the fabric, perhaps with some other less hydrophobic dye present, which is worthy of further investigation. The fabrics that liberated the most colour were black cotton, dark navy cotton, burgundy cotton and royal blue cotton. This may be because for deeper shades, dye is applied in higher amounts.[79] λmax-vis values for individual fabrics are shown in Table 2.1; λmax-vis for the combined model wash solution was 548 nm.

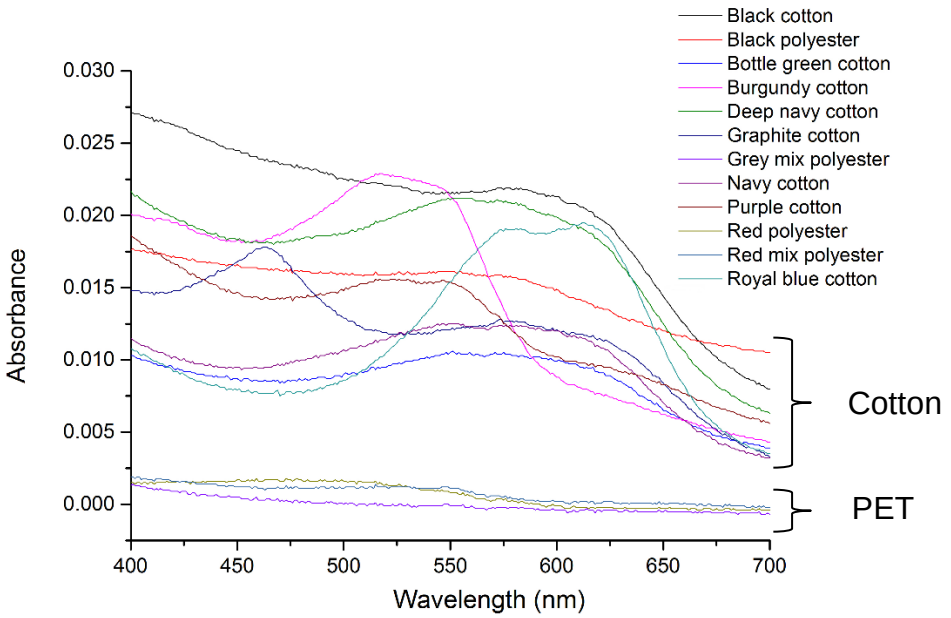


Figure 2.7: UV/vis measurements of wash liquors of each t-shirt colour after being stirred in water at 40 °C, 150 rpm for 1.5 hours.

Figure 2.9 and Figure 2.10 show Raman spectra of some of the t-shirts making up the retail dark load; these were compared to spectra of known dyes on fabric. Raman spectroscopy is a sensitive technique that is capable of measuring the light scattered from a dye in a fabric.[80] Certain functional groups have characteristic spectral features, similar to FT-IR. Because of this, the dyes in the model load can either be fully identified through matching spectra with a known dye from a library, or specific functional groups can be picked out using the peaks. Partial matches may also be made when significant but not total similarity between spectra from a t-shirt matches with peaks from the dye library. This would suggest that either the identified dye is present on the t-shirt in combination with one or more dyes, or that the functional group that corresponds to the peak is present in a dye on the t-shirt and is in a similar environment to the dye from the library.

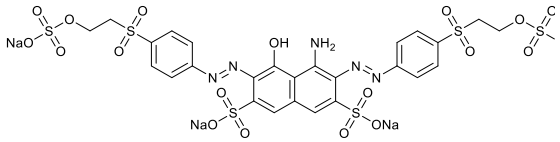
The presence of water-soluble functional groups such as –OH and $–SO_3$ ruled out certain dye types such as vat dyes. Peaks at 487 cm^{-1} were found to be attributed to an SO_2 group, from peak tables and spectra of known dyes. Peaks between 1190 cm^{-1} and 1230 cm^{-1} were attributed to the

sulfatoethylsulfone (–OSO_2O–) group. This functional group is mostly found in certain reactive dyes and so is indicative that a reactive dye is present.

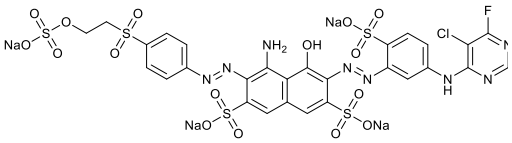
The spectroscopic data in Table 2.5 shows that predominantly reactive dyes were used on the model load garments (Figure 2.8). This suggests that the UV/Vis measurements represent hydrolysed reactive dyestuffs and that, even after production of these garments, a significant level of hydrolysed dye remains on the garment which then leaches into wash systems.

Table 2.5: Spectroscopic data of the t-shirts comprising the model retail load. Where full identification cannot be obtained, some partial matches have been found. It was not possible to obtain Raman spectra of the grey mixed jersey and the red mixed jersey shirts due to fluorescence.

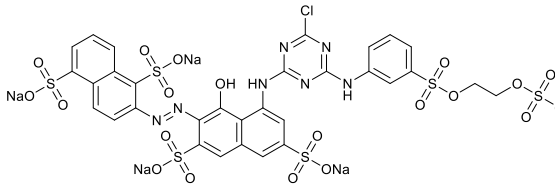
T-shirt fabric	T-shirt colour	Raman peak (cm^{-1})	Functional groups	λ_{max} (nm)	Identified dye
100% cotton	Black	1577, 1501	Aromatic/hetero ring	577	Partial match C. I. Reactive Black 5 (**2.1**)
		1288	$Ph–NR_2$		
		1245	Ph–OH		
		1192	$–OSO_2O–$		
		489	SO_2		
100% cotton	Bottle green	1849	C=O	612	C. I. Reactive Blue 225 (**2.2**)
		1612, 1499	Aromatic ring		
		1576	N=N		
		1423	CH_2/CH_3		
		1344, 1456	$Ph–OH/SO_2–OH$		
		1322, 1293	$Ph–NR_2$		
		1211	C–C/sulfone		
		1137, 745, 489, 455	SO_2		
100% cotton	Burgundy	1618, 1591, 1504, 1471	Aromatic/hetero ring	518	C. I. Reactive Red 195 (**2.3**)
		1419	CH_2		
		1283	$Ph–NR_2$		
		1184	$–OSO_2O–$		
		487	SO_2		
100% cotton	Deep Navy	1590	Phenyl/naphthyl ring	557	C. I. Reactive Black 5 (**2.1**)
		1502	CC, CN aromatic		
		1415	N=N		
		1347, 1137, 490	SO_2		
		1216, 1184,	$–OSO_2O–$		
100% cotton	Light Graphite	1601, 1025	Aromatic ring	463, 574	Partial match C. I. Reactive Violet 5 (**2.4**)
		1436	Amide/ $–OSO_2O–$		
		1392	Aromatic azo		
		1318, 1280	$Ph–NR_2$		
		1114, 1075	Sulfone		
100% cotton	Navy	1592	Phenyl/naphthyl ring	552	C. I. Reactive Black 5 (**2.1**)
		1287	$Ph–NH_2$		
		1213, 1189	$–OSO_2O–$		
		489	SO_2		
100% cotton	Purple	1442, 1386	Aromatic azo	523	Partial match C. I. Reactive Blue 224
		1427	CH_2/CH_3		
		1290, 1285, 1272	$Ph–NH_2$		
		1225	Ph–OH		
		1015	Aromatic ring		
100% cotton	Royal blue	1429	CH_2	613, 581	C. I. Reactive Blue 224
		1387	Aromatic azo		
		1225	Ph-OH		
		1286	$Ph-NH_2$		
100% polyester	Black	1588	Aromatic/hetero ring	546	
		1447	Phenol O–H		
		1334, 1271	$Ph–OH/Ph–NR_2$		
		1230	Ph-OH		
		1172	Aromatic ring		
		1136	SO_2		
100% polyester	Red	1539, 1001	Aromatic ring	479	C. I. Disperse Red 356 (**2.5**)
		1427	CH_2/CH_3		
		1388, 1343	$C–CH_3$		
		1199	C–C		
		1150	Aromatic ring/C–O–C		
		883	C–O–C		
50% polyester, 25% cotton, 25% rayon	Grey	N/A	N/A	548	
50% polyester, 25% cotton, 25% rayon	Red	N/A	N/A	478	C. I. Disperse Red 356 (**2.5**)



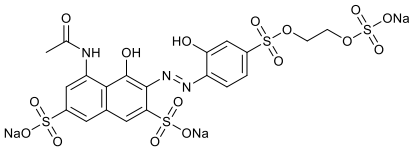
2.1 M_w: 991.80 g mol^{-1}



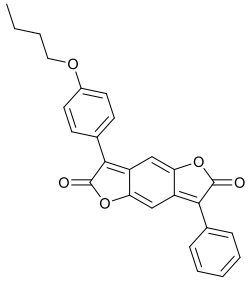
2.2 M_w: 1047.22 g mol^{-1}



2.3 M_w: 1136.32 g mol^{-1}



2.4 M_w: 735.59 g mol^{-1}



2.5 M_w: 412.43 g mol^{-1}

Figure 2.8: Chemical structures of dyes identified in model wash load by Raman spectroscopy.

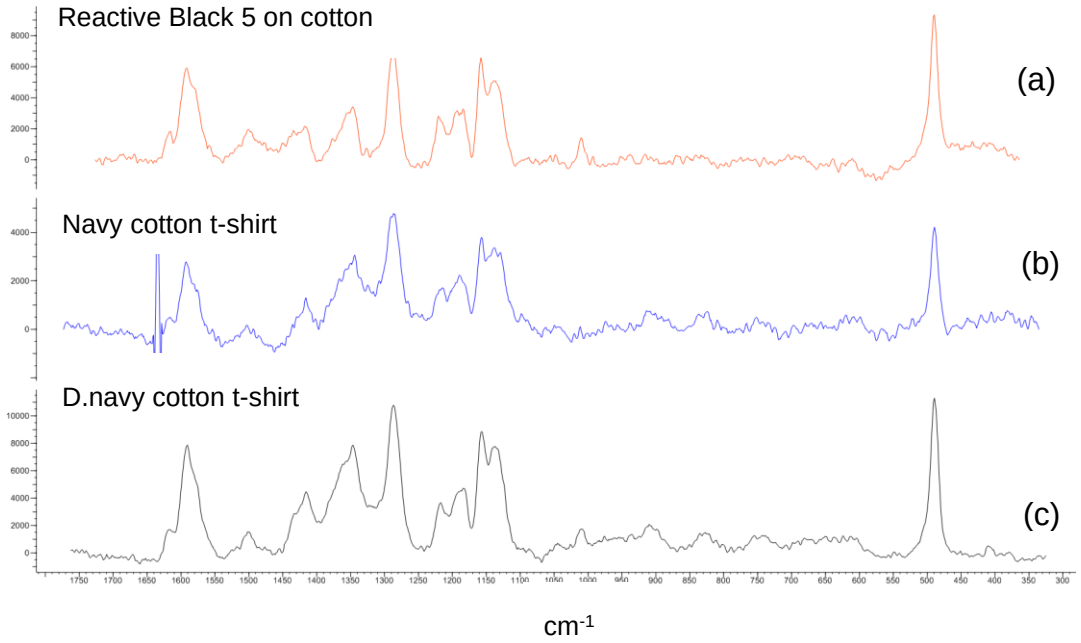


Figure 2.9: Raman spectra of (a) C. I. Reactive Black 5 on cotton (standard), (b) navy cotton t-shirt, and (c) deep navy cotton t-shirt.

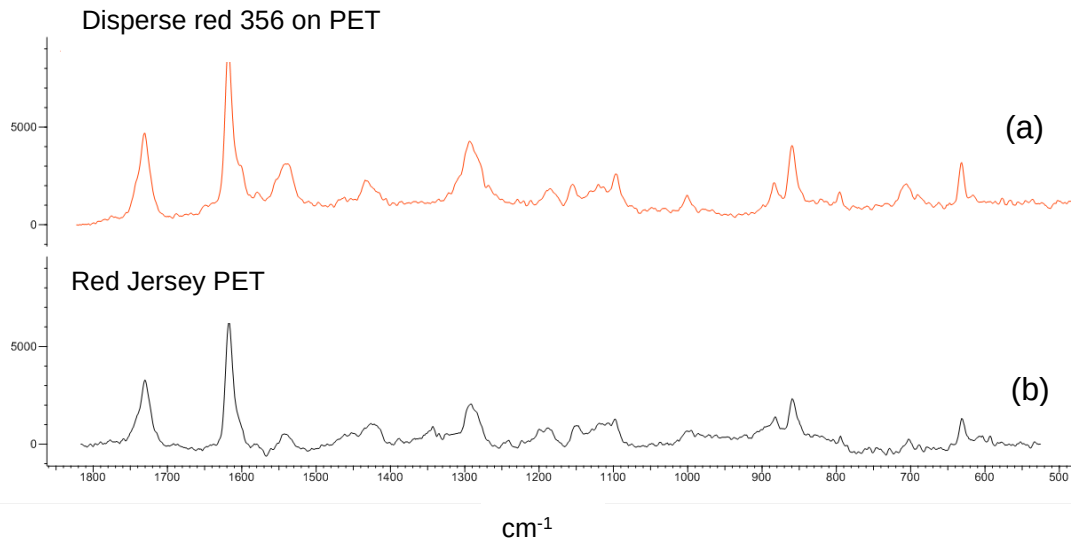


Figure 2.10: Raman spectra of showing identification of (a) C. I. Disperse Red 356 on polyester, and (b) red polyester t-shirt.

2.3.3. Effect of temperature on dye desorption and re-adsorption

Swatches from the model wash load were stirred in water at either 20 °C, 40 °C or 60 °C and mean *A* at 548 nm ($\lambda_{max\text{-}vis}$ of wash liquor) observed against *t* for each temperature. The precise composition of the dye mixture evolved from the model wash load was not known, however, to allow for a quantitative comparison of dye desorbed and adsorbed, properties of C.I. Reactive Black 5 were used as it was observed from Raman studies that this dye was released in significant quantities; whilst this does not represent an absolute quantification of moles of dye released, it allows for quantitative comparison between conditions. Concentration (*c*) was calculated from *A* values based on the Beer-Lambert law ($A = \varepsilon.c.l$) using the molar extinction coefficient (ε) for C.I. Reactive Black 5 in water (45.5 dm^3 $mmol^{-1}$ cm^{-1}),[81] based on a pathlength (*l*) of 1 cm. Figure 2.11 shows the concentration of dye released/desorbed (*q*) with increasing *t* for each temperature. *q* is calculated as follows whereby V is volume and m is mass:

$$q = \left(\frac{\left(\frac{A}{\varepsilon}\right)V}{m}\right) \qquad (2.1)$$

The desorption data appears to show that there is a small, but significant difference between the level of dyestuffs being released at 20 °C and 40 °C. This is likely due to the increased thermal energy in the system and so dye

particles may move more. However, the difference in dyestuff released at 40 °C and 60 °C is not substantially different for all time points, suggesting that beyond a certain temperature, similar amounts of dyestuffs are desorbed and re-adsorbed onto fabric within a certain period of time. For all temperatures, there is a steady increase in dyestuffs released over time, which is to be expected. Slight fluctuations in the absorbance readings are likely due to some re-adsorption of the dyestuffs onto the fabrics in the wash.

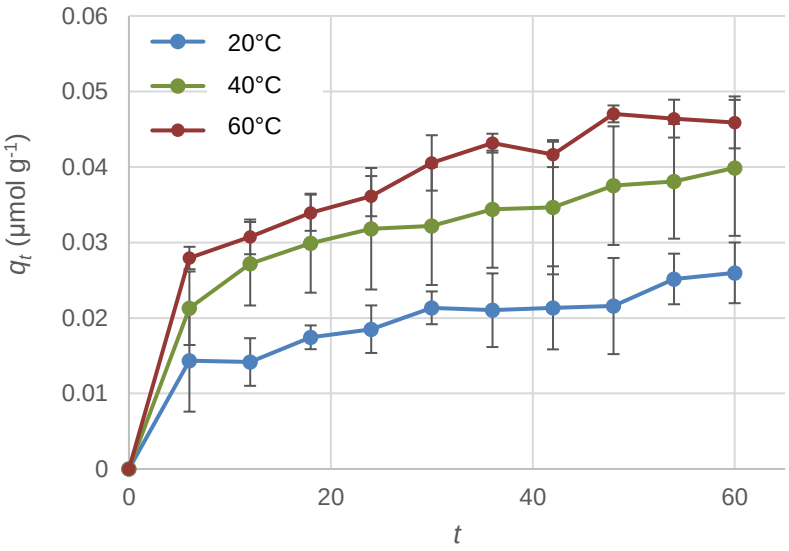


Figure 2.11: Mean q_t values of wash liquor dye desorption from model wash load over time at 20 °C (blue), 40 °C (green) and 60 °C (red). Error bars show ± standard deviation of three repetitions.

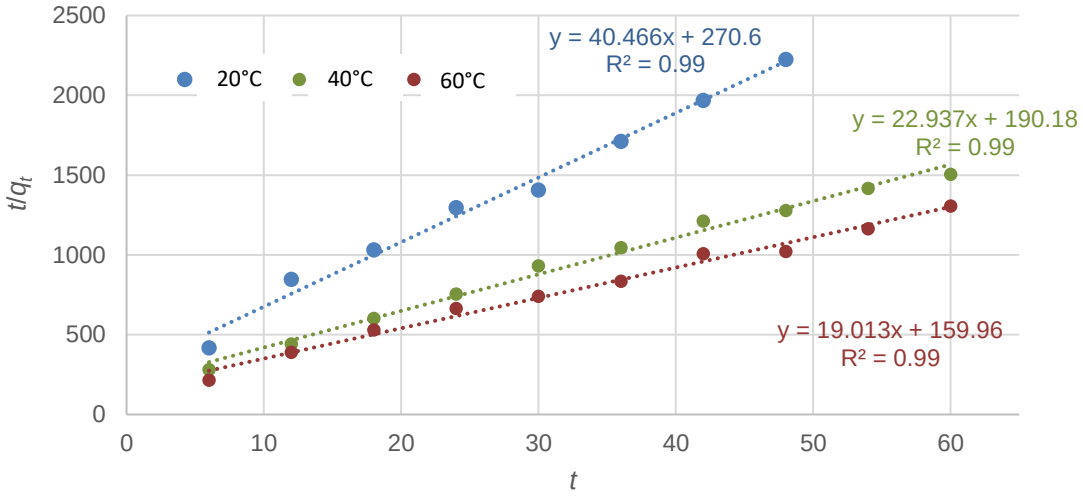
The data was fitted to a pseudo-second order kinetic model,[82] as described in equation 2.2:

$$\frac{\partial q_t}{\partial t} = k(q_e - q_t)^2 \qquad (2.2)$$

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 2.2 becomes equation 2.3:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (2.2)$$

A plot of t/q_t against t that produces a straight line, confirms the model, where absorbance at equilibrium (q_e) = 1/slope, and the pseudo-second order rate constant (k_2) = slope^2/intercept. Initial desorption rate h_0 (mol g^{-1} min^{-1}) = $k_2 q_e^2$.

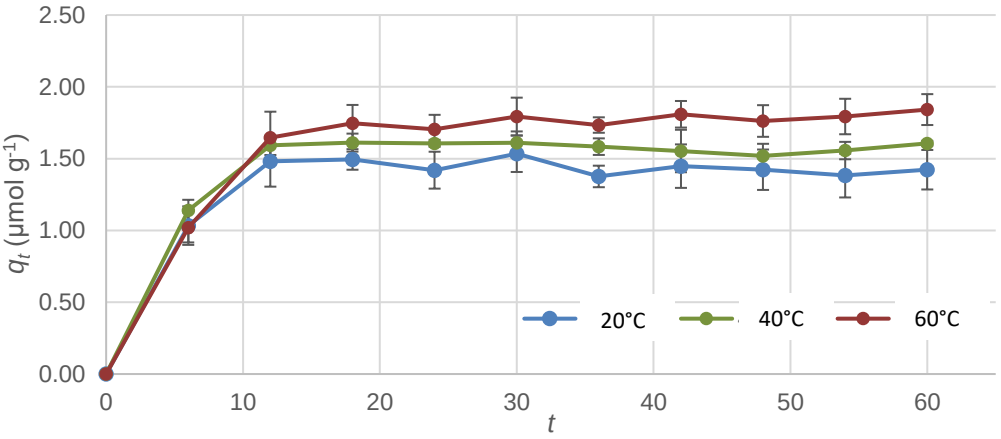


T (°C)	R^2	q_e (µmol g^{-1})	k_2 (g µmol^{-1} min^{-1})	h_0 10^{-3} (µmol g^{-1} min^{-1})
20	0.99	0.025	6.05	3.78
40	0.99	0.044	2.77	5.36
60	0.99	0.053	2.26	6.35

Figure 2.12: Plot of t/q_t *vs*. time (*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 2.12 shows high correlation (R^2 > 0.98) of the data with the pseudo-second order model at each temperature. In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases.[83] Adsorption of dyestuffs onto a white swatch of 100% cotton fabric was investigated to provide kinetic information at a predetermined temperature of 20 ° C, 40°C or 60°C ± 2°C. Wash liquor from the model retail load was used as a source of dyestuff of which; a UV/vis measurement was taken to obtain the initial absorbance. Aliquots of wash liquor were

taken over time to obtain the change in absorbance as adsorption onto the cotton substrate occurs.



T (°C)	R^2	q_e (µmol g^{-1})	k_2 (g µmol^{-1} min^{-1})	h_0 (µmol g^{-1} min^{-1})
20	0.99	0.228	5.73	0.30
40	0.99	0.253	4.87	0.31
60	0.99	0.305	2.73	0.25

Figure 2.13: Mean *qt* 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. Inset table shows data from plot of t/q_t *vs*. time (*t)* confirming pseudo-second order re-adsorption of dyes different temperatures.

Data from Figure 2.13 suggests that the concentration of dyestuffs in solution decreases over time and plateaus for all temperatures over 1 hour. The small fluctuations in absorbance are likely due to the adsorption and desorption that occurs while the acceptor fabric is in solution. There is very little significant difference between the values for the three temperatures. As with the Desorption data, the kinetics of this system also follows a pseudo second order as seen in Figure 2.12. By using this data, the effect of time on dye release and adsorption in this system, at a given temperature, can also be investigated. The data suggests that for all temperatures, an increase in time leads to an increase in dye desorption over the course of 60 minutes and beyond. 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. After this time, the q_t levels out, suggesting that an equilibrium between desorption from the cotton substrate and re-adsorption occurs. At 60 °C however, q_t is still increasing slightly after 60 minutes. This suggests that temperature and time can have a combined effect, with an increase in both parameters producing an increased adsorption.

2.3.4. Effect of Ionic strength on dye desorption and re-adsorption

Ionic strength of a solution (μ) is defined by equation 2.4:[84,85]

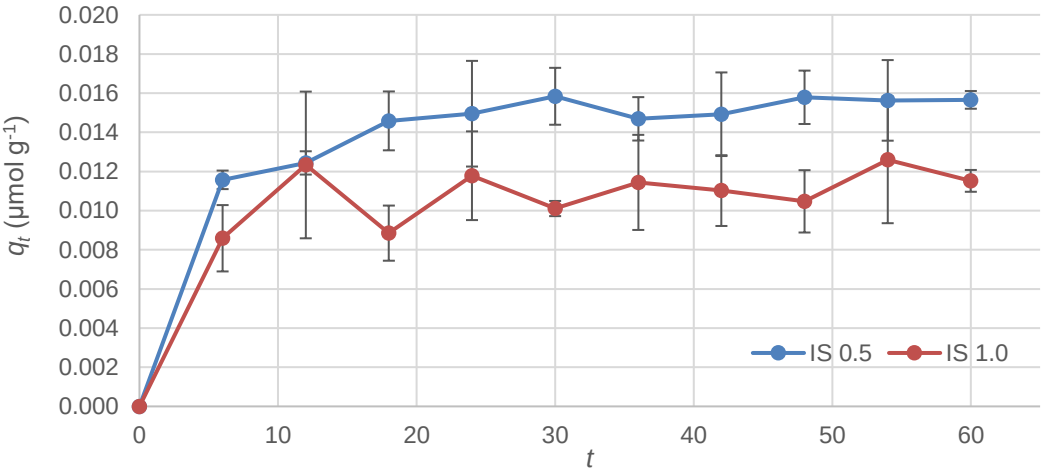
$$\mu = \frac{\sum cv^2}{2} \tag{2.4}$$

where c is molar concentration and v is the valence of ions present of each of the ions in solution. Sodium chloride, NaCl, is a 1:1 salt and so the ionic strength is the same as the concentration. For example, a 1 M concentration of NaCl:

$$\mu = \frac{\left[([\mathrm{Na^+}])(+1)^2+([\mathrm{Cl^-}])(-1)^2\right]}{2} \tag{2.5}$$

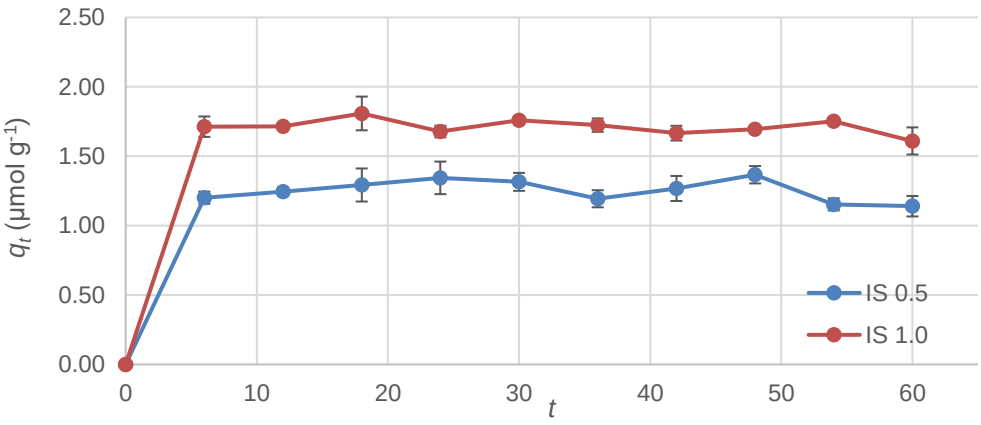
$$\mu = \frac{\left[(1)(+1)^2+(1)(-1)^2\right]}{2} \tag{2.6}$$

$$\mu = 1 \tag{2.7}$$



μ	R^2	q_e 10^{-3} (µmol g^{-1})	k_2 (g mmol^{-1} min^{-1})	h_0 10^{-3} (µmol g^{-1} min^{-1})
0.5	0.997	2.73	0.81	6.05
1.0	0.972	2.01	1.03	4.16

Figure 2.14: Mean q_t values of wash liquor dye desorption from model wash load at ionic strength 0.5 (blue) and 1 (red) over time. Error bars show ± standard deviation of 3 repetitions. Inset table shows data from plot of t/qt vs. time (*t*) confirming pseudo-second order desorption of dyes at different ionic strengths.



μ	R^2	q_e 10^{-3} (µmol g^{-1})	k_2 (g mmol^{-1} min^{-1})	h_0 10^{-3} (µmol g^{-1} min^{-1})
0.5	0.974	0.200	6.72	0.27
1.0	0.997	0.284	3.66	0.29

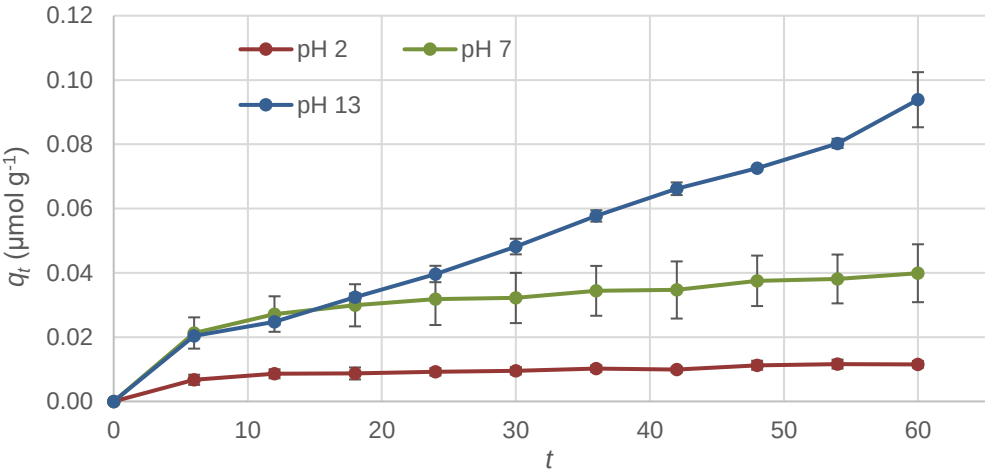
Figure 2.15: Mean q_t values over time as dye is removed from wash liquor solution by adsorption onto acceptor fabric swatch at $\mu = 1$ (red) and $\mu = 0.5$ (blue). Error bars show ± standard deviation of 3 repetitions. Inset table shows data from plot of t/q_t *vs*. time (*t)* confirming pseudo-second order re-adsorption of dyes at different ionic strengths.

The kinetics of dye desorption (Figure 2.14) and adsorption (Figure 2.15) for both ionic strengths followed pseudo-second order reaction. At higher ionic strength, there is more substantivity for the dye particles to the cotton fibre, for both dye desorption and dye adsorption. This is likely due to the presence of Na^+ ions reducing repulsion between the negatively charged cotton fibre and the anionic dyes. As discovered from Raman measurements, the dyes in the retail load are predominantly reactive dyes. A component of the reactive dyeing process is to add an electrolyte such as sodium chloride which shields the electrostatic repulsion between fibre and dye.[86] At a lower ionic strength, more dye is leached into the aqueous environment and remains there. The implications of this for the reduction of dye transfer are that an increase in ionic strength, for example by the release of electrolyte from a detergent pod, could stop dye donors from losing the same extent of dye. This would also decrease the level of fading a garment experiences with each wash. However, any dye that is liberated during the wash would be even more likely to adsorb onto other garments

and discolour them. Therefore, there could be an optimum ionic strength that allows minimal dye release and so minimal dye adsorption onto acceptor garments.

2.3.5. Effect of pH on dye desorption and re-adsorption

pH was also investigated for its effect on dye desorption from the fabric swatches into solution, and dye re-adsorption from the wash liquor onto the white acceptor fabrics.



pH	R^2	q_e (µmol g^{-1})	k_2 (g µmol^{-1} min^{-1})	h_0 10^{-3} (µmol g^{-1} min^{-1})
2.0	0.984	0.013	10.18	1.72
7.6	0.991	0.044	2.77	5.36

pH	R^2	q_0 (µmol g^{-1})	k_0 10^{-3} (µmol g^{-1} min^{-1})
13.0	0.989	0.006	1.40

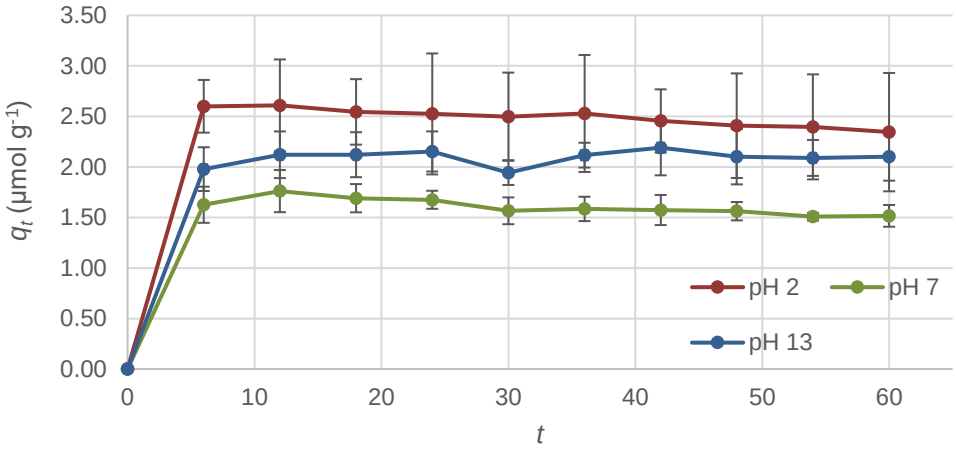
Figure 2.16: Mean q_t values of wash liquor from model wash load over time at pH 2 (red), pH 7 (green) and pH 13 (blue). Error bars show ± standard deviation of 3 repetitions. Inset table shows data from plot of t/q_t *vs*. time (*t)* confirming pseudo-second order desorption of dyes different pH 2 and pH 7.6, and pseudo-zero order desorption of dyes different pH 13.

Figure 2.16 shows the increase in dye desorption as pH is increased. For pH 2 the level of dyestuffs released from the dyed fabrics plateaus very quickly, after around 12 minutes. At this low pH, the acidic protons in solution help to

reduce repulsion between the anionic dye and the negative charge of cotton in an aqueous environment, resulting in less dye migration from the fibre. A protonated form of the dye may also have lower solubility in water. At pH 7, there is still a gradual increase in dye release after an hour, which mirrors the corresponding data from the same condition, 40 °C, in Figure 2. However, at pH 13 there is a significant, linear increase in dye release over time, which exceeds one hour; the kinetics of this system were found to be pseudo-zero order and can be modelled using equation 2.8:

$$q_t = q_0 - kt \tag{2.8}$$

Where, k is the rate constant of sorption (mol g^{-1} min^{-1}), q_t and q_0 (mol g^{-1}) are the concentrations of dissolved sorbate adsorbed at a given time (t) and at t = 0 (initial), respectively. A plot of q_t *vs.* t yielding a straight line confirms the pseudo-zero order nature of this dye desorption, where the gradient of the line = k, and the intercept = q_0. This trend is due to the repulsion between the anionic dyes and the cellulosic fibre in the alkaline aqueous media.



pH	R^2	q_e (µmol g^{-1})	k_2 (g µmol^{-1} min^{-1})	h_0 (µmol g^{-1} min^{-1})
2	0.999	0.391	3.51	0.54
7	0.999	0.244	6.91	0.41
13	0.994	0.352	2.78	0.34

Figure 2.17: Mean q_t values over time as dye is removed from wash liquor solution by adsorption onto acceptor fabric swatch at pH 2 (red), pH 7 (green) and pH 13 (blue). Error bars show ± standard deviation of 3 repetitions. Inset table shows data from plot of t/q_t *vs*. time (*t)* confirming pseudo-second order re-adsorption of dyes different pH 2, pH 7, and pH 13.

Figure 2.17 shows that at pH 2 more dyestuffs are removed from solution as they are adsorbed onto the acceptor fibre compared to higher pHs. As with desorption, the presence of acidic protons in the solution may mask the charge repulsion between the anionic sulfonic acid groups and the anionic hydroxyl groups in cellulose, increasing adsorption. There is a small difference in adsorption at pH 13 and pH 7, with slightly more adsorption occurring at the higher pH. While there are some fluctuations, dye adsorption seems to plateau for both pH 2 and pH 13 over 60 minutes. At pH 7, there is more dye de-adsorption over the 60 minutes than at pH 2 or pH 13. Implications for dye transfer reduction include introducing a possible acidic component into a wash system which can help keep surface dyes attracted to fibre and lower their water solubility to prevent dye release into aqueous media.

2.4. Conclusions

A novel model wash load was assembled from commercially available garments to accurately mimic an average of consumer wash loads. Trends from dye transfer onto acceptor fabrics were compared as well as the individual L*, a* and b* values, to ensure a good representation of consumer data. Dyestuffs were released predominantly from cotton garments, although a significant amount of dyestuffs was released from the black polyester garment, suggesting an additional dye was present along with a hydrophobic disperse dye. Characterisation of the dyes on these t-shirts through Raman and UV/vis spectroscopy highlighted a significant use of reactive dyes in consumer garments in an average UK wash load. Implications of this means that future waste-water treatment and dye transfer inhibition should focus on this dye group and hydrolysed reactive dyes more so than other less commonly used dye groups. Findings from research carried out on the less commonly used direct dyes, known for low wash-fastness, should be assessed for their impact.

The effects of temperature of wash, time of wash, ionic strength and pH on dye desorption and dye re-adsorption of the model wash load were investigated in a small scale, nil-detergent study. It was found that increased temperature, increased time and higher pH led to increased dye desorption from the donor fabrics in the retail model. Increased ionic strength led to less dye desorption from the model wash load. Increased temperature and higher ionic strength led to higher dye re-adsorption onto a cotton acceptor. Time had little effect on dye re-adsorption, with dye re-adsorption increasing over time at wash temperature of 60 °C. The effect of pH on dye re-adsorption suggested that a lower pH led to more dye adsorption than alkaline or neutral pH. These findings have implications for future detergent development to reduce the deterioration of clothing from dye fading, and to reduce dyes entering waterways.

The model wash load was accepted as a suitable model to represent real consumer wash loads, however other fabric types are also common such as denim and so should also be investigated.

Chapter 3- Denim Investigation and Analysis

3.1. Introduction

As well as the textiles tested in Chapter 2, denim is also a popular textile and so, is also worth investigating for the extent of dye transfer that it produces. The name denim is thought to originate from *serge de Nîmes*, a fabric from the Nîmes region of France.[87] The term 'jeans' is thought to originate from the French word for the Italian city Genoa (*Gênes*).[88] Levi Strauss added copper rivets to parts of the material prone to wear when making overalls for workers in the nineteenth century and from this, paved the way for the modern denim jeans that are popular apparel today.[87] It is estimated that 10% of all aggregate cotton generated in the world is manufactured into denim.[88] Denim is produced by ring-dyeing cotton warp yarns with indigo and weaving them with white cotton weft yarns(Figure 3.1). Indigo is a natural dye derived from *Indigofera tinctoria*; however, it is also easily synthesised and so modern denim is more usually dyed with the synthetic dye (Figure 3.2). Denim materials may also be further shaded with C.I. Sulphur dyes such as C.I. Sulphur Black 1 to provide darker coloured material.[89] Denim is durable and has been used for clothing such as overalls for physical labour. It is also a very fashionable material and can be modified and dyed in a range of ways to create appealing consumer garments. In 2017, over 24 million people in the UK purchased a pair of jeans, with the vast majority purchasing garments costing £25 or less.[90]

Figure 3.1: Close up picture of the back of denim material showing indigo dyed cotton warp and white cotton weft.

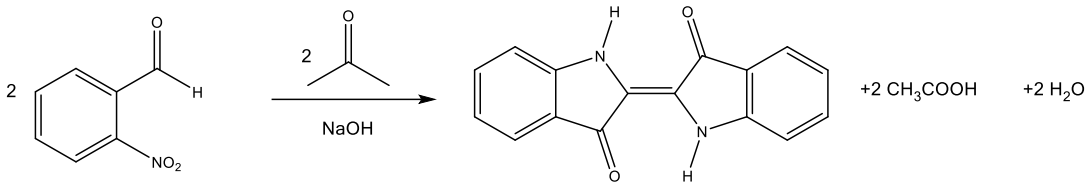


Figure 3.2: Baeyer-Drewson synthesis of indigo from 2-nitrobenzaldehyde and acetone.[91]

Indigo (C.I. Vat Blue 1) is a vat dye. This class of dye requires a reduction step to make them water soluble for the dyeing process. During dyeing, indigo (Figure 3.3, (1)) is reduced first to acid leucoindigo (Figure 3.3, (2)), using reducing agents such as sodium hydrosulfite (sodium dithioniate), however it still has limited solubility in water and low substantivity for cellulosics.[92] Then alkali is added to form alkaline leucoindigo, first the monophenolate ionic form (Figure 3.3 (3)), then the biphenolate ionic form (Figure 3.3 (4)), which has much improved water solubility. This reduction process to leuco-indigo alters the chromophore of the dye and so acid leucoindigo appears as off-white and alkaline leucoindigo appears as pale yellow. The leucoindigo has weak attraction to cellulosic fibre by van der Waals and dipolar forces, allowing for substantivity for the fibre. After sorption of the reduced form, the dye is then oxidised, typically through exposure to oxygen in the air, but oxidising agents such as hydrogen peroxide may also be utilised. The dye is oxidised back to water-insoluble indigo and is mechanically trapped into the fibre.

While other technologies have been investigated to prevent to use of reducing agents in order to dye with indigo, they are still in their infancy and have not been adopted by industry yet.[91] The long process of reduction of indigo to leucoindigo is necessary because the blue form of the dye is not water soluble. Therefore, it is counter-intuitive to the teachings of dyeing with indigo how dye can transfer from denim in an aqueous environment such as in a domestic wash, where reducing agents are not present.

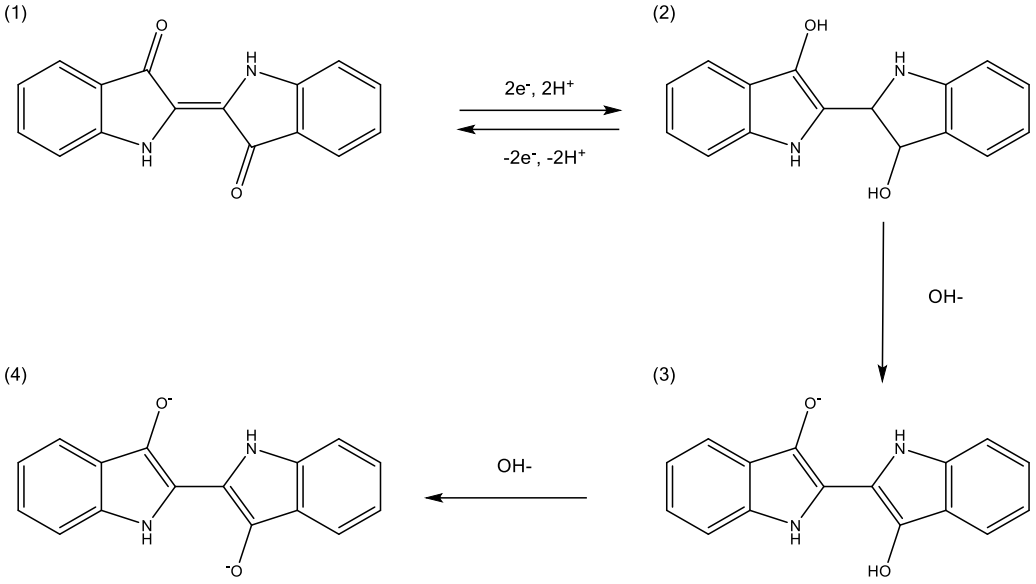


Figure 3.3: Reduction of indigo to leucoindigo.

Denim has long been suspected of causing significant dye transfer during laundering. The mobility of the blue indigo molecules has been highlighted in literature by the phenomenon of ‘backstaining’. Backstaining is a process by which the white parts of the denim garment, such as the white weft, pocket lining and wash labels are discoloured blue after laundering.[93] It is thought that this occurs due to the presence of cellulases in detergents. The purpose of these enzymes in detergents is to bio-polish the textile, by degrading small amounts of cellulose that have pilled and also to provide a soft handle for fabrics. These cellulases have aromatic and non-polar residues containing amino acids such as tyrosine, tryptophan and phenylalanine which allow for π-π interactions with indigo.[94] It is thought that the cellulase molecules bind to indigo molecules while being adsorbed on the surface of cellulose fibres, acting as a bridge between the indigo molecules and the cellulose. Not all of the cellulose molecules are washed off, giving a blue discoloration to the cellulose.[95] However, it is not fully understood if backstaining is the only mechanism of dye transfer from denim during laundering. The cellulases only have affinity for cellulosics and so, other fibres would not experience dye transfer through backstaining. As well as this, backstaining requires cellulases to be present, but dye transfer may still

occur in a nil detergent system or in a wash with a detergent that does not contain cellulases, such as a non-biological detergent.

The purpose of the experiments in this chapter was to gain information about how dye transfer from denim occurs in an aqueous environment. The experiments set out to give at least some characterisation of the staining species, understand functionalities that the species may interact with, and investigate the effect that certain parameters such as temperature and pH have on the level of dye transfer.

3.2. Experimental

3.2.1. Materials and solvents

Technical denim (E-277) was purchased from CFT.BV, the Netherlands as a control sample of denim, and was cut into 10 cm x 4 cm strips. A multifibre roll was purchased from James Heal and cut into 10 cm x 4 cm strips. Shop bought denim samples were purchased as the following: (Shop 1 denim) George skinny denim jeans from ASDA UK, (Shop 2 denim) Maine New England blue regular leg jeans from Debenhams UK and (Shop 3 denim) Light denim wash boot-cut jeans with stretch from Sainsbury's Tu range, all in Men's size XL, all to represent real denim goods available to consumers in the UK. A selection of undyed, white acceptor fabrics were used in accordance with standard practice at Procter & Gamble dye transfer procedures. They were comprised of the following:

Table 3.1: Acceptor fabric details.

Acceptor number	Acceptor fabric	Retailer
1	100% Cotton	Fruit of the Loom
2	100% Cotton	Anvil
3	100% Cotton	Gildan
4	100% Cotton	B & C
5	100% Cotton	Russell
6	100% Cotton	Russell
7	100% Polyester	Gildan
8	50% Polyester, 25% cotton, 25% rayon	Anvil
9	100% Polyester	Fruit of the Loom
10	65% Polyester, 35% Cotton	Kustom Kit
11	100% Polyester	Spiro
12	100% Polyester	Xpres
13	65% Polyester, 35% Cotton	Russell
14	100% Cotton	Tee Jays
15	100% Polyester	Spiro
16	95% Polyester, 5% Spandex	Tee Jays
17	52% cotton, 48% polyester	Bella Canvas
18	100% polyester	Gildan

Indigo, indigo carmine, acetonitrile, acetone, dichloromethane, sodium hydrosulfite, citric acid, sodium hydrogen phosphate, sodium carbonate,

sodium bicarbonate, arginine, glutamic acid and phenylalanine were purchased from Sigma-Aldrich. Sodium hydroxide and polyhexamethylenebiguanide hydrochloride were purchased from Fischer Scientific. DMSO-d_6 was purchased from Fluorochem. Detergent was Ariel Original washing liquid, purchased from ASDA, UK and dose scaled down according to the instructions on the packaging.

3.2.2. General Procedures and Instrumentation

Wash tests were carried out using a James Heal 1315 B Gyrowash at 40 rpm for 30 minutes at either 20 °C, 40 °C or 60 °C depending on the experiment. The Gyrowash allows for small scale simulation of domestic washing with easy collection of wash liquor. The wash method was an adaptation of ISO 105-C10:2007 colourfastness test: 25 steel balls were used unless otherwise stated in the experiment.[96] 50 mL of distilled water was added to the canister. After the wash stage, wash liquor was replaced with 50 mL fresh distilled water and a rinse step was carried out at 40 rpm for 10 minutes at the same temperature of the wash. Fabric samples were left to air dry for 24 hours before measurement on a Data Colour Spectraflash 600 (Plus) CT spectrophotometer, generating L*, a* and b* values.

Validation of technical and shop-bought denim was carried out using a Copley Scientific tergotometer. This is another piece of equipment that allows for small scale simulation of a wash and easy collection of wash liquor. Each pot contained 300 mL city (Newcastle-upon-Tyne, UK) tap water and stirred at 40 °C at 150 rpm for 90 min. UV/vis measurements were taken using Jenway 6850 UV/Vis spectrophotometer. Thermal analysis was carried out on a TGA Q50 V6.7 Build 203. TGA measures mass loss of a sample as a function of either temperature or time. By increasing the temperature that a sample is exposed to, changes in mass such as water evaporation and decomposition can be observed. Measurements were taken at a ramp increase of 10 °C min^{-1} under nitrogen between 25 °C and 500 °C.

FT-IR measurements were carried out using a Perkin Elmer FT-IR system spectra BX. DLS measurements were taken on a Malvern Zetasizer ZS 2,

refractive index of 1.5 was used for all sample measurements. HPLC was carried out using a Dionex Ultimate 3000 series. The sample was filtered with a 0.45 micrometre syringe and injected at a flow rate of 1 mL min^{-1}.

HPLC method was carried out at 30°C with the mobile phase consisting of acetonitrile (ACN) and water. The program began at 20% ACN and linearly increased to 95% ACN over 20 minutes. After this time the percentage of ACN was linearly decreased from 95% to 20% over a further period of 20 minutes.

NMR spectra were obtained from a Bruker Ultrashield 500 MHz spectrometer. UV/vis spectra, except for technical material validation, were obtained from a Jasco V-630 spectrophotometer.

Buchner filtration was carried out using a grade 3 Duran SCHOTT sintered funnel with pore size of 16-40 µm.

Samples in falcon tubes were immersed in liquid nitrogen till frozen then freeze-dried using a VirTis BenchTop Pro with Omnitronics from SP Scientific.

Electrospray Ionisation (ESI) LC-MS was carried out on an Agilent Technology 1200 series Bruker Daltronics HCT extra. Mobile Phase - Acetonitrile/Water both with 0.1% Formic Acid added. Gradient - 2 -95% MeCN over 1 min. Column - Phenomenex Kinetex C18, 50 x 2.1mm, 2.6um particle size. Flow Rate - 1.3 mL min^{-1}.

SEM was carried out using a Hitachi TM-1000 model using magnification between 100x and 1800x, accelerating voltage 15 kV. Microscopy was carried out using an upright Leica microsystem using a magnification of 30x.

To heat wash liquor aggregates, 100 mL of filtered wash liquor, in which aggregates had formed, was stirred and heated to 65 °C. During reduction experiments, wash liquor was added to solution of sodium hydroxide and sodium hydrosulfite and was stirred under reflux for 4 hours.

3.3. Results and Discussion

3.3.1. Denim wash tests

3.3.1.1. Validation of test material

Technical denim provided by CFT. BV, a test materials manufacturer was validated against a selection of commercially available denim jeans from UK stores. The use of a technical denim material would allow for full knowledge of the dye used and a homogeneous colour throughout the material, which is not affected by aesthetic effects as found in real denim garments such as distressing or stonewashing.[97]

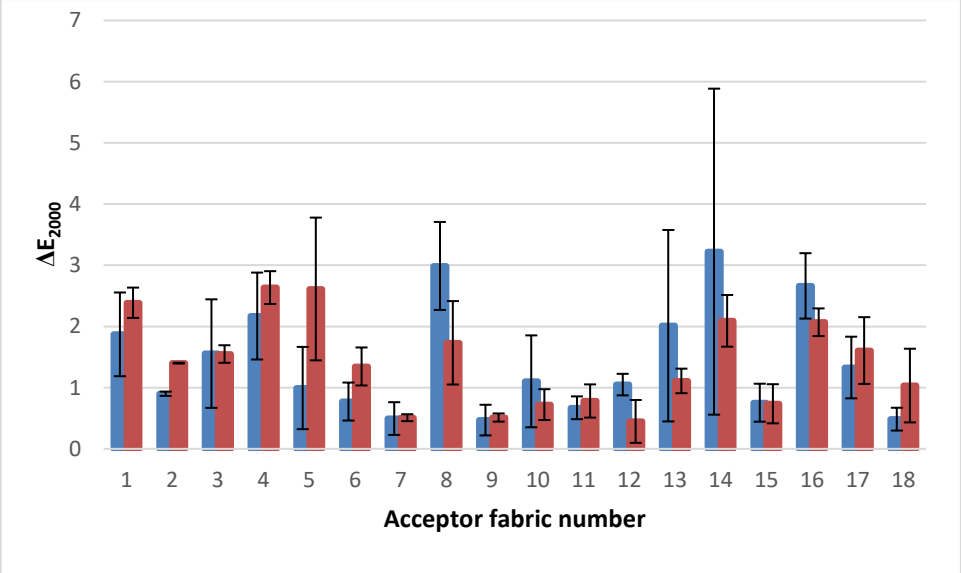


Figure 3.4: Comparison of ΔE_{2000} values between acceptor fabrics washed with technical denim (blue) and a selection of shop-bought denim samples (red). Washed at 40°C for 30 minutes with liquid detergent. Error bars show ± standard deviation of three repeats.

There were some similar levels of discoloration from the technical denim and the shop-bought denim samples across the different tracer acceptors (Figure 3.4). This data, taken together with the L*, a*, b* suggests that the technical denim can be accepted as a suitable model for real consumer shop-bought garments and accurately represents clothing within a consumer washload.

Comparison of separate L* (Figure 3.5), a* (Figure 3.6) and b* (Figure 3.7) values are also a good validation of using technical denim to represent commercially available garments. Not only does the technical material transfer in similar proportions to acceptor fibres as the commercial denim, but the colour that is transferred is also very similar in the colour space.

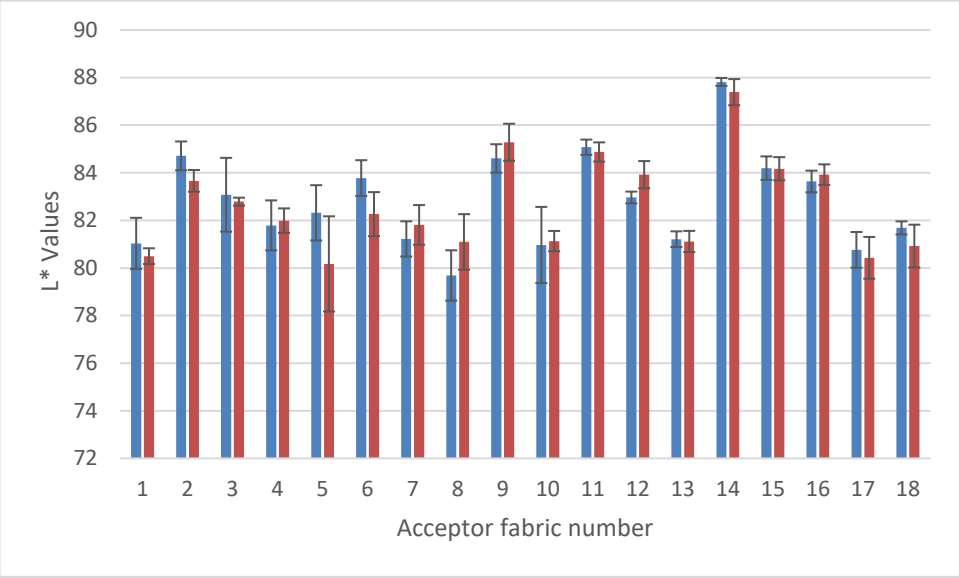


Figure 3.5: Comparison of L* axis values for technical denim (blue) and shop-bought denim (red). Error bars show ± standard deviation of three repetitions.

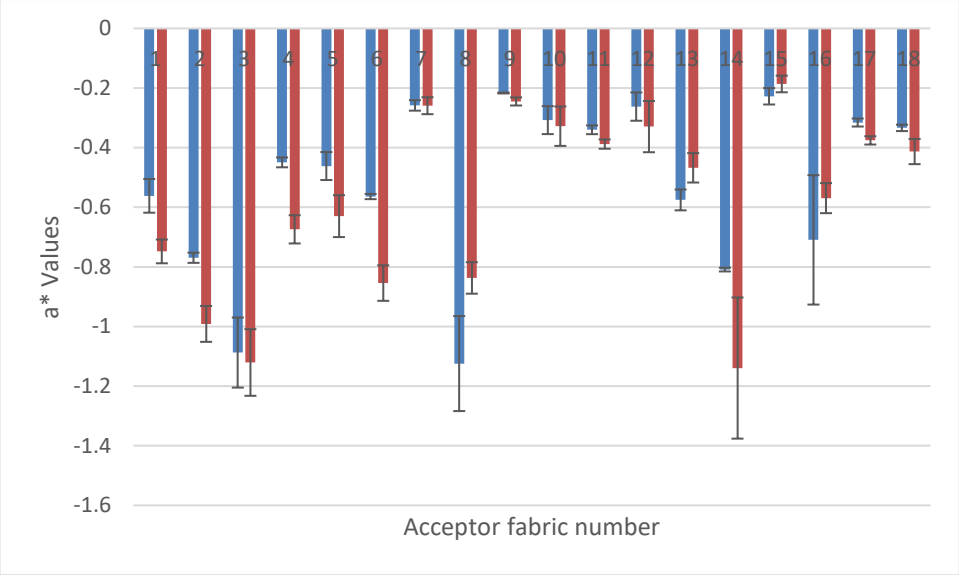


Figure 3.6: Comparison of a* axis values for technical denim (blue) and shop-bought denim (red). Error bars show ± standard deviation of three repetitions.

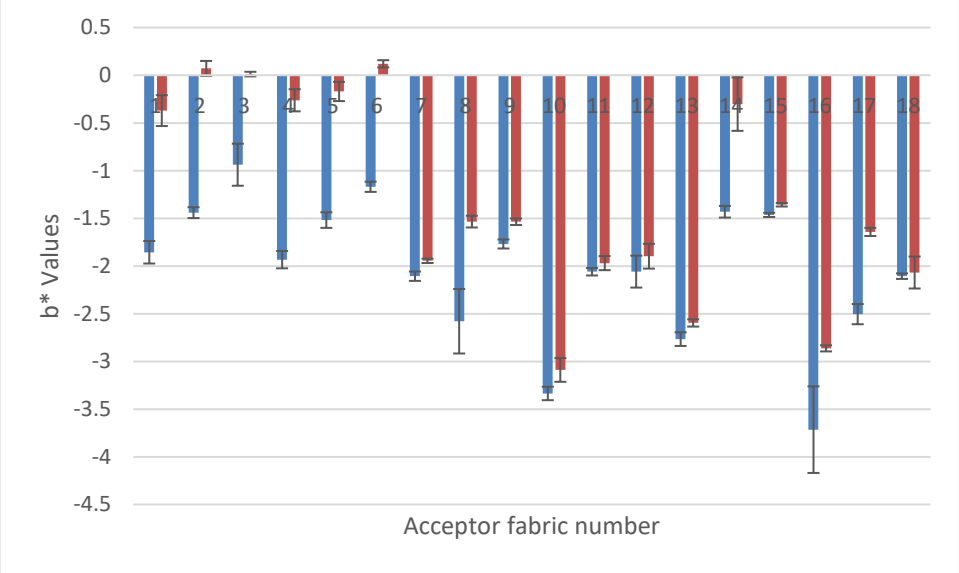


Figure 3.7: Comparison of b* axis values for technical denim (blue) and shop-bought denim (red). Error bars show ± standard deviation of three repetitions.

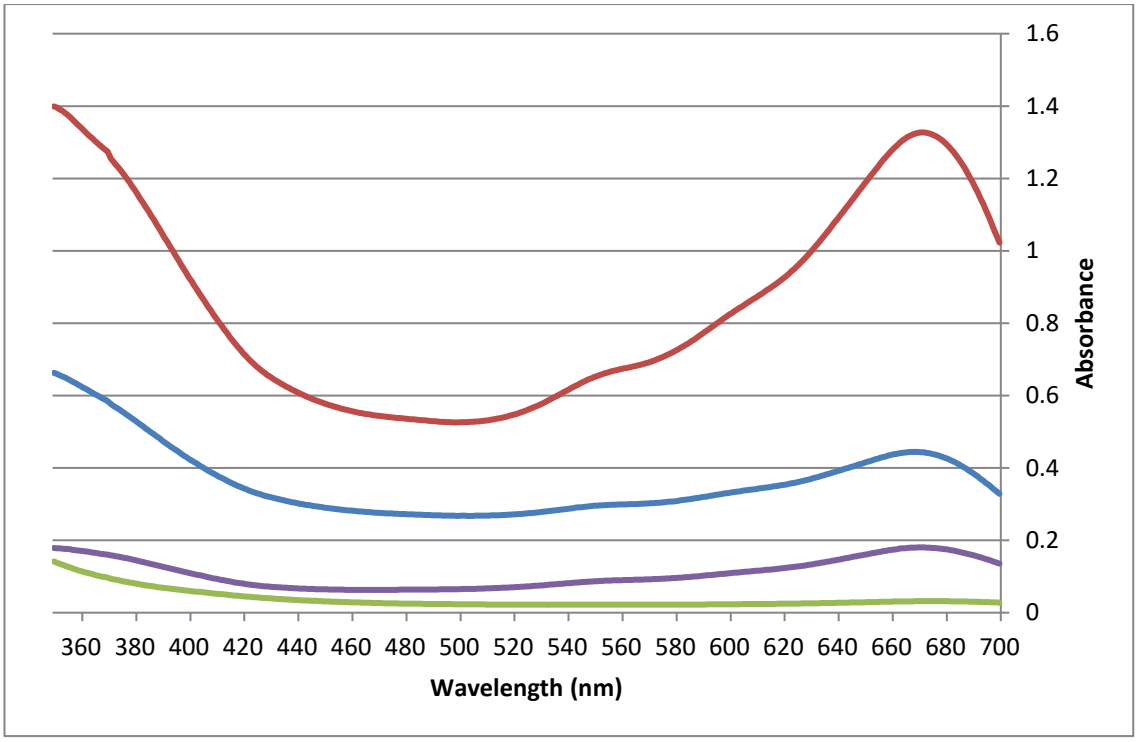


Figure 3.8: UV/vis spectra of technical denim sample (purple) compared to commercially available denim samples- Shop 1 Blue, Shop 2 red and Shop 3 green.

As a final validation, UV/vis spectra were measured of the separate denim samples (Figure 3.8). The $\lambda_{max\text{-}vis}$ value for the technical denim was significantly similar to two of the denim samples. This suggests that the colour of dyestuffs released from the technical denim is also similar to those released from the commercially available garments. After these comparisons, it can be concluded that the technical denim releases a similar shade of dyestuffs to the commercially available garments. These dyestuffs redeposit onto different acceptor fibres at the same relative magnitude of dyestuffs from the commercially available garments. Therefore, the technical denim is a suitable model fabric to use for denim dye transfer which allows uniformly dyed denim to be investigated. As the technical denim is known to be dyed with indigo dye, these validations also suggest the presence of indigo dye in the commercially available garments.

3.3.1.2. Initial wash tests

A small scale wash test was performed to investigate dye transfer without using large quantities of materials for each test. The test was carried out using a procedure adapted from ISO 105-C10:2007 colourfastness test. Denim was washed with multifibre acceptor strips comprising of different textiles in a nil detergent condition Figure 3.9 in order to understand the level of dye transfer in an aqueous environment from the denim alone and not influenced by other components in the wash, such as those present in detergents. Washing with multifibre strips allowed for investigation of dye transfer from denim onto a wider range of acceptor fabrics. The difference in colour and thus level of discoloration was measured by ΔE_{2000} (Figure 3.10).

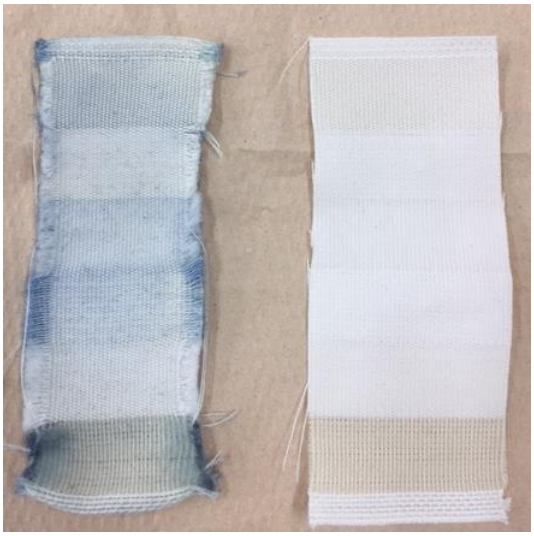


Figure 3.9: Multifibre strips after a nil-detergent wash with denim fabric (left) compared with an unwashed multifibre sample. Fibres from top to bottom are: secondary cellulose acetate, bleached cotton, nylon 6,6, polyester, acrylic, and wool.

As can be seen in Figure 3.9, a visible amount of dye is transferred from the denim fabric causing discoloration. The discoloration is not uniform across the acceptor fibres, suggesting the discoloration can be attributed to affinity of the staining species for specific fibre characteristics, instead of a layer of dyestuffs covering the surface of all the acceptor fibres held by weak van der

Waals forces. This confirms that some dye transfer occurs which cannot be attributed to cellulase backstaining as no cellulases were present in this wash. The presence of discoloration of non-cellulosic materials further confirms this finding. The most stained fibre types were wool, polyester and diacetate, while polyamide also showed significant staining (Figure 3.10). This suggests that there may be some hydrophobic quality to the staining species which is why these particular fibres were more stained than hydrophilic cotton. However, as this species appears to travel in the wash liquor, it is unlikely to be completely hydrophobic. The high transfer onto wool and significant transfer onto polyamide suggest that the amide group, which is capable of being a hydrogen bond donor and acceptor, may play a role in why the staining species is attracted to these fibres.

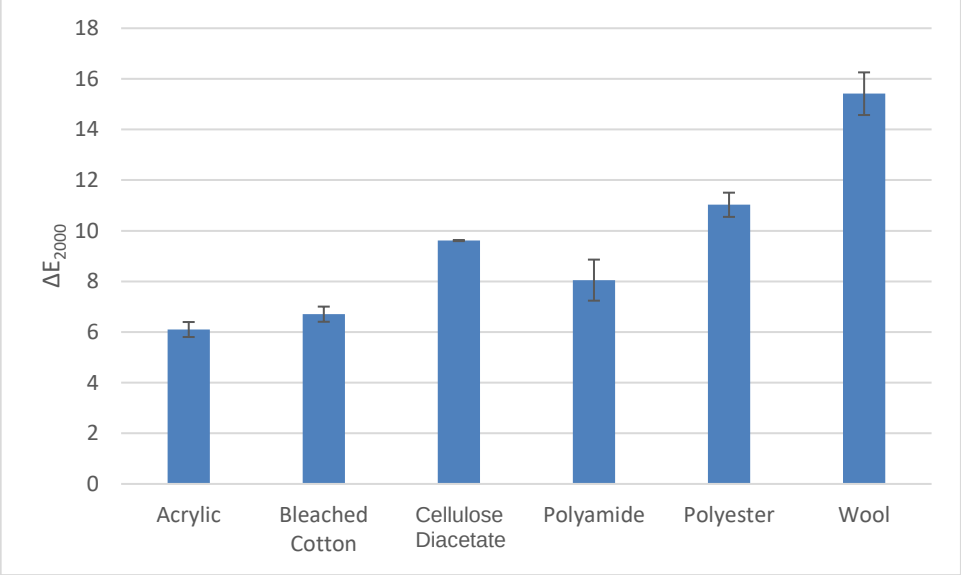


Figure 3.10: ΔE_{2000} values for different fibres on multifibre washed with denim, with nil-detergent. Error bars show ± standard deviation of three repetitions.

A blue wash liquor was produced during the initial wash of denim in water with agitation (Figure 3.11). It appeared a deep blue transparent liquid with small fibres present. These fibres settled towards to bottom of the sample vessel within 1 hour.

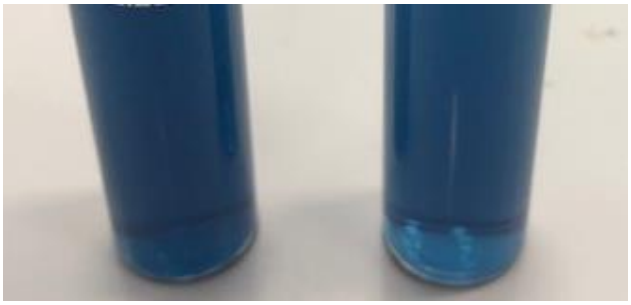


Figure 3.11: Denim wash liquor (nil detergent) before filtration (left) and after filtration through 16-40 micrometre funnel (right).

This wash liquor was filtered using a 16-40 µm sintered funnel to separate the solid from the liquid, and these separate components were then each washed with a new multifibre acceptor fabric. This was performed to investigate whether coloured fibres in the wash liquor, or whether the wash liquor itself were responsible for dye transfer. The filtered wash liquor appeared as a slightly paler blue transparent liquid and all visible fibres had been removed after this filtration. It was found that the wash liquor liquid was responsible for the staining, and not just a carrier for a solid staining species, suggesting that the staining species was water soluble or contained staining particles of less than 16 µm in size. This is counter-intuitive to what is known about indigo. In its parent blue form, indigo is not water-soluble in any significant concentration, and so should not be able to form a visibly blue solution with water. This suggests that the blue species may not be indigo or indigo alone and so chemical analysis is needed to provide characterisation. It is also possible that, while appearing as a solution, the wash liquor may actually be a colloid or fine dispersion and so, particle sizing is also important to understand the species.

3.3.1.3. Indigo wash test

As it was recorded by the manufacturer that the validated technical denim was indeed dyed with indigo dye, it was necessary to investigate the behaviour of commercial indigo in the wash test. In order to examine the behaviour of commercially sold indigo and dye transfer in aqueous solution, a nil detergent wash test was conducted with a multifibre strip and 0.05 g of

powdered indigo from Sigma Aldrich, whereby the indigo powder was added to the wash canister instead of a denim strip. As can be seen in Figure 3.12, the multifibre strip was significantly discoloured after this wash with commercial powdered indigo. However, the low affinity that indigo is known to have for fibres without any reducing agent, indicates that the dye powder formed a layer on top of the multifibre, held in place by weak interactions such as Van der Waals forces. Further evidence for this coating can be seen in the top fibre, cellulose diacetate. Where a loose thread covered the strip, upon its removal, a paler region on the strip can be seen, where it was shielded from the dyestuffs by the thread. Indigo was easily removed from the multifibre strip while handling, again suggesting the interaction between the dye and the fibre was weak.

Figure 3.12: Multifibre strip following wash test with commercial powdered indigo and water.

However, the pattern of discoloration across the fibres, while of higher magnitude, is similar to the discoloration of the multifibre from the denim strip and so behaves in the same way. This could suggest that actually, the staining species may be indigo and that these observed weak van der Waals interactions also play a role in staining from the denim species.

3.3.1.4. Heating of wash liquor

After a sample of denim wash liquor was filtered and left to stand for 24 hours, the wash liquor produced blue precipitates due to aggregation of particles. The wash liquor was heated and agitated at 65 °C, above the typical wash temperature used, in an attempt to breakdown these aggregates. However, this was not possible, suggesting that should a precipitate form during a wash, breakdown of the precipitate would not be possible by temperature alone. This may be of interest to remove the staining species from wash liquor. Coagulation and flocculation are techniques whereby particles are precipitated together, and this has been used as a previous method of removal of dyestuffs from dyehouse wastewaters.[98,99] If it were possible to accelerate an aggregation of staining species in the wash, the resulting precipitate may be able to withstand washing temperatures and thus, this could reduce dye transfer by removing the staining species from the liquor.

3.3.1.5. Reduction of wash liquor

Reduction of the wash liquor was also investigated. If indigo was present in the sample, it maybe be possible to reduce it to its leuco-form and remove the blue colour from the wash liquor. Sodium hydrosulfite is a commonly used reducing agent for indigo and so was added in excess to the wash liquor and the pH was increased with sodium hydroxide to mimic the industrial process of indigo reduction.[92] However, the wash liquor did not seem to reduce and the blue colour remained. This could suggest that either the blue colour of the liquor was not from indigo, or that the indigo was not able to be reduced by traditional methods, possibly due to the carbonyl group being unavailable for reduction due interaction with other species.

3.3.2. Sample Analysis

Dynamic Light Scattering (DLS) is a technique which measures laser light scattered by particles in solution to provide information about the size of these particles.[100] The z-average value for the unfiltered denim wash liquor

was 213.53 d.nm (diameter in nanometres) as determined by a Zetasiser particle sizer. This suggests that the particles within the wash liquor were of a colloidal range, with dispersed particles that do not settle in a short time frame.[101] Colloidal dispersions are irreversible systems; they cannot be easily reconstituted to their original state.[102] This explains why the previous heating of the denim wash liquor sample did not break down the solid aggregates. However, there was evidence that over an extended time frame, a matter of months, the dispersed particles in the denim wash liquor did aggregate and form blue precipitates, as seen in Figure 3.13. As indigo in its parent blue form is not water soluble, it makes sense that, should indigo be present, the DLS measurements confirm that the wash liquor is not a solution. However, there may still be some water-soluble species present within the wash liquor as the Polydispersity Index (PDI) width, a measure of size distribution within a sample, was incredibly broad at 137.2. An ideal PDI value for a measured value is around 0.1-0.4, which would signal that the sizes of the observed particles are similar to each other.[103] The broad particle size distribution of the denim wash liquor suggests that there are particles of many different sizes present, possibly due to aggregation and so there may be water soluble species present as well as non-water soluble particles. If a complex was present, with one part being water soluble, it is possible for the complex as a whole to experience enhanced water solubility.[104]

Due to the unknown nature of the staining species, assumptions were made when measuring DLS. A refractive index of 1.5 was used, as this is similar for other species such as cotton, which denim is made of which has a refractive index of around 1.6.[105] This may not be the correct value and so, particle sizes may not be exact. However, by using this refractive index for future samples, a comparison between these samples is possible.

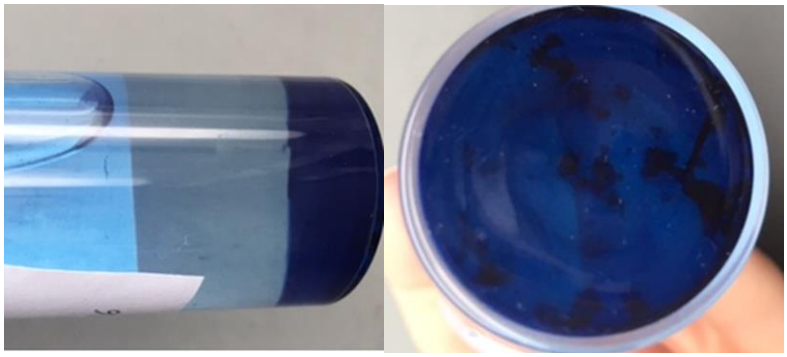


Figure 3.13: Images of filtered denim wash liquor in distilled water after 5 months. A blue solution can be seen (left) but blue precipitates have also formed at bottom of sample vial (right).

As identified in the initial wash tests on the denim fabric, it is the isolated denim wash liquor that causes the most amount of staining, even more so than the denim material. The wash liquor was filtered and analysed by UV/Vis spectroscopy (Figure 3.14) and showed a $\lambda_{max\text{-}vis}$ of 673 nm. That a reading was possible with UV/vis spectroscopy and at 673 nm, absorbing light in the red-orange region of the visible light spectrum, suggests that there is some solubility of the staining compound in water. The spectrum was compared to the water-soluble analogue of indigo, indigo carmine (Figure 3.15). However, UV/Vis spectra revealed that the two species were different as seen in Figure 3.16.

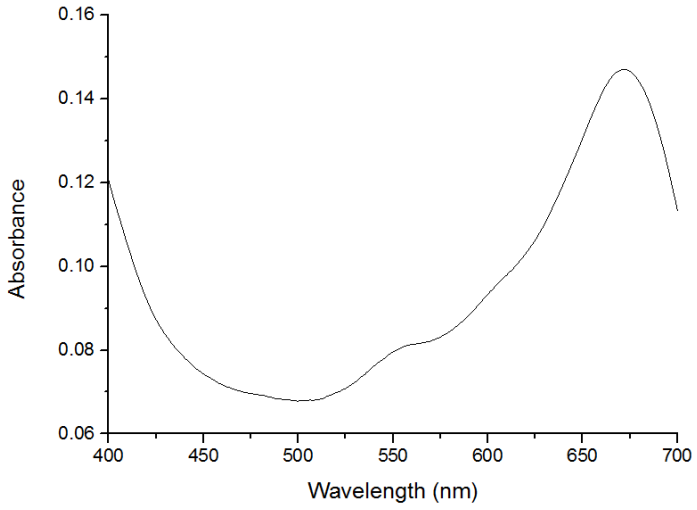


Figure 3.14: UV/Vis spectroscopy of filtered wash liquor solution from denim sample in water.

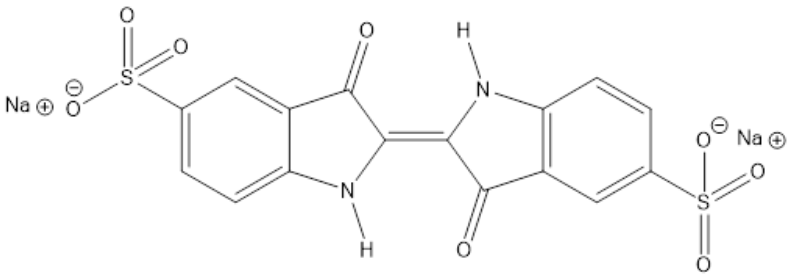


Figure 3.15: Structure of indigo carmine (C.I. Acid Blue 74). M_w: 466.35 $gmol^{-1}$.

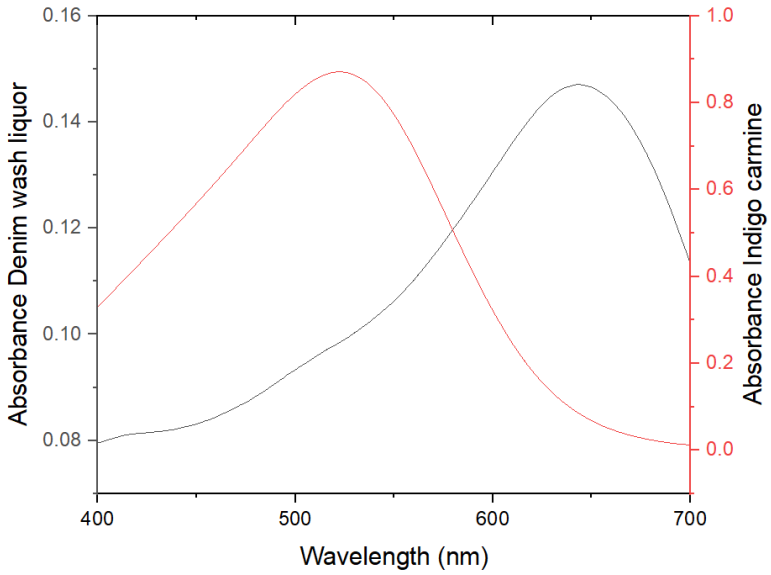


Figure 3.16: UV/Vis comparisons between denim wash liquor (black) and indigo carmine (red) in water.

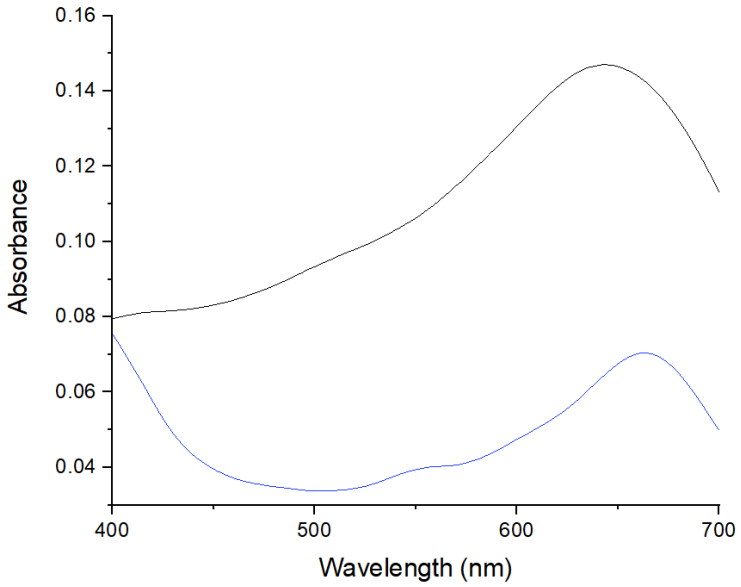


Figure 3.17: UV/vis spectra of denim wash liquor (black) and commercial indigo in water (blue).

The denim staining species spectra does not seem to match any $\lambda_{max\text{-}vis}$ value in the literature. However, the literature does not include UV/vis values for indigo in the solvent water. This is likely because indigo has such negligible solubility in water, that it is deemed non-water soluble. However, when trace amounts of commercial indigo were partially dissolved in water, the UV/vis trace also gave a $\lambda_{max\text{-}vis}$ reading of 673 nm (Figure 3.17). This suggests that while the species may not be indigo alone, the chromophore of the blue species is the same as the chromophore of indigo, shown in Figure 3.18.

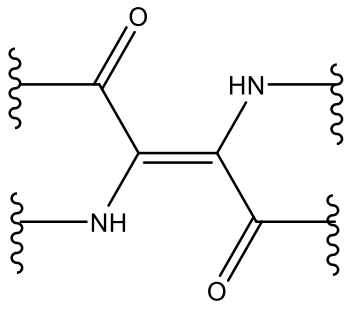


Figure 3.18: Chromophore of indigo.[106]

The wash liquor was run through a reverse-phase C18 High Performance Liquid Chromatography (HPLC) column using a solvent system and ramping method described in the literature to identify indigo, and degradation products of indigo.[107] The HPLC chromatogram in Figure 3.19 shows the presence of two main species which elute separately. In a reverse-phase column, the more polar species will elute first. Therefore, the two species found have slightly differing polarities.

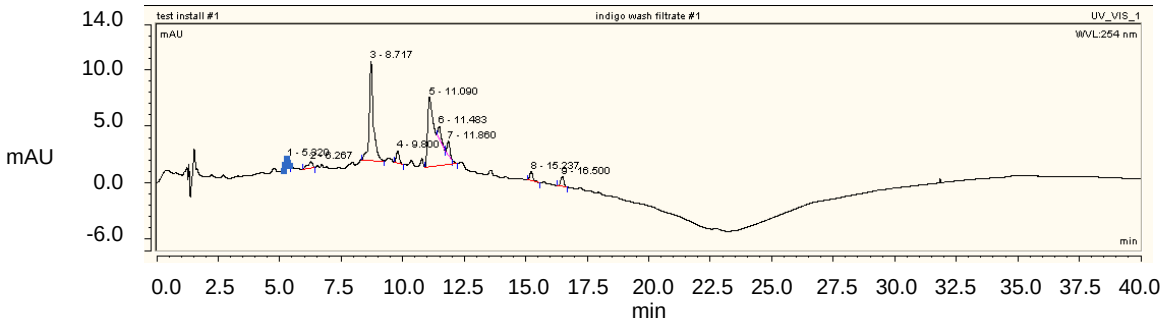


Figure 3.19: HPLC chromatogram of denim wash liquor after filtration with 16-40 µm filter.

The elution times were 8.7 mins and 11.1 mins for the main two compounds. Neither of these times correlates with any species of indigo or indigo degradation products in the literature. A peak for indigo would be expected at 21.8 minutes, but no such peak is present in this sample. This suggests that indigo as a separate species is not present in the sample. However, other analyses such as UV/vis have suggested that indigo or the chromophore of indigo is present. Therefore, it could be possible that indigo is present within a more polar complex and so elutes from the HPLC column earlier.

The denim wash liquor was filtered and measured by Electrospray Ionization Liquid Chromatography-Mass Spectrometry (ESI LC-MS) in both positive and negative ionisation modes. As per the HPLC data, two compounds were identified (Figure 3.20).

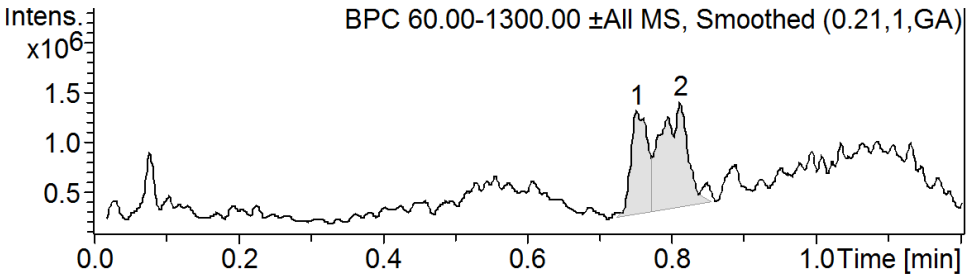


Figure 3.20: LC-MS chromatogram showing elution of two species.

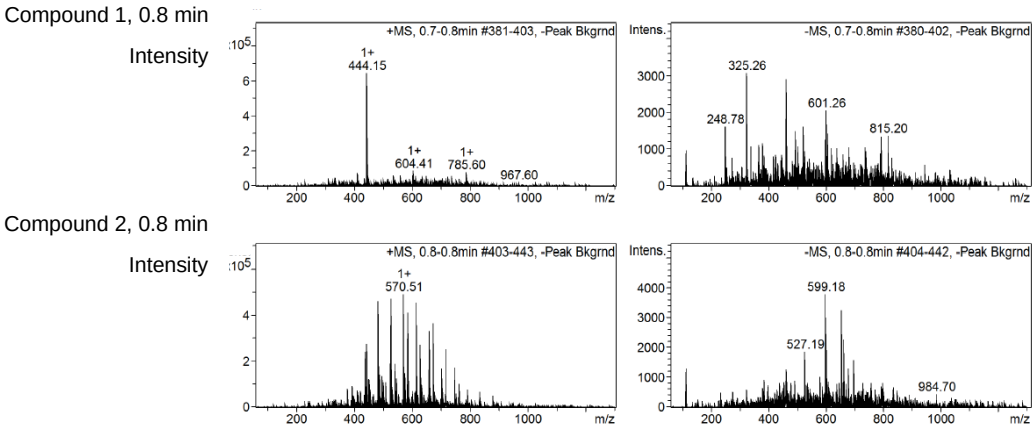


Figure 3.21: LC-MS mass spectra of both compounds in ESI positive mode (left) and ESI negative mode (right).

The first compound gave peaks of 967.60, 785.60, 604.41 and 444.15 (+) m/z and 815.20, 601.26, 325.26 and 248.78 (-) m/z (Figure 3.21). The second compound gave peaks of 570.51 (+) m/z and 984.70, 599.18 and 527.19 (-) m/z (Figure 3.21). Depending on the structure of the species and whether anionic species can be formed through loss of a functional group or proton, or addition of an adduct ion to produce a positive species, different ESI modes may show the presence of different compounds. No peaks corresponding to indigo from previous literature (263.2 m/z $[M+H]^+$) were found.[108] There are no obvious molecular fragments identified from this LC-MS analysis.

^{1}H-NMR spectroscopy of freeze-dried denim wash liquor in DMSO-d_6 revealed shifts in both the aliphatic and aromatic region (Figure 3.22). Spectra were difficult to gain due to low solubility in solvents. Indigo is

usually measured in DMSO-d_6 but this solvent was still not able to provide strong enough spectra for the unknown staining species. The ^{1}H-NMR spectra obtained of the unknown staining species does not agree with literature spectra of indigo.[108] This suggests that the protons present within the sample are in different environments to the protons in a pure indigo molecule.

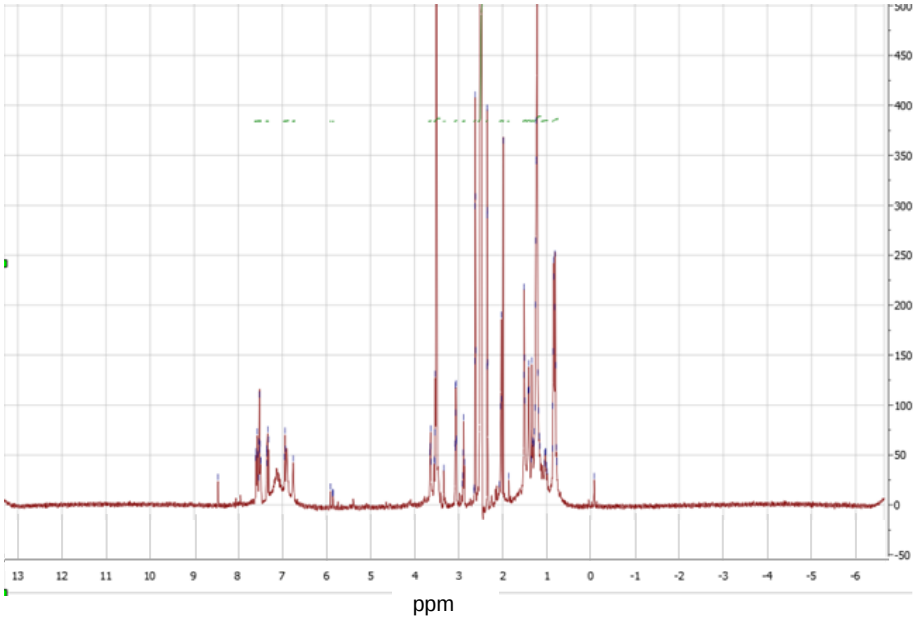


Figure 3.22: ^{1}H NMR of freeze-dried denim wash liquor in DMSO-d_6.

Fourier-Transform Infrared (FT-IR) spectroscopy of the freeze-dried denim wash liquor, shown in Figure 3.23, was compared to indigo (Figure 3.24), and it was found that there were some similarities between to two spectra, in particular, similarities were found at 1700 cm^{-1} and below. The fingerprint region of an FTIR spectra measures from 500 cm^{-1} to 1500 cm^{-1} and is named so as this region is very specific to different molecules.[109] That the spectra of the denim wash liquor sample and commercial indigo were very similar in appearance within the fingerprint region, suggests that there is evidence that indigo is part of the denim wash liquor and thus, staining species.

Peaks from the spectra were identified in Table 3.2 to provide further structural analysis of the denim staining species. Carbonyl peaks and carbon

ring structures were identified as well as the presence of nitrogen, suggesting the species was a mostly organic substance.

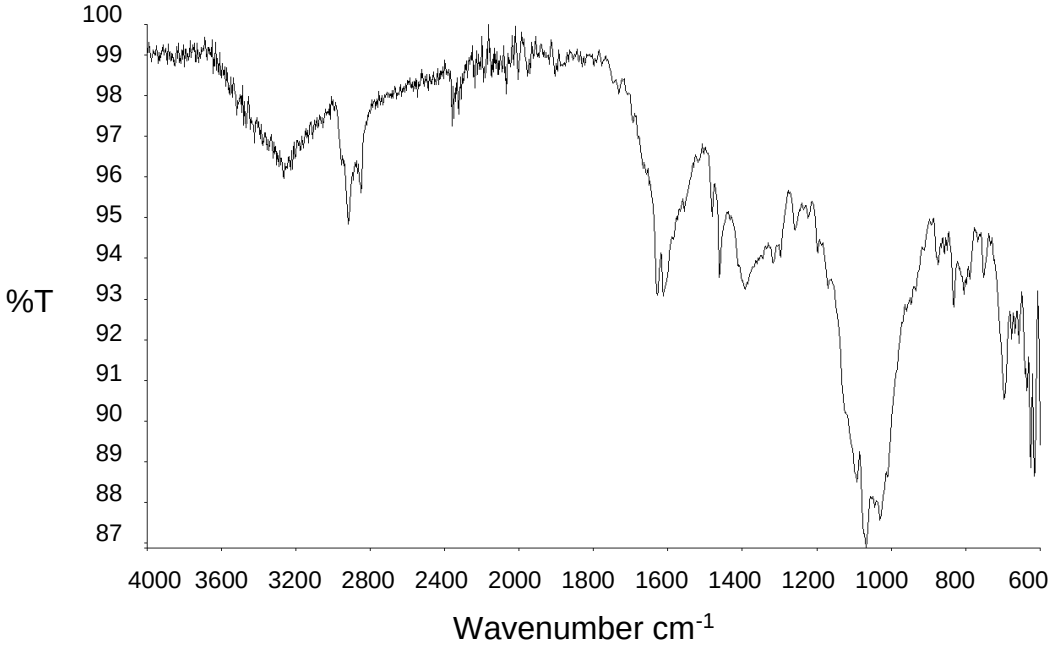


Figure 3.23: FT-IR spectra of freeze-dried filtered denim wash liquor.

Table 3.2: Peaks and corresponding functional groups from freeze-dried denim wash liquor sample.

Peak (cm^{-1})	**Functional Group**
3244	OH
2917	Methylene stretching
2362	N–H stretching
1627	C=O
1611, 1585, 1010	CC 6-membered ring
1481, 1461	CH, CC 6-membered ring
1389, 1124	NH, CN
1316, 1198	CC 6-membered ring, CC 5-membered ring, CH
1298, 752	CH
1169, 1070	CN, CH, NH
1095	CO, CN
878, 858, 711	CC 6-membered ring, CC 5-membered ring
790, 697, 640	CH bending

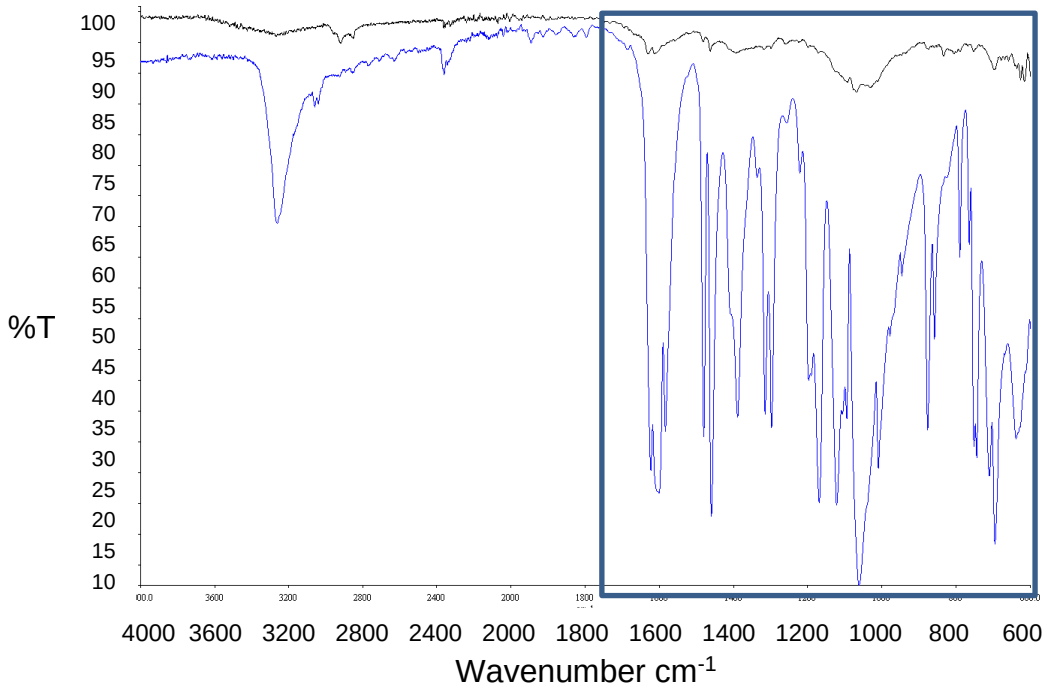


Figure 3.24: Comparison of FTIR spectra of freeze dried denim wash liquor (black) and indigo dye (blue). The blue box highlights area of similarity between spectra, however indigo signal is much stronger than that of freeze dried denim wash liquor.

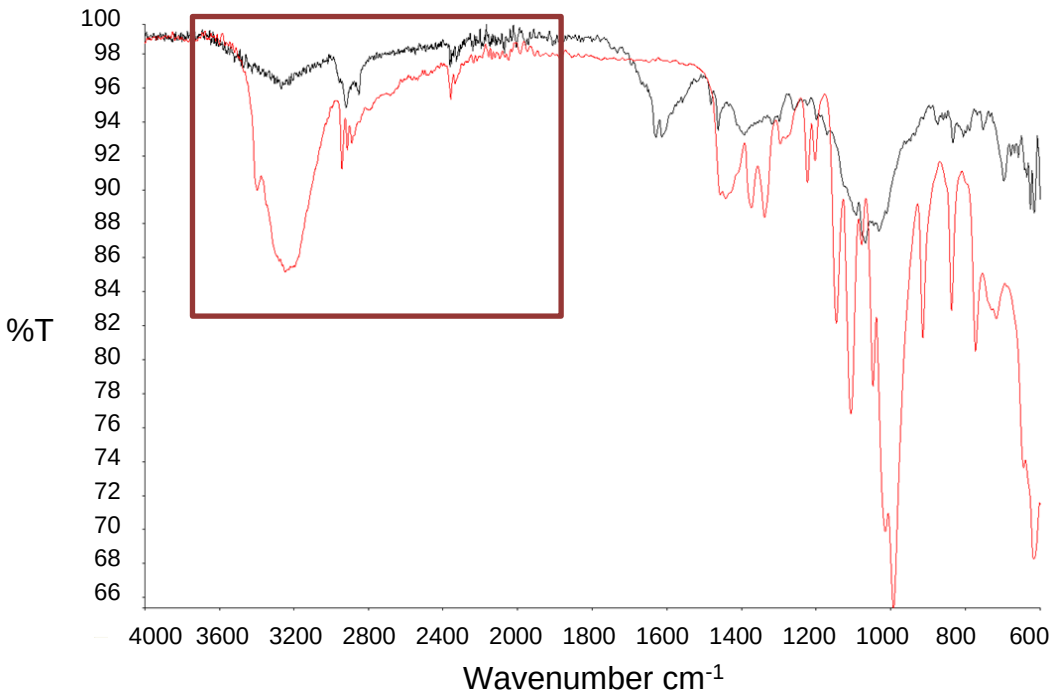


Figure 3.25: FTIR comparison of freeze dried denim wash liquor (black) and glucose (red). The red box highlights area of similarity between the two spectra.

However, at higher wavenumbers, the sample appears to resemble glucose, the monomer of cellulose which makes up cotton (Figure 3.25). This suggests that both cotton (cellulose) oligomers and indigo are present in the wash liquor. The O–H stretch of the denim wash liquor (DWL) sample has a slightly lower wavenumber than the O–H stretch in the cotton sample 3244 cm^{-1} compared to 3278 cm^{-1} respectively which may suggest hydrogen bonding at the DWL O–H.[110] While this is a very subtle difference in wavenumber, it is worth considering that the O–H groups of glucose will be hydrogen bonded within the commercial glucose sample. Therefore, the O–H peak of the glucose may already be at a lower wavenumber than the O–H peak an isolated glucose molecule.

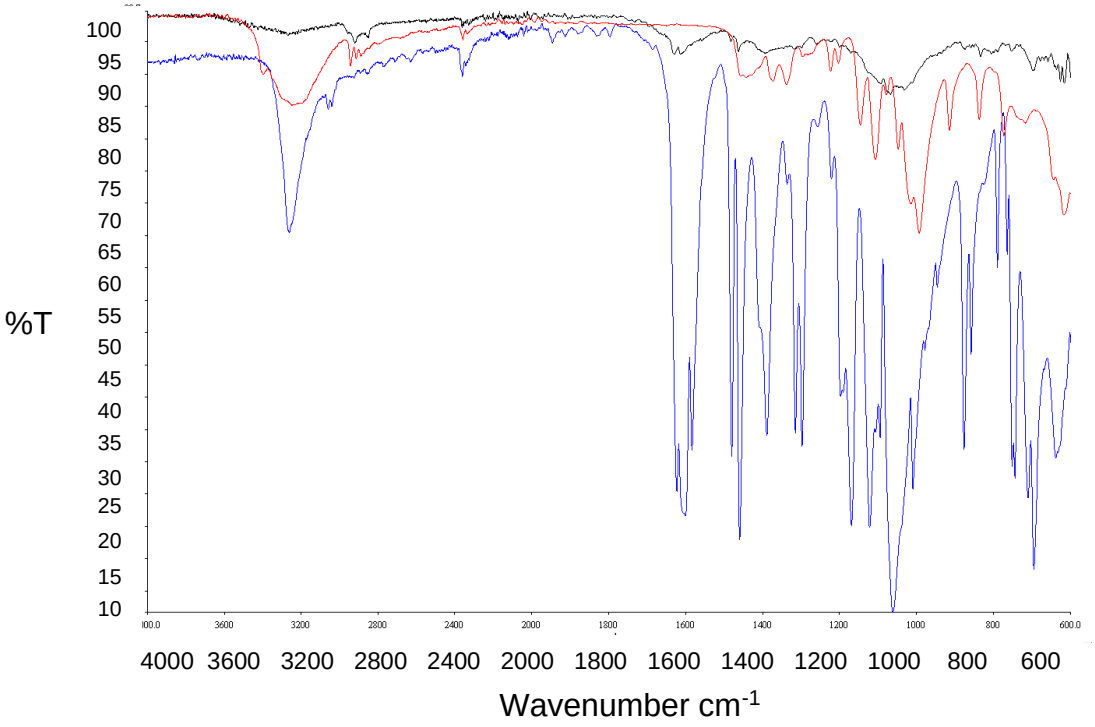


Figure 3.26: IR comparison between spectra of freeze dried denim wash liquor (black), indigo dye (blue) and glucose (red).

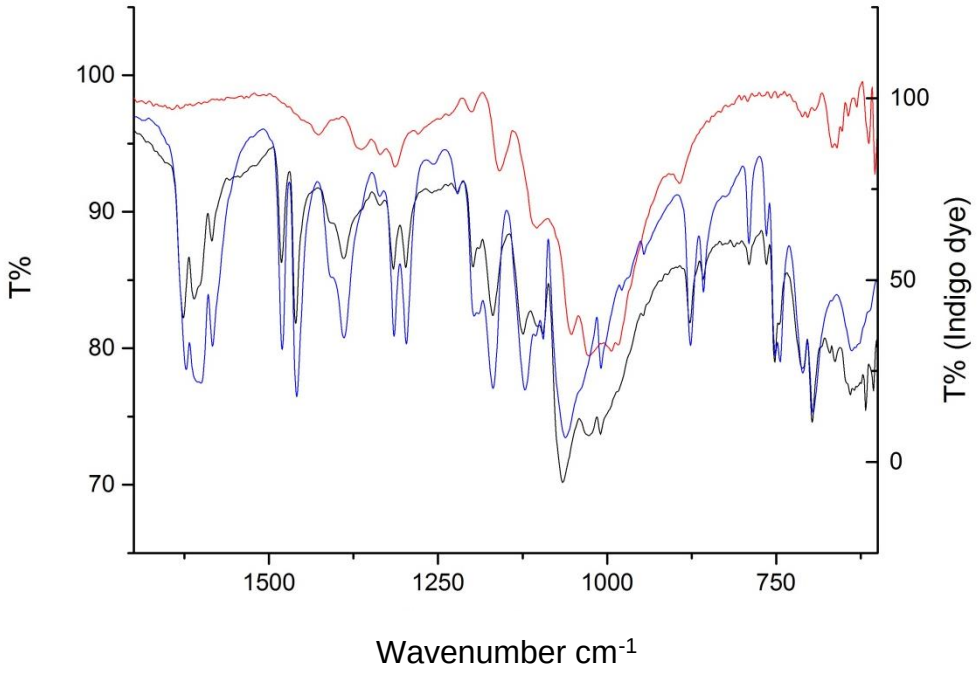


Figure 3.27: Close up of the fingerprint region showing similarity of spectra between the freeze-dried denim wash liquor (black), indigo dye (blue) and glucose (red). By plotting T% of indigo on secondary Y-axis, the similarities between spectra can be viewed more easily.

When comparing all three species (Figure 3.26, Figure 3.27), every peak from the denim wash liquor sample can be attributed to either the cellulose oligomer or indigo spectra. Therefore, the data seems to suggest that the denim staining species is a complex between indigo and cellulose oligomers. This would explain why the $\lambda_{max\text{-}vis}$ of the staining species in water is the same as indigo in water but why, through association with cellulose oligomers, the species exhibits different properties to indigo in other analyses such as ^{1}H NMR and HPLC. If the association involves the carbonyl region of the indigo molecule to the cellulose oligomers, this may also explain why the staining species was not able to be reduced by sodium hydrosulfite.

Scanning Electron Microscopy (SEM) of the filtered freeze-dried denim wash liquor seems to show two separate structure types within the sample. One is clustered, and one is more fibrous (Figure 3.28). The fibrous, rope-like structure seems to resemble cellulose nanofibrils, which are produced mechanically, for example by ball milling. In the denim washes using the Gyrowash, the steel balls will have had a similar mechanical affect and so it is likely that cellulose nanofibrils will have been produced and that they are visible in the SEM.[111]

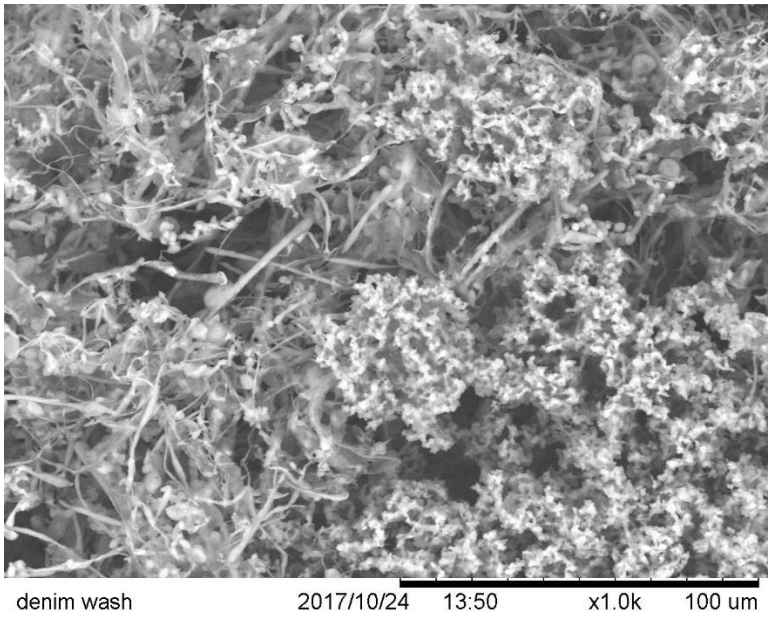


Figure 3.28: SEM of freeze-dried denim wash liquor.

The length of the cellulose nanofibrils related to the extent of mechanical breakdown of the cellulose fibre, with longer fibril length suggesting less breakdown. The denim sample has fibres of varying lengths from 27.1 µm to 61.3 µm, as measured by the SEM. This suggests the mechanical agitation of the denim sample by the steel balls was not uniform throughout the fabric sample. Using light microscopy, it was observed that the freeze-dried solid appears a homogenous colour throughout (Figure 3.29). While FTIR suggested that the species was a complex between cellulose oligomers and indigo, the homogeneity of colour from light microscopy shows that the two components of the complex are well integrated together and there does not appear to be any separate regions of blue indigo or cellulose monomers. Even with the existence of the separate fibrils present in the SEM, these do not appear as a separate colour from the rest of the sample under light microscopy. This suggests a strong attraction between the two components of the complex and so, further explains why certain analyses such as NMR and HPLC do not match literature values for the individual components.

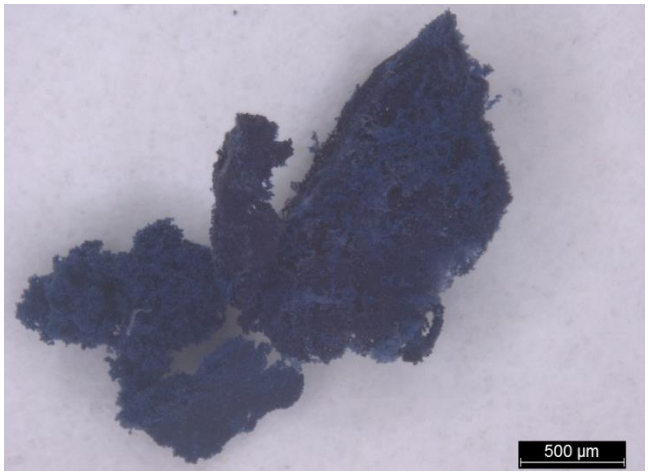


Figure 3.29: Light microscope picture of freeze-dried filtered denim wash liquor sample at a magnification of x30.

The sample was investigated for the presence of any crystalline material that would be suitable for an X-Ray crystallography measurement. The water in

the samples of denim wash liquor was evaporated slowly at room temperature to try and initiate crystallisation. Solvents were also investigated for possible recrystallisation and co-crystallisation. Freeze-dried denim wash liquor was insoluble in acetone and dichloromethane. As the wash liquor appears to have some material dissolved, it was used in vapour diffusion/co-crystallisation. The blue wash liquor was places into a small glass vial with the lid loosely screwed on. This small vial was then placed into a large vial containing DCM, a solvent that is more volatile than water and that does not seem to dissolve the wash liquor solid. The lid was screwed onto the large vial and the sample was set aside to observe if any solid could be collected. As the DCM diffuses into the inner vial, the staining species becomes less soluble in the solvent mixture between water and DCM. Theoretically, this would cause the solid staining species to precipitate, possible in a crystalline form. Some solid was collected from both air evaporation and vapour diffusion. However, after investigation with microscopy, it was determined that no crystalline material was obtained and so it was not possible to measure an X-Ray crystal structure.

Thermogravimetric analysis (TGA) of the sample suggests that the freeze dried denim solid starts to decompose at around 160°C and that there may be a second decomposition step at around 365 °C (Figure 3.30). Multiple decomposition steps may be indicative that more than one kind of species is present, and this would be expected should a cellulosic-indigo complex be present. The mass loss at around 160°C may reflect the beginning of sample melting. Any water in the sample would have evaporated before this temperature was reached. However, 160°C is too low a decomposition temperature for both indigo (390°C) and cellulosic oligomers alone (305°C cellulose), which have been identified as present through FT-IR.[112],[113] This is further evidence of the presence of a mixture between these two species and that there may be some electrostatic interaction between them. Sharper, higher melting points are associated with purer compounds, which suggests that a low and broad decomposition may be attributed to a mix of compounds. If there was no association between the two species, then it may be expected that two single decomposition points would be present

relating to the reported decomposition points of indigo and cellulose oligomers respectively.

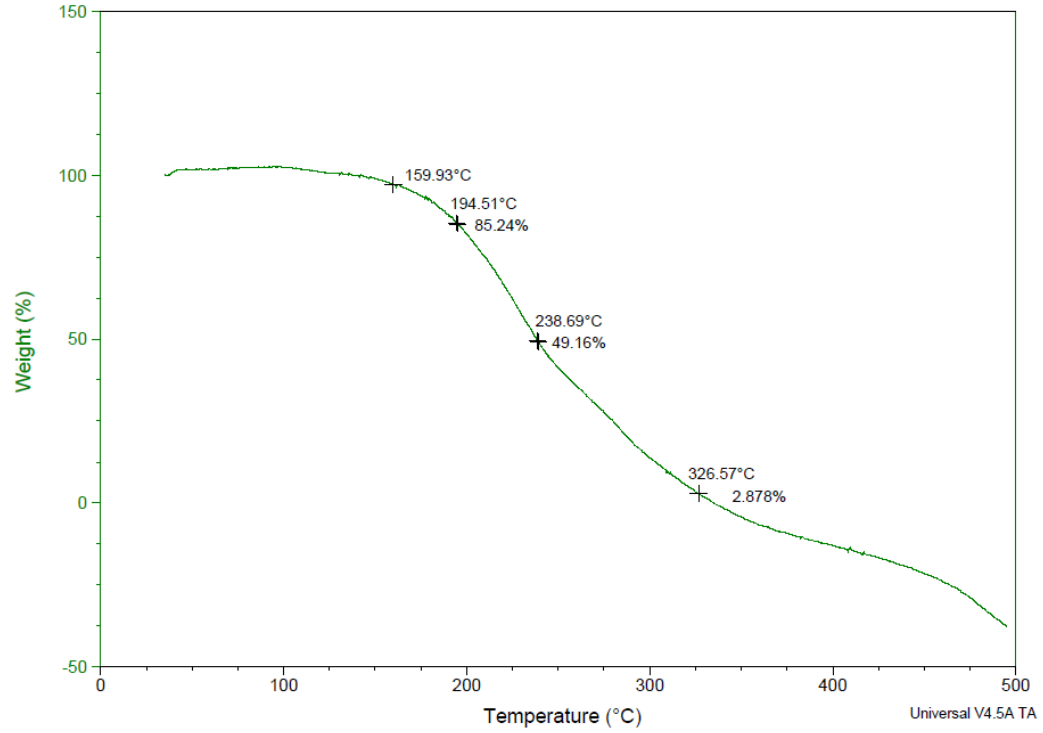


Figure 3.30: Thermogravimetric analysis of freeze-dried denim solid.

3.3.3. Further wash tests to understand behaviour of denim staining species

Further wash tests using distilled water were carried out to understand how the staining species behaves under different conditions such as temperature, agitation and pH.

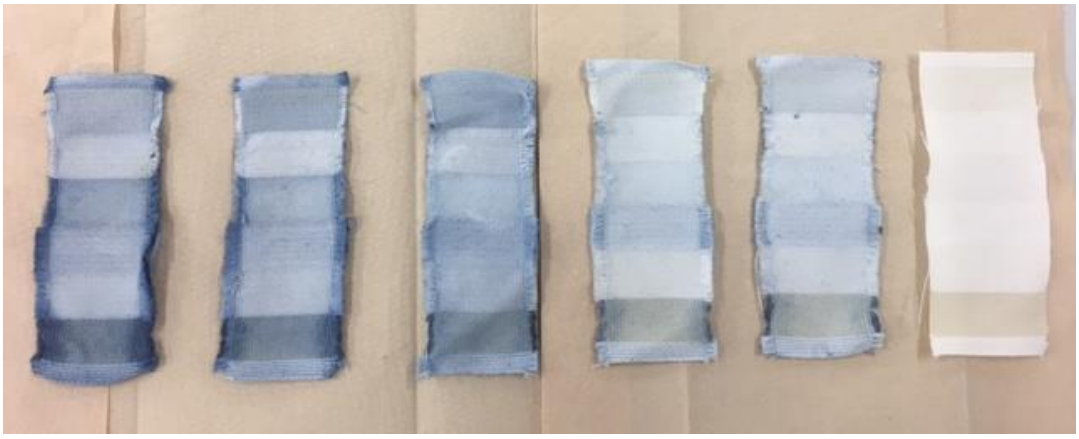


Figure 3.31: Multifibre after washing with denim in water at altered pH. From left to right: pH 3, pH 5, pH 7, pH 9, and pH 10.6, unwashed multifibre.

3.3.3.1. Effects of pH on dye transfer

pH was altered to measure the effect on dye transfer. It was observed that the wash liquor at lower, more acidic pH was less intensely coloured and the multifibre washed at lower pH were more stained (Figure 3.31 and Figure 3.32). This suggests that at lower pH, either the staining species is protonated and so is less water soluble, or the acidic protons help to mask repulsion between anionic fibres and an anionic staining species, causing higher dye transfer. However, at higher pHs than neutral pH 7, the staining species is deprotonated and so is more water soluble and therefore remains in solution rather than re-depositing onto acceptor fibres, and possible repulsion between the staining species and anionic fibres is increased. Cellulose diacetate, polyester and, to some extent, acrylic are more hydrophobic fibres, unlikely to attract charged particles in solution. However, at pH7, the dyestuffs may be neutral and exhibit no charge and therefore, associate with the more hydrophobic fibres. This could explain the increased dye transfer at a neutral pH for these fibres.

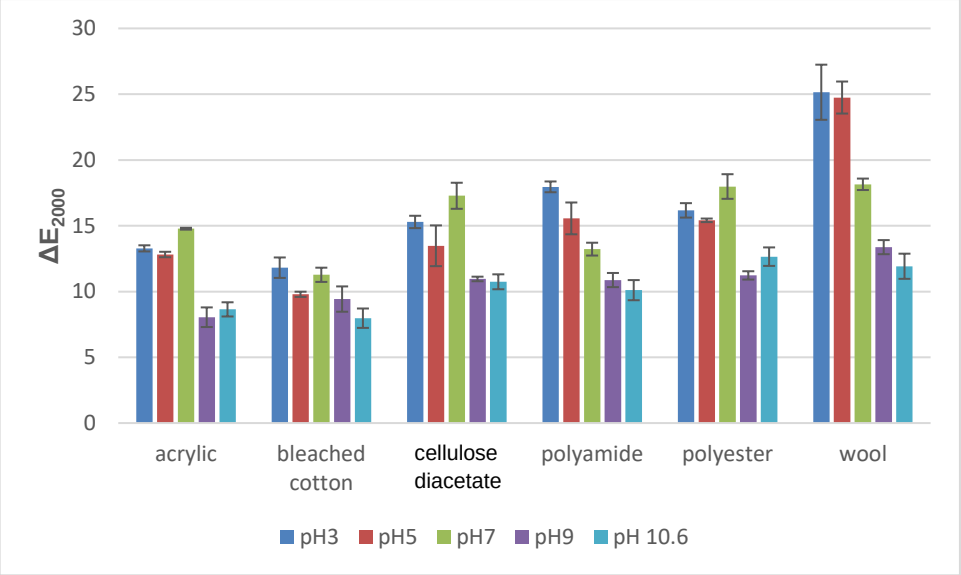


Figure 3.32: Effect of increased pH on dye transfer from denim. Error bars show ± standard deviation of three repetitions.

3.3.3.2. Effects of agitation on dye transfer

Agitation was increased by increasing the number of steel balls in the wash canister from 0 to 35 with denim, distilled water and a multifibre strip (nil detergent). The general trend in Figure 3.33 is that with increased agitation, there is increased dye transfer. However, there also seems to be a peak in dye transfer with 5 steel balls bearings, which then drops with 10 steel balls. This may occur due to the space inside the canister that allows the dyestuffs to move more freely with 5 steel balls than 10. However, when agitation is increased from 10 steel balls onwards, the degree of dyestuff released is great enough that space inside the canister for dyestuff movement is no longer a limiting factor on dye transfer

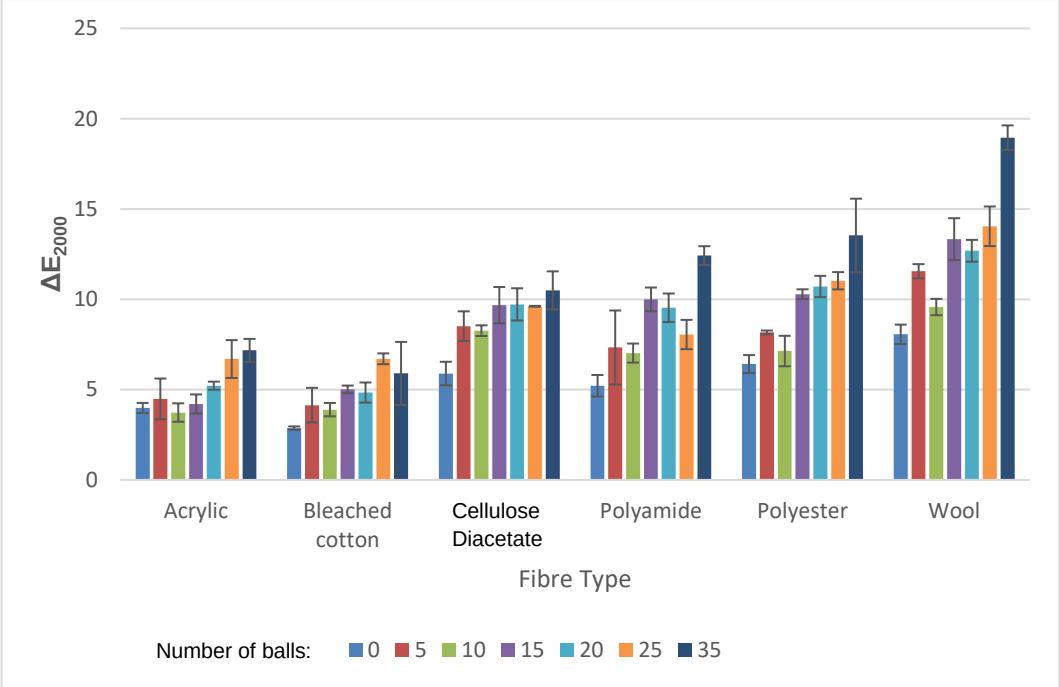


Figure 3.33: Effect of increased agitation on dye transfer from denim. Number of steel balls increased from 0 to 35. Error bars show ± standard deviation of three repetitions.

3.3.3.3. Effects of Temperature on dye transfer

Dye transfer increases with higher temperature (Figure 3.34). Collision Theory states that increased temperature increases the rate of reaction. This is because at higher temperatures, particles in the system have high kinetic energy and so can move around more and are more likely to collide with other particles in the system with sufficient energy and react.[114] In a similar sense, the staining species particles will move around more at a higher temperature of wash due to increased kinetic energy of these particles. The more the staining species particles move, the more likely they are to come into contact with and redeposit onto acceptor fabrics.

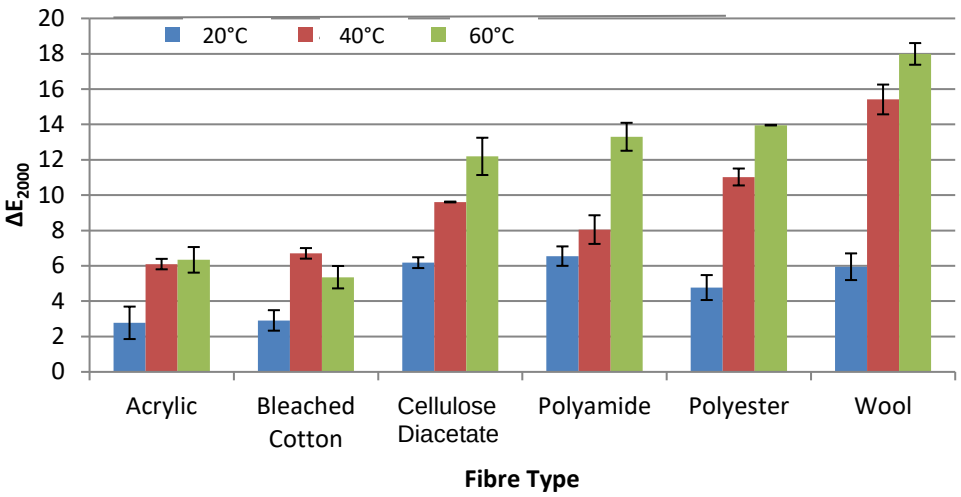


Figure 3.34: Dye transfer from denim onto acceptor fibres washed at different temperatures. Error bars show ± standard deviation of three repetitions.

3.3.3.4. Effects of detergent addition to wash on dye transfer

The presence of detergent in a wash system alters the extent of staining from denim to different degrees across the acceptor fibres (Figure 3.35). Detergents contain existing technologies to reduce dye transfer such as DTI polymers and surfactants for dye encapsulation. These technologies reduce the level of dye transfer from the denim across all acceptor fibres to some extent. DTI polymers complex with vagrant dyestuffs through attractive supramolecular interactions and hold them in solution to prevent re-deposition on acceptor textiles.[50,51] Surfactants can encapsulate vagrant dyestuffs, holding it in a surfactant micelle and so, preventing re-deposition onto acceptor textiles. The detergent used also has a pH of around pH 8. The pattern of dye transfer across the acceptor fibres when detergent is used is very similar to the pattern of dye transfer from denim at higher pH levels as would be expected.

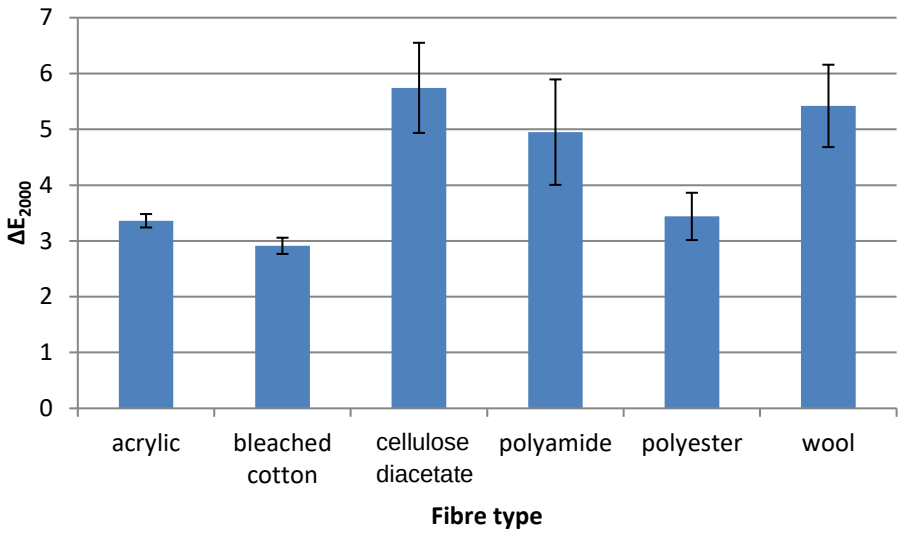


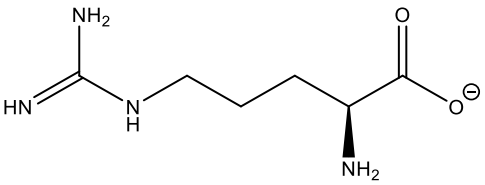
Figure 3.35: Dye transfer from denim onto different acceptor fibres washed with detergent and rinse step. Error bars show ± standard deviation of three repetitions.

3.3.4. Supramolecular recognition of sample with amino acids and PHMB

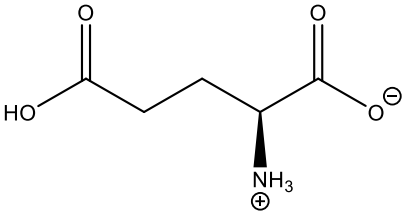
When considering the data from the denim wash tests, it is apparent that the staining species from denim adhered in some way to proteinaceous fibres wool and polyamide over other fibre types. Amino acids, which like these fibres contain an amide moiety, were investigated for their attraction to the staining species for further complex formation, and to act as a possible competitive inhibitor, to prevent the same level of dye transfer onto fibre.

Amino acids are naturally occurring molecules which are capable of bonding through many different kinds of intermolecular forces such as electrostatic, π-π, π-cation and π-anion. α-amino acids contain a central α-carbon which is bonded to both an amine and a carboxylic acid functional group; the α-carbon is also bonded to a hydrogen and the side chain of the amino acid. With the exception of glycine, which has the side chain of H, this central carbon is chiral and so both D- and L-isomers of the molecule may be formed; in nature, typically the L-isomer is produced.[115] Depending on the side group of the amino acid, these biomolecules may be used as sensors for other species.

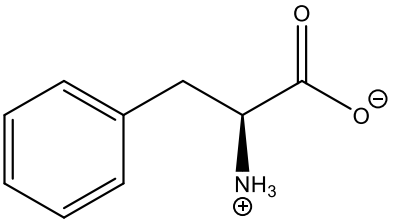
Whilst it was assumed that the staining species would form attractive intermolecular interactions with the amino acids (Figure 3.36), it was not known which type of side chain would be most complimentary and produce strong interactions. Therefore arginine (cationic, guanidinium side chain; **3.1**), glutamic acid (anionic side chain; **3.2**) and phenylalanine (aromatic side chain; **3.3**) were all investigated.



(**3.1) (M_w: 174.20 gmol^{-1}**)



(**3.2) (M_w: 147.13 gmol^{-1}**)



(**3.3) (M_w: 196.19 gmol^{-1}**)

Figure 3.36: Chemical structures of (3.1) L-arginine, (3.2) L-glutamic acid and (3.3) L-phenylalanine.

Polyhexamethylenebiguanide hydrochloride (PHMB) (Figure 3.37) was also investigated due to the presence of its guanidinium moieties which are cationic and so may have attractive interactions with the staining species which may have anionic properties, as evidenced by the pH wash test, especially when detergent is present. This allowed for a comparison between small molecules such as arginine and larger polymers as to which produced lower dye transfer. An initial experiment for attractive interactions

comprised of the addition of each amino acid to separate samples of filtered denim wash liquor (nil detergent). Visual observations were made and absorbance measurements were taken.

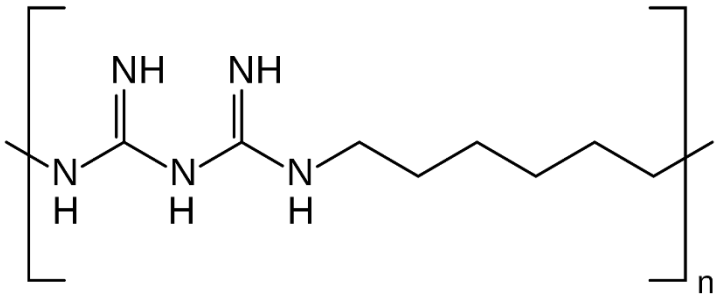


Figure 3.37: Structure of PHMB.

3.3.4.1. UV/vis measurements of denim wash liquor with amino acid/PHMB addition

As can be seen from Figure 3.38, all additions to the wash liquor resulted in much lower absorbance readings, as the wash liquors were much less intensely coloured. This is because the additions to the wash liquor caused more dyestuff to precipitate, possibly through complex formation with the additives. Arginine gave the lowest absorbance, followed by phenylalanine, glutamic acid and PHMB respectively. This suggest that a larger, water-insoluble complex was formed between the staining species and the arginine, removing the blue staining species from solution and thus leading to lower absorbance measurements. Arginine has a guanidinium side group, which has been mentioned in previous literature to form strong supramolecular interactions with anionic species such as electrostatic interactions and hydrogen bonding.[116] Because of the finding that amino acids and PHMB promote aggregation and precipitation of the dyestuff with the additives, it was proposed that they may reduce dye transfer in a domestic wash by acting the same way.

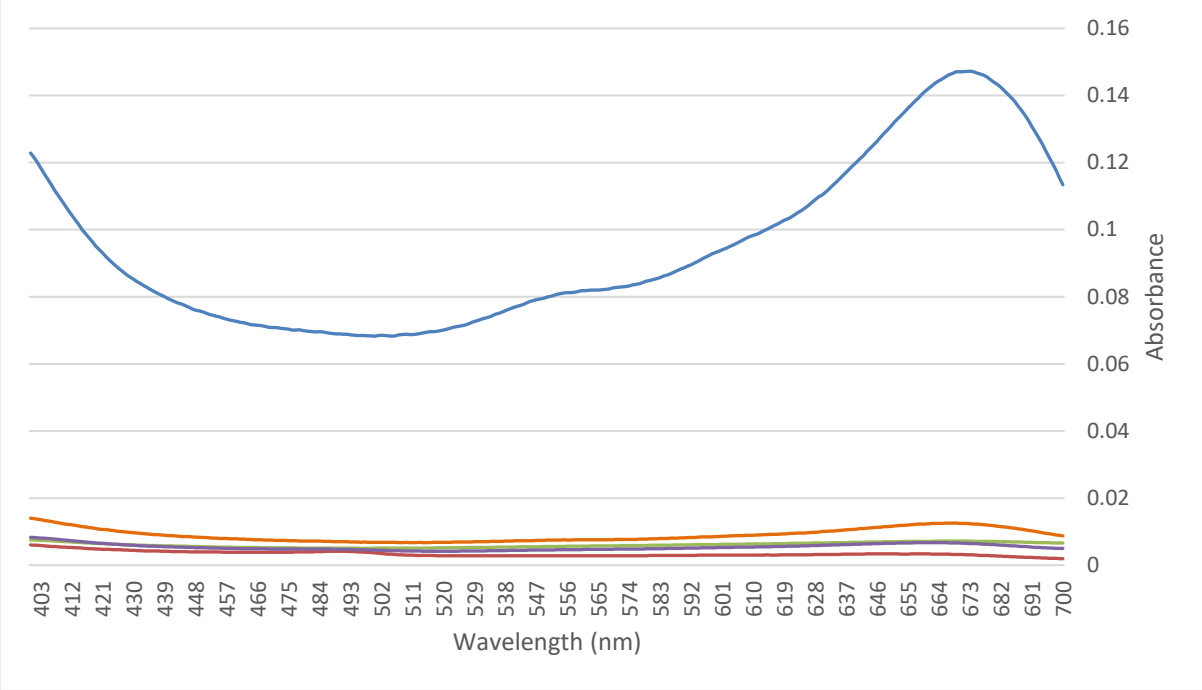


Figure 3.38: UV/Vis spectra of denim wash liquor alone (blue) and in combination with glutamic acid (green), PHMB (orange), arginine (red) and phenylalanine (purple).

As can be seen in Figure 3.39, the samples with the additives in show a distinct difference to the precipitate and the liquid liquor, with them being less intensely coloured than the original denim wash liquor sample. The denim wash liquor with Glutamic acid only appears slightly less intensely coloured however, as the UV/vis data shows a low absorption, this suggests that the precipitates are smaller in this sample and so may not appear as a separate solid like the other samples. Phenylalanine is known to self-assemble into fibre like structures and this may explain the contrasting appearance of the freeze-dried phenylalanine sample to the other amino acid samples (Figure 3.39).[117]

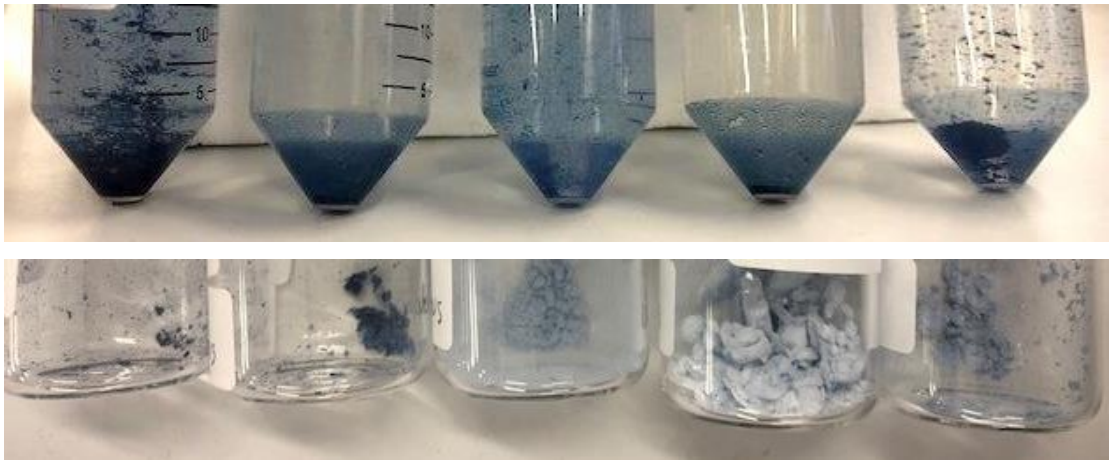


Figure 3.39: Comparison of wash liquors (top) and freeze dried samples (bottom). L-R: Denim wash liquor, denim wash liquor with arginine, denim wash liquor with glutamic acid, denim wash liquor with phenylalanine, denim wash liquor with PHMB.

3.3.4.2. Dynamic Light Scattering (DLS) to determine particle size of species in denim wash liquor with amino acid/PHMB addition

Using DLS, the Z-average allows for a comparison of particle size between samples, however, it may be skewed by an outlier. For samples which are multimodal or that have high PDI values, the intensity mean may be the best parameter to compare as this value refers to the particle size that has the most particles corresponding to it in solution. DWL-PHMB DWL-Glu, DWL-Phe and DWL-Arg all had multimodal (more than one peak). DLS measurements and all measured samples have high PDI values to a similar magnitude. Therefore, it is better to compare these samples by their intensity mean (Table 3.3).

Table 3.3: Different DLS parameter data for denim wash liquor solutions with and without amino acid and PHMB additives.

Sample	Z-average (d.nm)	Intensity mean (d.nm)	Number mean (d.nm)	Volume mean (d.nm)	PDI width
Denim wash liquor	213.5	538.0	61.8	2907.0	137.2
Denim wash liquor with Arginine average	411.0	1095.3	77.8	3637.0	373.4
Denim wash liquor with Glutamic acid average	269.4	500.7	66.9	2666.0	167.3
Denim wash liquor with Phenylalanine average	654.6	910.2	385.9	2035.7	407.4
Denim wash liquor with PHMB average	256.2	232.6	58.8	217.8	157.7

Phenylalanine, having a benzyl functional group is a larger molecule than glutamic acid or arginine. By comparing the different aspects of the DLS data, it can be inferred that while the DWL-Phe sample contained large molecules in terms of intensity mean, there were more molecules in the sample, and they took up less volume. This may suggest that there were lots of molecules in close association with each other. Indeed, due to the hydrophobic effect, phenylalanine is known to self-assemble in aqueous solution, through π-π stacking of the aromatic ring.[117] However, the DWL-Arg sample shows a large intensity mean particle size and a large volume mean despite having a small number mean. This suggests that there were fewer particles than in the DWL-Phe sample, but that these particles were larger in size due to more aggregation between arginine and the denim staining species.

DWL-Glu seems to have similar DLS measurements as the original Denim wash liquor sample, suggesting that that no significant aggregation occurred to increase observed particle size. Pairing this with the UV/Vis data, this suggests that the staining species has been precipitated out with glutamic acid, but the precipitates stay small and do not self-assembly into larger aggregates, perhaps due to electrostatic repulsion between carboxylate groups of glutamic acid.

PHMB is a macromolecule which explains why the DWL-PHMB number mean is so low in comparison to the other samples, as there will be less molecules of PHMB in a certain volume than in the same volume of discrete amino acids. PHMB is capable of forming interactions through hydrogen bonding, electrostatic interactions and hydrophobic interactions.[118] Because of this, the polymer chains may interact together to form condensed particles resulting in smaller intensity mean and smaller volume measurements. Therefore, it is difficult to tell whether the denim staining species is also involved within the PHMB complex, however UV/vis data suggests that the presence of PHMB does precipitate out the staining species, and so it is likely that the staining species is involved with the PHMB complex.

3.3.4.3. Liquid Chromatography Mass Spectrometry (LC-MS) to elucidate species present in denim wash liquor with amino acid/PHMB addition

Liquid chromatography-mass spectroscopy techniques such as ESI-LC-MS are soft enough ionisation methods which may allow for analysis of supramolecular interactions between species.[119] As well as m/z values for possible fragments, the elution of species during the liquid chromatography component provides information on the number of species and their relative polarities.

Seven species were found in the LC-MS measurement of denim wash liquor with arginine (Figure 3.40), however they eluted closely together. All samples elute at a later time than the original denim wash liquor suggesting they are less polar. This agrees with the DLS data reputed in section 3.3.4.2 that more non-water soluble species were formed when arginine was added to the denim wash liquor.

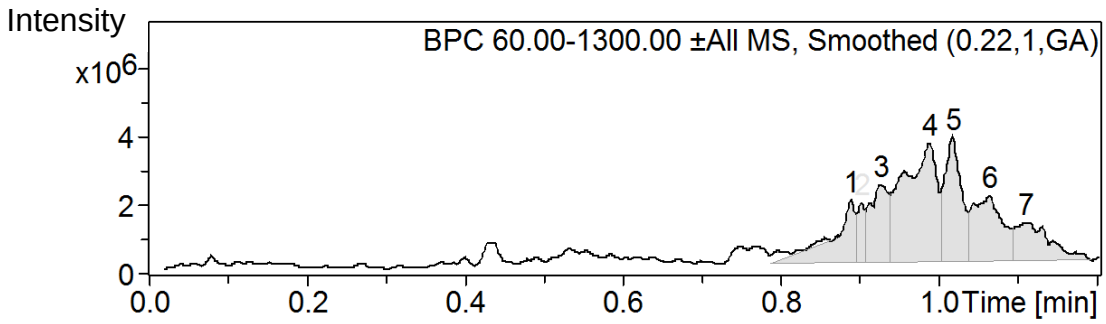


Figure 3.40: LC-MS chromatogram of DWL-Arg.

Table 3.4: LC-MS peaks from DWL-arginine sample. Asterisks denote peaks from sodium formate artefact.

Compound	Positive ESI Peaks (m/z)	Negative ESI Peaks (m/z)
1	1170.11, 1011.97, 663.48, 506.59, 290.03	1021.50, 743.15, 524.24, 443.14, 270.89
2	1012.09, 796.67, 708.63, 506.63, 321.00, 229.93	1064.00, 881.59, 647.23, 521.89*, 443.14
3	1014.00, 784.55, 663.61, 506.54, 229.87	653.34, 443.20
4	1169.66, 1012.94, 663.58, 506.52, 183.81	1117.64, 809.62, 665.44, 491.96
5	1168.60, 1011.74, 784.36, 663.53, 506.53	666.40, 491.93, 270.35
6	1170.80, 1011.87, 729.65, 506.59, 312.01	810.38, 653.60, 364.90, 248.80*
7	1168.97, 1012.00, 729.65, 506.55, 312.05	987.71, 810.40, 666.37, 492.08, 134.66

Table 3.5: LC-MS peaks from denim wash liquor and commercial arginine. Asterisks denote peaks from sodium formate artefact.

Sample	Positive ESI Peaks (m/z)	Negative ESI Peaks (m/z)
Denim wash liquor compound 1	967.60, 785.60, 604.41, 444.15	815.20, 601.26, 325.26, 248.78*
Denim wash liquor compound 2	570.51	984.70, 599.18, 527.19
Commercial arginine	728.68, 413.31, 148.75	689.62, 612.17, 520.78*, 270.66

Due to the high p*K*a of the guanidinium side group, arginine by itself is more likely to be protonated than deprotonated and so, the positive ESI measurement may provide the better environment to observe the mass spectrum.[120] The large majority of the peaks found from the DWL-Arg LC-MS (Table 3.4) were original peaks that could not be traced back to the separate spectra of the denim wash liquor and commercial arginine (Table 3.5). This suggests that some significant interaction took place during the addition of arginine to the denim wash liquor, producing unique fragmentation peaks and peaks with larger m/z. Nine different species eluted from the DWL-Glu sample (Figure 3.41). One compound in particular elutes much earlier than the others, suggesting that it is more polar than the other compounds. The DLS data suggested that electrostatic repulsion between glutamic acid molecules prevented any significant aggregation of particles and so, this polar compound may be the result of a smaller, ionically charged species.

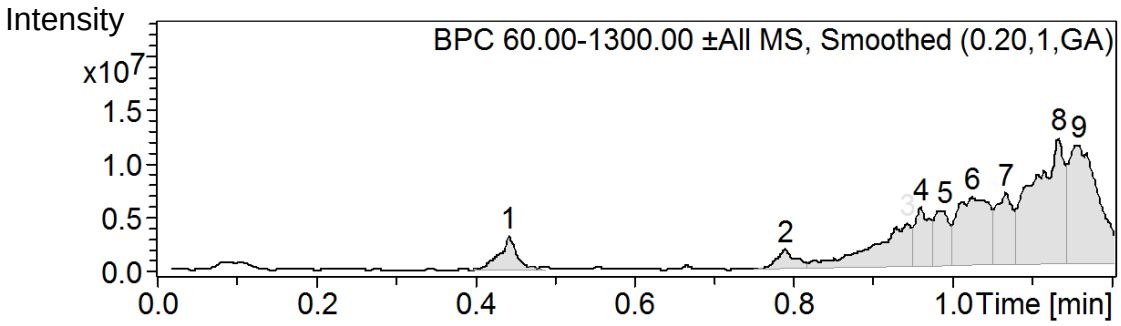


Figure 3.41: LC-MS chromatogram of DWL-Glu.

Table 3.6: LC-MS peaks from DWL-glutamic acid. Asterisks denote peaks from sodium formate artefact.

Compound	Positive ESI peaks (m/z)	Negative ESI peaks (m/z)
1	907.47, 548.29, 453.32, 229.80	958.40, 573.31, 487.37
2	584.45, 444.16, 229.86	677.28, 321.20
3	1012.29, 728.60, 506.51, 229.84	677.68, 443.28
4	1012.06, 700.87, 506.48	667.19, 514.80, 338.80, 137.60
5	1012.09, 804.66, 627.32, 506.53, 312.01	951.66, 829.58, 453.69*, 273.64
6	1011.66, 506.68,	955.64, 833.60, 587.32*, 134.81
7	1011.67, 728.79, 506.59,	803.44, 627.65, 520.72*
8	1012.26, 851.20, 506.67	805.62, 590.40*
9	1011.81, 506.50	867.26, 665.55, 587.20*, 271.63, 135.67

Table 3.7: LC-MS peaks from denim wash liquor sample and commercial glutamic acid. Asterisks denote peaks from sodium formate artefact.

Sample	Positive ESI Peaks (m/z)	Negative ESI Peaks (m/z)
Denim wash liquor compound 1	967.60, 785.60, 604.41, 444.15	815.20, 601.26, 325.26, 248.78*
Denim wash liquor compound 2	570.51	984.70, 599.18, 527.19
Commercial glutamic acid compound 1	713.49	656.80*, 520.84*, 384.86*, 248.78*
Commercial glutamic acid compound 2	713.49, 351.25	901.33, 792.79, 577.20, 443.20
Commercial glutamic acid compound 3	1012.05, 701.62, 506.59	777.68, 443.25
Commercial glutamic acid compound 4	1011.84, 728.52, 506.60	743.43, 384.79*, 134.53
Commercial glutamic acid compound 5	1011.69, 804.40, 728.51, 507.57, 413.19, 312.06	743.61, 668.40, 492.07
Commercial glutamic acid compound 6	824.57, 499.45	805.65
Commercial glutamic acid compound 7	997.57, 728.55, 506.57, 413.22	1095.74, 979.60, 687.67, 587.19*, 509.65, 136.80
Commercial glutamic acid compound 8	728.90, 506.51, 229.85	805.61, 590.45*, 270.66

Several peaks from the positive ESI measurement of DWL-Glu (Table 3.6) match up with peaks from commercial glutamic acid, and also a peak from the original denim wash liquor (Table 3.7). Only a couple of peaks in the negative ESI measurement of DWL-Glu match up with peaks from commercial glutamic acid, and no peaks from the original DWL were found. This suggests that during the addition of glutamic acid to the denim wash liquor, some interaction took place to produce a certain amount of species which gave unique m/z peaks, as shown by the lower UV/vis absorption for DWL-Glu. However, not all the glutamic acid interacted and so produced m/z peaks characteristic of commercial glutamic acid.

LC-MS of the DWL-Phe sample gave three distinct compounds with different polarities (Figure 3.42). Compound two appears to elute at the same time as the denim wash liquor's compound two. This suggests they might be of the same polarity and possibly even the same compound.

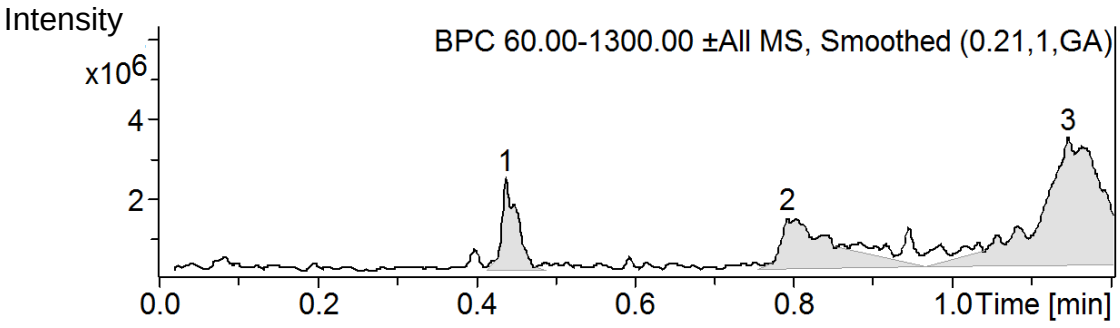


Figure 3.42: LC-MS chromatogram of DWL-Phe.

Table 3.8: LC-MS peaks from DWL-phenylalanine sample. Asterisks denote peaks from sodium formate artefact.

Compound	Positive ESI peaks (m/z)	Negative ESI peaks (m/z)
1	548.29, 311.97	529.28, 325.03
2	548.48, 444.18	737.26, 599.19, 321.22
3	1011.89, 804.52, 611.12, 506.54	833.52, 677.58, 587.50*, 370.83, 134.80

Table 3.9: LC-MS peaks from Denim wash liquor sample and commercial Phenylalanine. Asterisks denote peaks from sodium formate artefact.

Sample	Positive ESI Peaks (m/z)	Negative ESI Peaks (m/z)
Denim wash liquor compound 1	967.60, 785.60, 604.41, 444.15	815.20, 601.26, 325.26, 248.78*
Denim wash liquor compound 2	570.51	984.70, 599.18, 527.19
Commercial phenylalanine compound 1	713.44, 607.65, 444.13, 229.80	520.78*, 384.92*, 248.81*, 152.67
Commercial phenylalanine compound 2	713.50, 607.38, 455.03	792.80*, 447.18, 329.23, 248.78*, 152.80

Some of the DWL-Phe m/z peaks (Table 3.8) did seem to correspond to m/z peaks from the denim was liquor in the negative ESI mode (Table 3.9). This suggests that the interaction that occurred between the phenylalanine molecules and the DWL molecules were weak and interrupted during the LC-MS process of ionisation, and so the DWL were able to elute unaltered from the original sample. Compound two, which eluted at the same time as the original denim wash liquor, did share an m/z peak of 599.2 which further suggests that this may be the same species, having not interacted with phenylalanine.

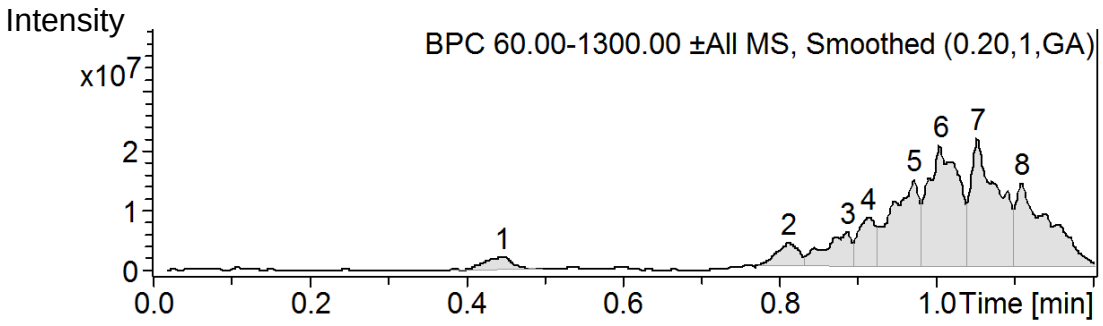


Figure 3.43: LC-MS chromatogram of DWL-PHMB.

Table 3.10: LC-MS peaks from DWL-PHMB sample. Asterisks denote peaks from sodium formate artefact.

Compound	Positive ESI peaks (m/z)	Negative ESI peaks (m/z)
1	475.30, 367.28, 183.84	707.24, 593.25, 515.24, 363.19
2	614.50	599.20, 321.22
3	1011.96, 700.60, 506.58	982.71, 747.55, 599.20, 234.40
4	1011.75, 700.53, 506.56	453.19*
5	1012.07, 506.62	877.66, 636.69, 491.94, 248.80*
6	1012.88, 506.55	959.58, 809.44, 677.57, 509.07, 270.40
7	1012.80, 705.64, 506.54	911.66, 815.58, 665.40, 520.98*, 448.75, 372.80, 280.80
8	1168.96, 1011.76, 663.48, 506.55	833.62, 677.61, 587.69*, 448.78

Table 3.11: LC-MS peaks from denim wash liquor sample and commercial PHMB. Asterisks denote peaks from sodium formate artefact.

Sample	Positive ESI Peaks (m/z)	Negative ESI Peaks (m/z)
Denim wash liquor compound 1	967.60, 785.60, 604.41, 444.15	815.20, 601.26, 325.26, 248.78*
Denim wash liquor compound 2	570.51	984.70, 599.18, 527.19
Commercial PHMB compound 1	367.27	593.30, 479.27
Commercial PHMB compound 2	636.37, 363.18	693.80, 483.45, 367.33
Commercial PHMB compound 3	778.42, 495.42, 367.35	823.58, 555.59, 362.73, 248.83*, 153.59
Commercial PHMB compound 4	698.21, 573.00, 418.20	803.59, 662.48, 521.20*, 363.89, 248.81*, 152.72
Commercial PHMB compound 5	794.00, 713.46, 351.84, 183.86	992.79, 769.57, 363.15, 152.76
Commercial PHMB compound 6	1057.61, 713.42, 400.83, 280.83	1018.76, 769.59, 520.77*, 362.80, 248.80*, 152.80
Commercial PHMB compound 7	713.50, 608.47	1018.80, 656.86*, 521.22*, 385.97*, 248.83*
Commercial PHMB compound 8	713.52, 408.20	1018.82, 656.90*, 498.96, 386.75*, 197.60
Commercial PHMB compound 9	1011.69, 728.71, 506.58, 229.85	677.62, 587.24*, 134.66

Many m/z peaks of the DWL-PHMB sample (Figure 3.43, Table 3.10) can be attributed to commercial PHMB, in both positive and negative ESI mode, and some m/z peaks can also be attributed to DWL in the negative ESI mode (Table 3.11). This suggests that while there are new m/z peaks that may reflect the presence of fragmentation from complexes between the DWL and PHMB, there are still a significant proportion of un-interacted starting materials due to lower affinity between the DWL and PHMB species. This could explain why the UV/vis absorbance for DWL combined with PHMB is slightly higher than the other amino acid additives.

3.3.4.4. SEM and light microscope photographs

Samples were freeze-dried to analyse the solid present. While solvent removal can alter supramolecular interaction, freeze-drying has been previously found to preserve structural details better than drying a sample at room temperature.[121]

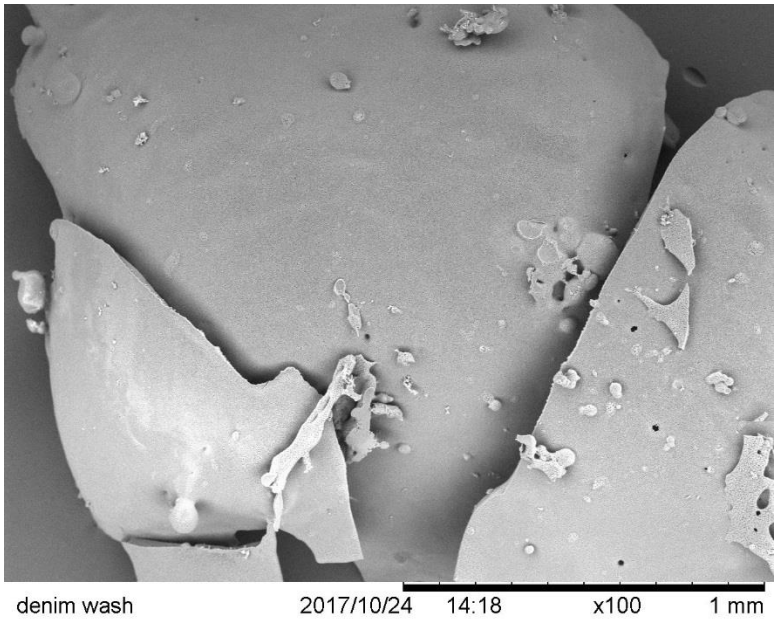


Figure 3.44: SEM of denim wash liquor and arginine complex removed from solution at a magnification of x100.

The SEM of arginine and the denim staining species appears plate-like; very smooth and homogeneous (Figure 3.44). Very few pores can be seen. At

higher magnification it was not possible to gain any further detail. In contrast to the other amino acids and PHMB complexes, it appears as though a solid structure has been produced. Figure 3.45 shows that the Denim wash liquor and arginine complex appears to be amorphous in structure.

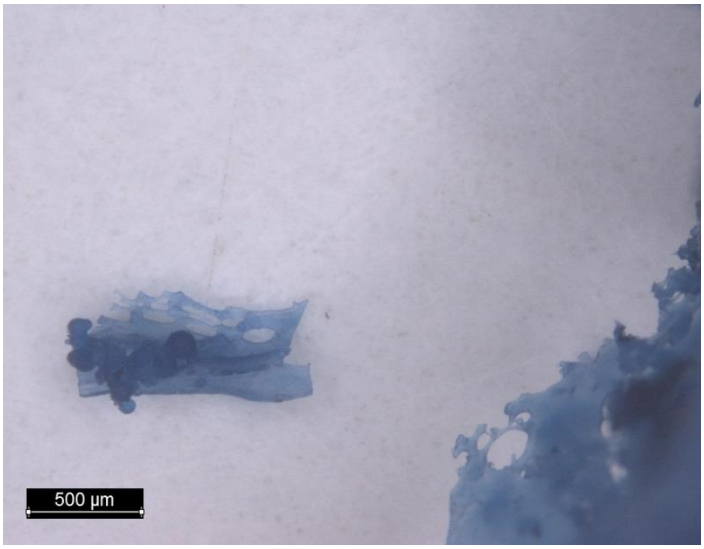


Figure 3.45: Light microscope picture of denim wash liquor and arginine complex at a magnification of x30.

It was observed that after the addition of arginine to the denim wash liquor, the liquid appeared a paler blue than the original wash liquor sample. This was confounded by a lower absorbance measurement (Figure 3.38). In the arginine wash liquor DLS data, a larger volume mean was recorded (Table 3.3). This suggests that larger particles were present in this wash liquor, compared to the others. These large particles may form due to attractive supramolecular interactions between the staining species and the arginine. As the particles increase in size they precipitate from solution. It is this removal of the staining species from solution that is likely to lower dye transfer.

The DWL-Glu sample shows a more extended cluster morphology, with fewer individual fibres visible than the original freeze-dried denim wash liquor sample (Figure 3.46) signalling a physical interaction between

glutamic acid and the wash liquor. There is also less noticeable open space in the structure. This is surprising, as the DLS data in Table 3.3 suggested that the particles within the sample were small and had not formed large aggregates. However, the sample may appear this way because it has been freeze-dried and separate particles are layered in the SEM picture.

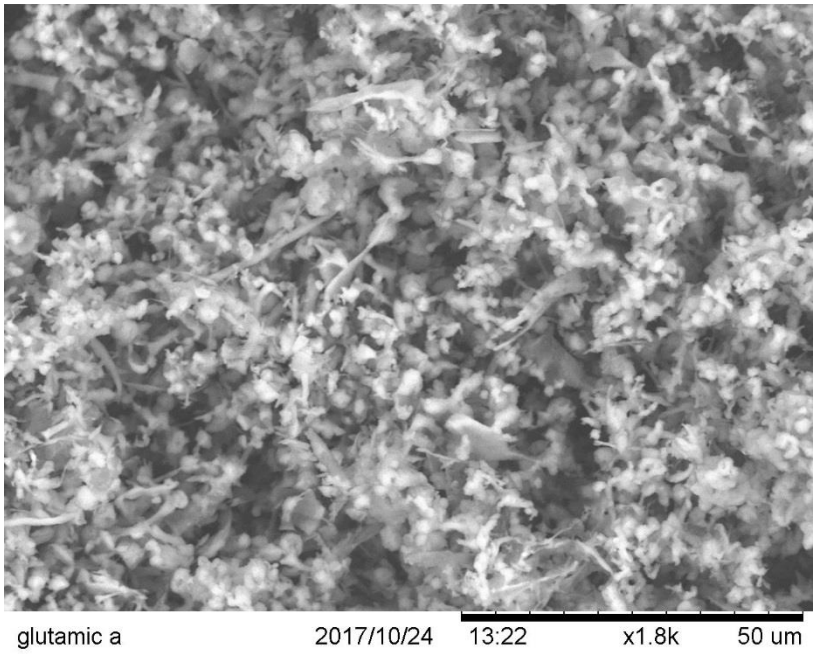


Figure 3.46: SEM of denim wash liquor and glutamic acid complex at x1800 magnification.

The light microscope picture also shows a paler sample than the original freeze-dried denim wash liquor, again signalling a physical change (Figure 3.47).

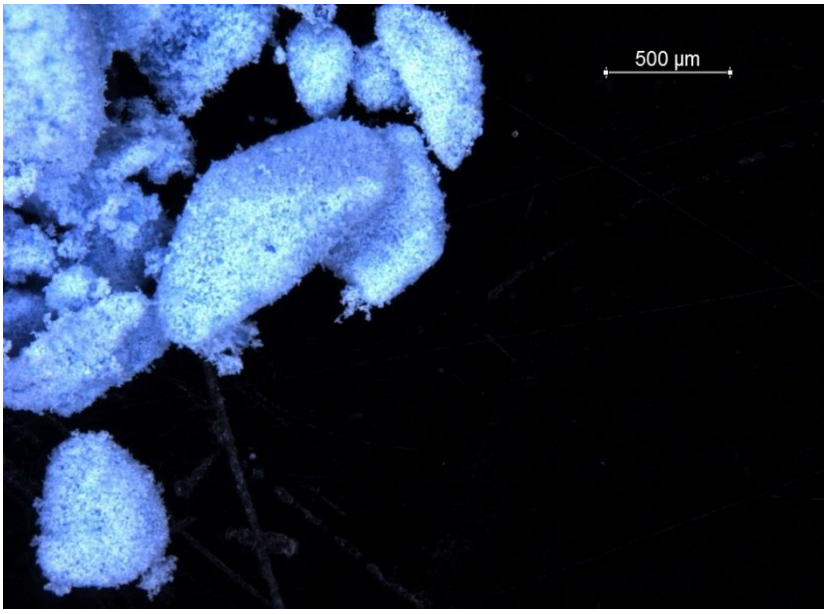


Figure 3.47: Light microscope picture of denim wash liquor and glutamic acid complex at a magnification of x30.

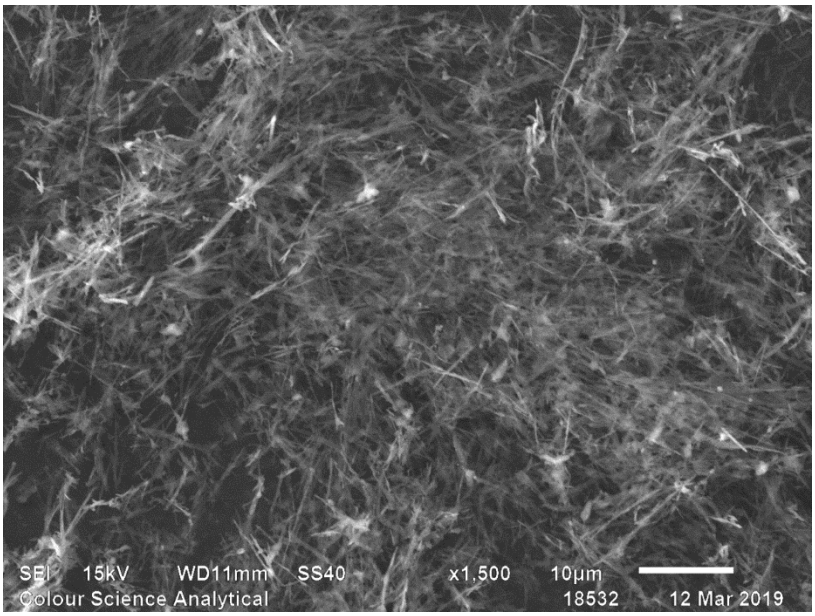


Figure 3.48: SEM of Denim wash liquor and phenylalanine.

Conversely to the DWL-Glu sample, the DWL-Phe sample show much more fibre-like structures and no areas of clusters suggesting the fibre-like self-

assembly of phenylalanine has been observed.[117] The sample appeared needle like (Figure 3.48).

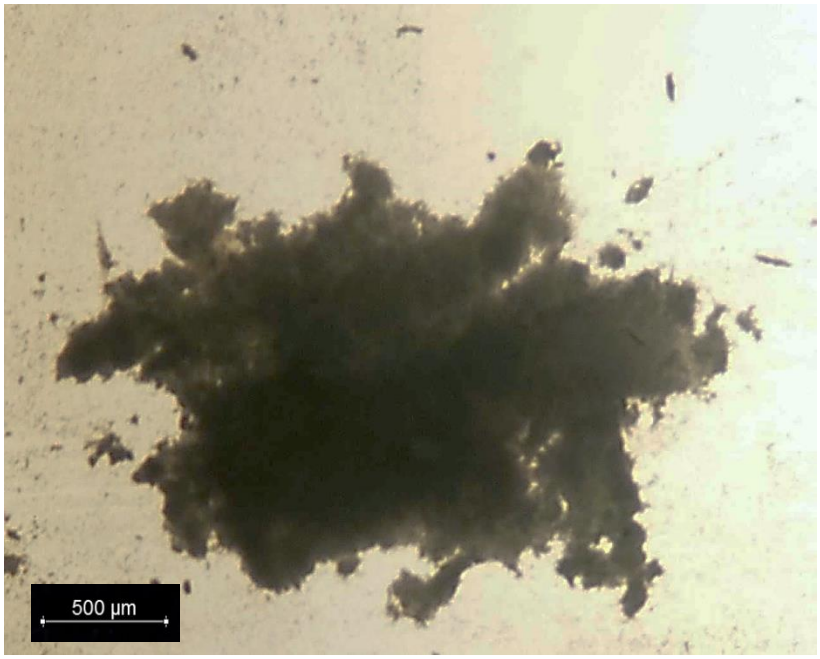


Figure 3.49: Light microscope picture of denim wash liquor and phenylalanine at a magnification of x30.

Around the edges of the sample, the needle like structure can be observed as spikes in the outlines (Figure 3.49).

Figure 3.50 show cluster structures interlocked with fibre structures. There are also large pore areas creating a relatively open structure. This closely resembles the original solid obtained from freeze drying the denim wash liquor alone (3.29). This initially suggests that there has been little physical change between the original denim wash liquor and the DWL-PHMB complex. However, the UV/vis data in particular suggests that PHMB was able to interact and precipitate the staining species out of solution.

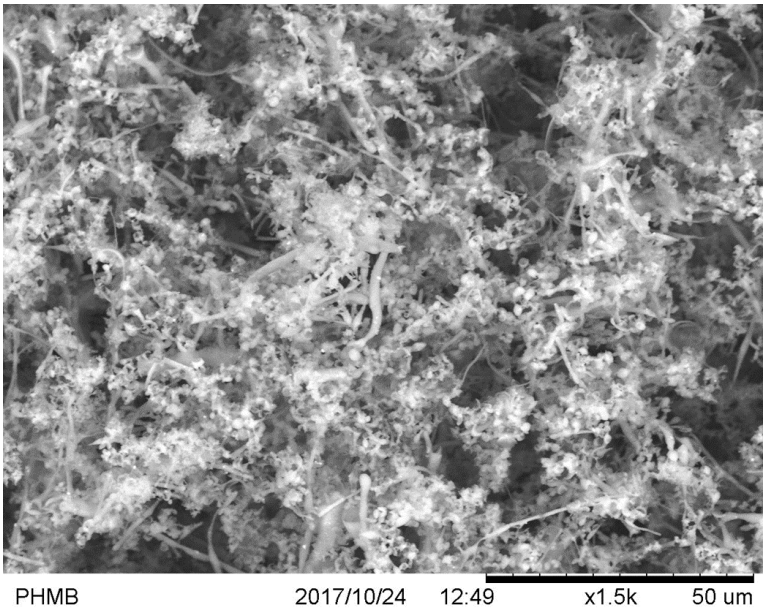


Figure 3.50: SEM of denim wash liquor and PHMB complex.

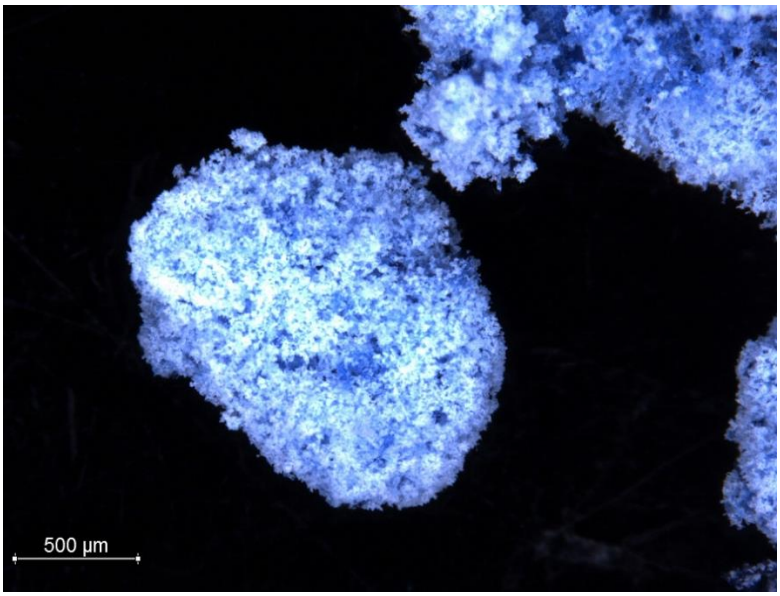


Figure 3.51: Light microscope picture of denim wash liquor and PHMB complex at a magnification of x30.

Some of the larger pores can be seen from the light microscope picture (Figure 3.51). The sample is homogeneous in colour, which is a paler shade of blue to the original freeze-dried denim wash liquor sample (Figure 3.29). This suggests that there has actually been a physical change made to the sample when PHMB was added and this may have occurred by affecting the

chromophores of the staining species to produce a slightly less intensely coloured species.

3.3.4.5. IR Analysis

The DWL-Arg sample closely resembles the spectra of commercial arginine but also exhibits some peaks attributed to the original denim wash liquor, such as 1070 cm^{-1} as highlighted in the green box on Figure 3.52. Therefore, presence of both the original species in some capacity was detected. There is some evidence of hydrogen bonding as some peaks in the DWL-Arg sample have slightly lower wavenumbers than the corresponding arginine peaks. The carbonyl peak at around 1600 cm^{-1} is lower in the DWL-Arg sample (1614 cm^{-1}) than in commercial arginine (1634 cm-1), suggesting the C=O group is involved in hydrogen bonding with the DWL species (Purple box in Figure 3.52).[122] There is also a slightly decreased O–H peak of the DWL-Arg sample compared to the commercial arginine sample, again suggesting this group is hydrogen bonded to the DWL species. This decrease occurs due to a slight weakening of the C=O/O–H covalent bonds in the DWL sample which is induced by hydrogen bonding.[123]

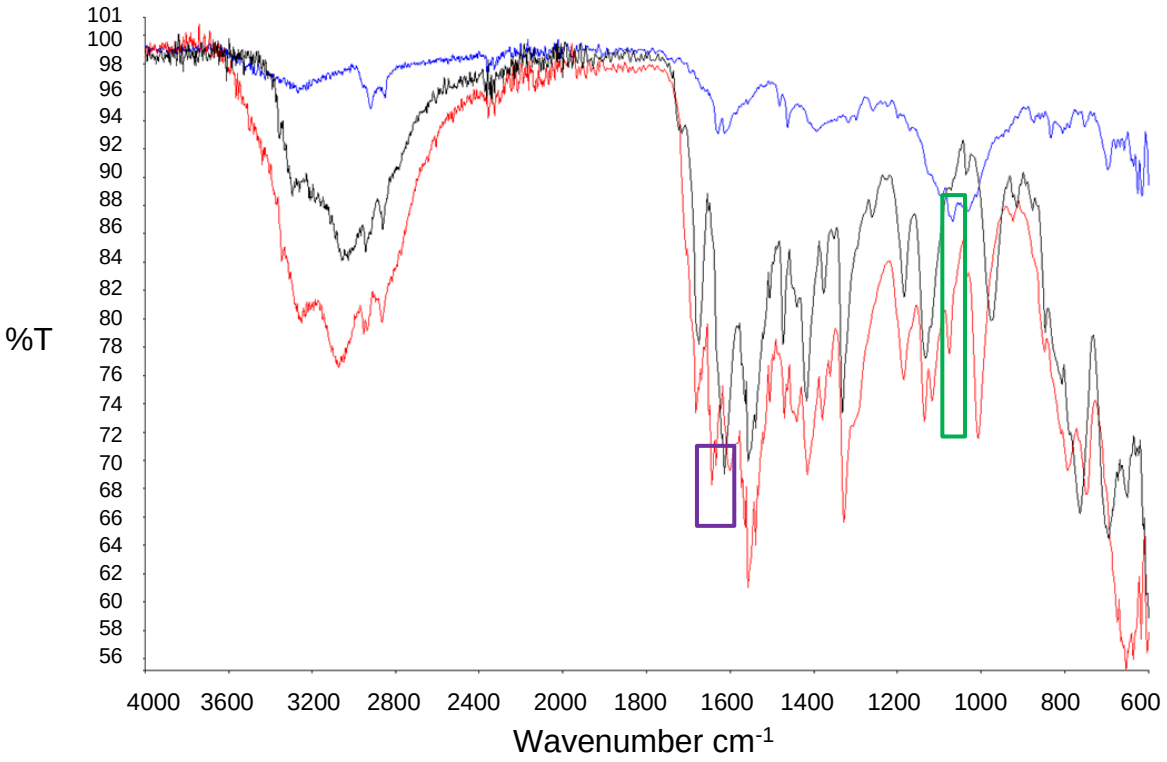


Figure 3.52: Comparisons of IR spectra of denim wash liquor solid (blue), DWL-Arg (red) and commercial arginine (black). Green box highlights similar peak between denim wash liquor solid and DWL-Arg. Purple box highlights reduction in carbonyl peak from 1634 cm^{-1} in commercial arginine sample, to 1614 cm^{-1} in DWL-Arg sample.

Figure 3.53 shows the strong glutamic acid characteristics of the DWL-Glu sample. This is evidenced by the similarity of peaks between the DWL-Glu sample and the commercial glutamic acid sample. There doesn not seem to be any peaks characteristic of the denim wash liquor in the DWL-Glu sample, however this could be a result of overlapping peaks such as those in the 900-1100 cm^{-1} region (possible CO, CN,CH,NH peaks) and the 1600-1700 cm^{-1} region (C=O). The denim wash liquor peaks may be masked by glutamic acid peaks because the staining species has similar bonds and functional groups to glutamic acid. This could further explain the DLS data of why the particles were small, because there was some electrostatic repulsion between glutamic acid molecules and staining species molecules. However, this repulsion was not so strong that the two species didn't interact, as the UV/vis data shoes that they did to precipitate out of solution.

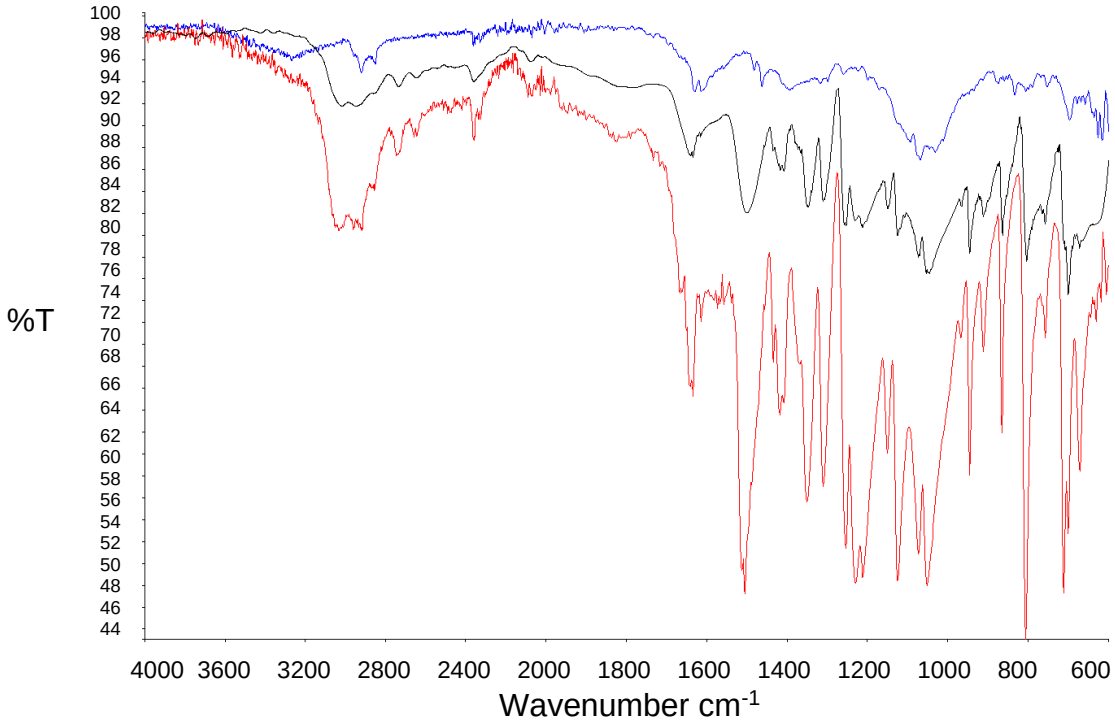


Figure 3.53: Comparison of IR spectra of denim wash liquor solid (blue), DWL-glutamic acid solid (red) and commercial glutamic acid (black).

The DWL-Phe sample shows only the peaks for phenylalanine (Figure 3.54). However, there is some possible slight broadening of peaks at wavenumbers where indigo exhibits peaks. This suggests that there was some indigo in the sample but the peaks from phenylalanine are much stronger, perhaps due to a higher stoichiometry of phenylalanine to indigo in the solid sample measured from phenylalanine self-assembly.

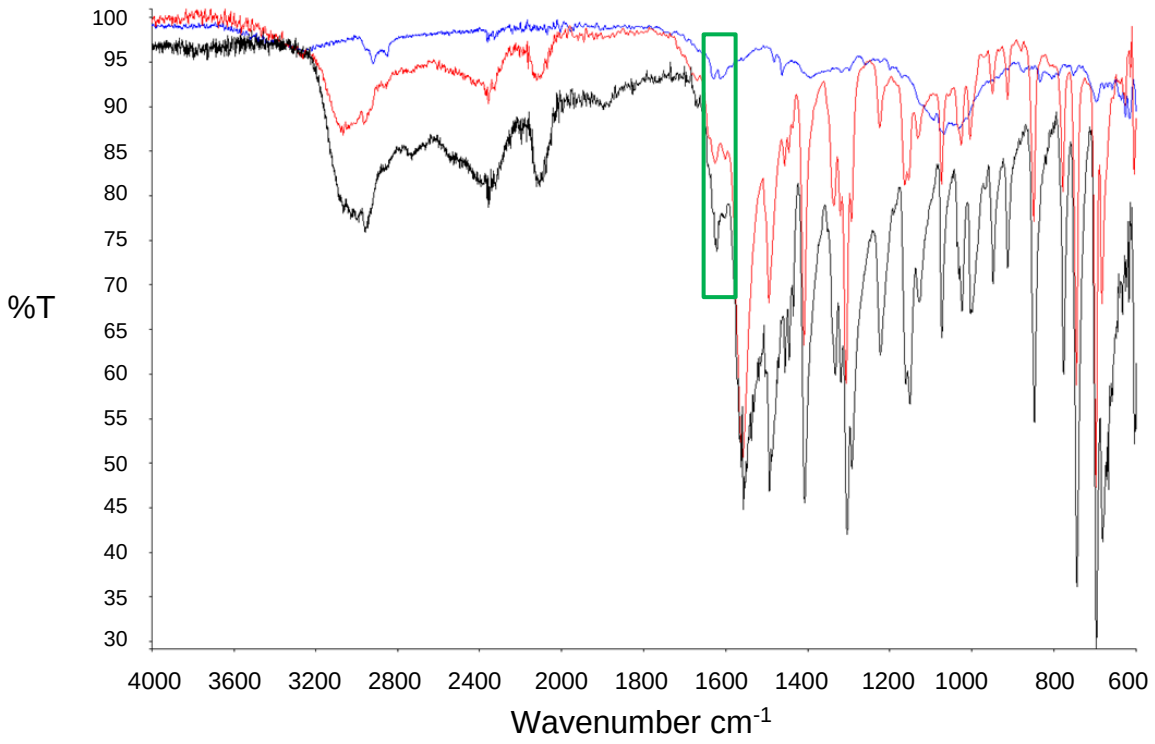


Figure 3.54: Comparison of IR spectra of denim wash liquor solid (blue), DWL-phenylalanine (red) and commercial phenylalanine (black). Green box highlights possible broadening of peak from DWL-Phe occurring from the overlapping of peaks from the denim wash liquor and commercial phenylalanine.

For the majority of the DWL-PHMB spectra, it closely resembles the spectra of commercial PHMB without any decreased wavenumbers to suggest additional hydrogen bonding between the PHMB and the DWL (Figure 3.55). However, the DWL-PHMB does include at peak at 1070 cm^{-1} from the DWL sample suggesting the presence of a CH/CN/NH peak, indicated by the green box in Figure 3.55. This is one area in the spectrum where the commercial PHMB peaks do not mask the peaks from the DWL and so the presence of this peak shows that the DWL species is present. However, the lack of change in wavenumber between the DWL-PHMB sample and either of the original DWL and PHMB samples suggests a low degree of supramolecular interaction in the combined sample.

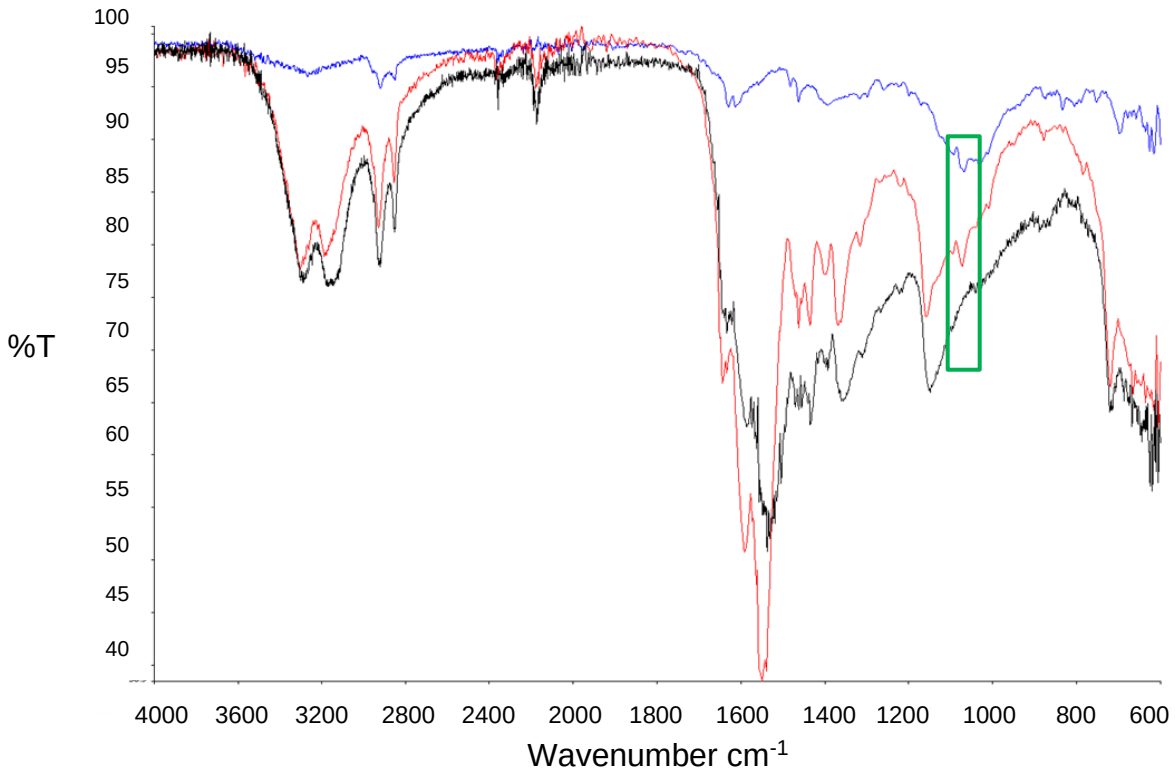


Figure 3.55: Comparisons of IR spectra of Denim wash liquor solid (blue), DWL-PHMB (red) and commercial PHMB (black). Green box highlights the presence of a peak at 1070 cm^{-1} in both denim wash liquor sample and DWL-PHMB sample.

3.4. Conclusions

From these analyses, some conclusions about the denim staining species can be made. The HPLC, IR and SEM data appears to show the presence of two species, indigo dye and cellulosic material. However, there does not seem to be any peak corresponding to indigo in the LC-MS data, which would be expected at m/z 263 [$M-H^+$] and a fragmentation pattern as recorded in the literature. This could be because the LC-MS was not sensitive enough to pick up a low concentration of indigo in the sample, or because of a change in structure which affected how any indigo present in

the sample fragmented. While there are two species present, magnification under a light microscope shows a homogenous colour. This, along with SEM results suggests that the coloured part of the molecule, determined from UV/vis spectroscopy and IR as being from indigo, is intrinsically complexed with the cellulosic portion of the species. It is likely that the staining species has some hydrophobic region to it due to the higher levels of transfer onto hydrophobic fibres but that it also has some anionic quality which allows hydrogen bonding to amide groups in fibres such as wool and polyamide.

3.4.1. Arginine

All additions of the amino acids and PHMB reduced the absorbance of the denim wash liquor, suggesting that all may have had an effect on precipitating the staining species from solution, so it was no longer measurable by UV/vis spectroscopy. The infrared spectrum of DWL-Arg shows peaks corresponding to the same functional groups as in arginine, but at lower wavenumbers. This is indicative to hydrogen bonding being present in the DWL-Arg sample that isn't in arginine alone. The DLS data suggests that the DWL-Arg species are larger particles than the DWL sample alone, and that these particles take up more volume in the sample. The SEM and microscope photographs show an amorphous, homogeneous structure which is plate like. The LC-MS data also shows the species elute at very similar times. These analyses suggest that arginine interacts with the denim staining species through hydrogen bonding to form large, homogeneous particles.

That the denim staining species forms strong intermolecular forces with arginine implies that the staining species functionality is complementary to the guanidinium side chain of arginine and so, further suggesting the staining species may be anionic, with hydrogen bond acceptor groups such as atoms with lone pairs of electrons (commonly found on N and O atoms).

DWL-Arg may be amorphous (suggested by the SEM) and so there may be more open spaces in the complex, explaining the larger DLS volume measurement for DWL-Arg in comparison to the other samples.

3.4.2. Glutamic acid

Infrared spectroscopy of DWL-Glu shows some possible evidence of hydrogen bonding between glutamic acid and the staining species at around 1200 cm^{-1}. The DLS data is similar to that of the original denim wash liquor and coupled with the SEM images suggests that the clusters in the DWL-Glu sample were more compact possibly due to electrostatic repulsion between the amino acid side groups in solution. However, this repulsion may also come from some anionic regions of the denim staining species within the interacted complex, as the FTIR peak measurements of the DWL-Glu samples seemed to overlap with commercial glutamic acid peaks, further indicating similar, anionic functionalities of the complex.

3.4.3. Phenylalanine

The appearance of the DWL-Phe sample was much paler in colour than the other DWL-amino acid/PHMB samples. When considering the Infrared spectrum, it is predominantly phenylalanine with no evidence of hydrogen bonding. This suggests that within a given sample of DWL-Phe, there is a much higher ratio of phenylalanine to the denim staining species. This may be reflected in the DLS data, where there are large particles in a smaller volume than other DWL-amino acid/PHMB samples. Phenylalanine is known to self-assemble and so the sample, which is mostly phenylalanine, closely associates. The lack of any visible cluster type species in the SEM image further confirms that the main presence is phenylalanine because the self-assembly of these molecules has increased the ratio of phenylalanine to the denim staining species in a sample of the isolated solid.

The denim staining species does not hydrogen bond with phenylalanine which may be due to repulsion between the species or steric hindrance from the aromatic ring in phenylalanine. It could also be that phenylalanine associates with other phenylalanine molecules much more strongly than with the denim staining species. The reduction of UV/vis absorbance may occur

due to some precipitation of the staining species alongside phenylalanine aggregates.

3.4.4. PHMB

There is an increase in the IR wavenumbers of some of the DWL-PHMB peaks compared to commercial PHMB, indicating a reduction in hydrogen bonding in the DWL-PHMB sample. PHMB as a polymer can form many intramolecular bonds and in aqueous solutions forms a kind of polymeric micellar structure due to alternating hydrophobic and hydrophilic regions.[124] The reduction in hydrogen bonding suggests that the denim staining species interacts with PHMB and disrupts existing intramolecular hydrogen bonds. This interaction forms small compacted cluster particles.

It is perhaps not surprising that PHMB interacts favourable with the denim staining species, as it shares a guanidinium functionality with arginine. PHMB being a longer, polymeric molecule may hinder the interaction between the two species, which explains the differences in results between arginine and PHMB.

Chapter 4- Technologies to reduce dye transfer of known textile migrant dyes

4.1. Introduction

Identification of dyes from the model wash load (Chapter 2, Table 2.1) and analysis and understanding of the staining species from denim (Chapter 3.4) provides valuable information that can inform future development of efficient technologies and mechanisms to reduce dye transfer from relevant textile dyestuffs. Data from previous chapters suggests that, in the case of denim, the staining species may adhere to amide-containing proteinaceous fibres over others. The model wash load data shows that length of wash and temperature of wash was influential on both dye release and dye re-adsorption. The purpose of this chapter was to utilize the findings from the previous chapters to determine whether dye transfer from both the model wash load and from denim could be reduced in a domestic wash setting.

4.2. Experimental

Both the model wash load and denim were measured for their level of dye transfer across a range of different undyed acceptor fibres. Wash parameters were changed and amino acids/PHMB were added to observe whether in dye transfer could be reduced in a wash simulation.

4.2.1. Materials and solvents

Technical denim (E-277) was purchased from CFT.BV, the Netherlands and was cut into 10 cm x 4 cm strips. Model wash load comprised the following 11 t-shirts:

Table 4.1: Table of dark model wash load details.

T-shirt Colour	T-shirt fabric	Retailer
Black	100% Cotton	Fruit of the Loom
Bottle Green	100% Cotton	Fruit of the Loom
Burgundy	100% Cotton	Fruit of the Loom
Deep Navy	100% Cotton	Fruit of the Loom
Light Graphite	100% Cotton	Fruit of the Loom
Navy	100% Cotton	Fruit of the Loom
Purple	100% Cotton	Fruit of the Loom
Royal Blue	100% Cotton	Fruit of the Loom
Black	100% Polyester	Fruit of the Loom
Grey and Red	50% Polyester, 25% Rayon, 25% Cotton	Bella Canvas
Red	100% Polyester Jersey	Gildan

T-shirts were either cut into 5 x 5 cm squares for small scale wash tests or used as whole article in full scale wash tests. Multifibre was purchased from James Heal and cut into 10 cm x 4 cm strips.

A selection of undyed, white acceptor fabrics were used in accordance with standard practice at Procter & Gamble dye transfer procedures. They were comprised of the following:

Table 4.2: Table of Acceptor fabric details

Acceptor number	Acceptor fabric	Retailer
1	100% Cotton	Fruit of the Loom
2	100% Cotton	Anvil
3	100% Cotton	Gildan
4	100% Cotton	B & C
5	100% Cotton	Russell
6	100% Cotton	Russell
7	100% Polyester	Gildan
8	50% Polyester, 25% cotton, 25% rayon	Anvil
9	100% Polyester	Fruit of the Loom
10	65% Polyester, 35% Cotton	Kustom Kit
11	100% Polyester	Spiro
12	100% Polyester	Xpres
13	65% Polyester, 35% Cotton	Russell
14	100% Cotton	Tee Jays
15	100% Polyester	Spiro
16	95% Polyester, 5% Spandex	Tee Jays
17	52% cotton, 48% polyester	Bella Canvas
18	100% polyester	Gildan

Each acceptor fabric was cut into a 5 cm x 5 cm square. One of each different acceptor fabric number was tagged onto a 27 cm × 30 cm piece of

knitted 100% cotton provided by Warwick Equest, in accordance with Procter & Gamble standard practice.

Citric acid, arginine, glutamic acid and phenylalanine were purchased from Sigma-Aldrich. Sodium hydroxide and polyhexamethylene biguanide hydrochloride were purchased from Fischer Scientific. Detergent was Ariel Original washing liquid, purchased from ASDA, UK and dose scaled down according to instructions on packing.

4.2.2. General Procedures and instrumentation

Small scale wash tests were carried out using a James Heal 1315 B Gyrowash at 40 rpm for 30 minutes at 40°C. Wash method was an adaptation of ISO 105:C06/A2S colourfastness test. 25 steel balls were used to provide agitation. 50 mL of distilled water was added to canister. 0.25 mL of liquid detergent was added to canister along with powdered amino acids or PHMB. Where pH has been altered, citric acid and sodium hydroxide were used to obtain desired pH. Fabric samples were left to air dry for 24 hours before measurement on Data Colour Spectraflash 600 (Plus) CT spectrophotometer, generating L*, a* and b* values.

Full scale was tests were carried out on a Miele 3622 washing machine using the following programmes:

Table 4.3: Table of washing machine cycles used.

Programme Name	Total cycle length (hours)	Spin cycle (rpm)
40°C Cotton Short	1.25	1600
40°C Express	0.5	1600
Cold Express	0.5	1600
40°C Automatic	1.18	1200
Cold Automatic	1.15	1200

40°C Cotton short is the control wash cycle used at Procter & Gamble to represent an average consumer wash. This was performed to provide initial data about the wash load that could represent a real domestic wash.

The Express washes and the Automatic washes were selected to provide data on how both temperature and time as independent variables separately affected the level of dye transfer. It was not possible to alter the rpm of the spin cycles to be the same for these washes, however the spin takes place after the wash water has been removed and so it is expected that limited dye transfer takes place during this portion of the cycle.

Detergents used were as following: 70 mL directly into each washing drum of Ariel Original Liquid detergent. After the wash, tracer fabrics were left to air dry for 24 h and then CIELab colour measured. ΔE_{2000} was calculated using equation 1.1 for each tracer fabric and the comparison unwashed tracer fabrics.

4.3. Results and Discussion

4.3.1. Reduction of dye transfer from Denim

4.3.1.1. Addition of amino acids and PHMB into the wash load

Amino acids have previously been incorporated into detergent products, often in oligomeric or copolymer form, for purposes such as soil anti-redeposition and improved fabric integrity.[125,126,127] Proline was found to have good anti-redeposition properties, due to hydrogen bonding with proposed staining species, such as carbon black.[127] The staining species from denim, hypothesised to be a complex between indigo and cellulose oligomers, had attractive interactions with amino acids and PHMB when they were added to the wash liquor, removing the staining species from solution. It was further investigated to see whether these interactions would reduce dye transfer in a simulated wash system with detergent.

Amino acids and PHMB were added to separate wash canisters with denim, detergent, water and a multifibre strip to make up a 10 mM concentration of the amino acid or PHMB in solution (arginine: 1.74 g mol^{-1}, glutamic acid: 1.47 g/mol, phenylalanine: 1.65 g mol^{-1}, PHMB: 2.31 g mol^{-1}). The samples were washed at 40 °C for 30 minutes with detergent, followed by a 10 minute rinse step with fresh water. After air drying for 24 hours, the multifibre L*, a* and b* values were measured and ΔE_{2000} values were calculated.

The level of dye transfer discoloration is shown in Figure 4.1

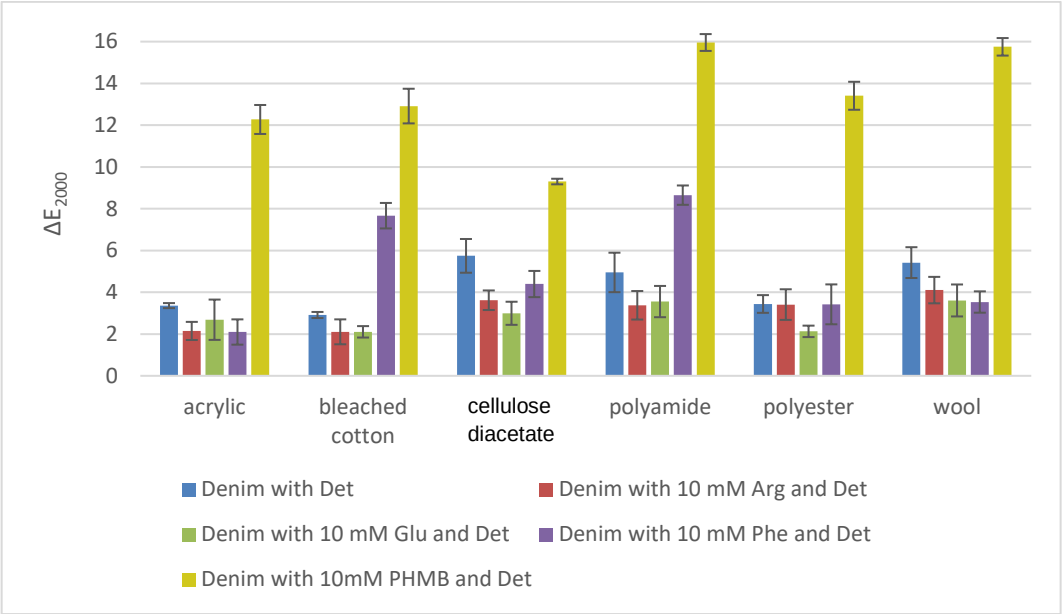


Figure 4.1: ΔE_{2000} comparisons of dye transfer from denim with detergent between different amino acid/PHMB conditions. No amino acid/PHMB (blue), 10 mM arginine (red), 10 mM glutamic acid (green), 10 mM phenylalanine (purple), 10 mM PHMB (yellow). Error bars show ± standard deviation of three repetitions.

. As can be seen, there is a significant reduction in dye transfer when Arginine and Glutamic acid are added to the wash systems. As this reduction in ΔE_{2000} is present for all fibre types, this suggests that the mechanism is due to induced removal of the staining species from wash liquor. If it were the case that the amino acids were interacting with the fibres and blocking deposition of the dyestuffs, reduction of dye redeposition would

not occur to the same extent for all the fibre types because they have different properties and thus, different affinities for the amino acids.

Phenylalanine however, did not provide reduction in ΔE_{2000} for all fibre types and in fact may have increased the levels of dye transfer, as seen for bleached cotton and polyamide. As previously discovered, the interaction between phenylalanine and the denim staining species was not very strong and that the phenylalanine molecules remained closely associated with each other. Therefore, phenylalanine may be acting as a blocking compound for acceptor fibres, except for the hydrophilic cotton and polyamide which will repel phenylalanine due to its hydrophobic side chain. If the other acceptor fibres are blocked from redeposition by phenylalanine, there will be more dye molecules within the volume of the wash canister that are free to redeposit onto the non-blocked fibres.

PHMB was seen to greatly increase dye transfer from denim onto all acceptor fibre types. It was found that PHMB is able to form a complex with the denim staining species and remove it from solution, thus decreasing the UV/vis absorbance. Therefore, the increase in dye transfer in the wash test suggests there is an interaction between PHMB and the detergent which may prevent complex formation between PHMB and the denim staining species. PHMB may also be interfering with the existing dye transfer inhibition technology within the detergent, such as forming hydrogen bonds with DTI polymers, thus leading to increased ΔE_{2000} values. As phenylalanine and PHMB were found not to decrease ΔE_{2000} and in some cases, increased levels of dye transfer, they were not further investigated.

4.3.1.2. Arginine concentration investigation

Arginine appeared to be successful at reducing dye transfer at a concentration of 10 mM in the wash liquor. Different concentrations of arginine were therefore investigated to observe if there was an optimum concentration that produced low ΔE_{2000} values across all acceptor fibres. 5 mM and 10 mM solutions were initially investigated. As both concentrations reduced dye transfer effectively for different fibres, a concentration of 7.5

mM was further investigated to understand how the half-way concentration behaved (Figure 4.2).

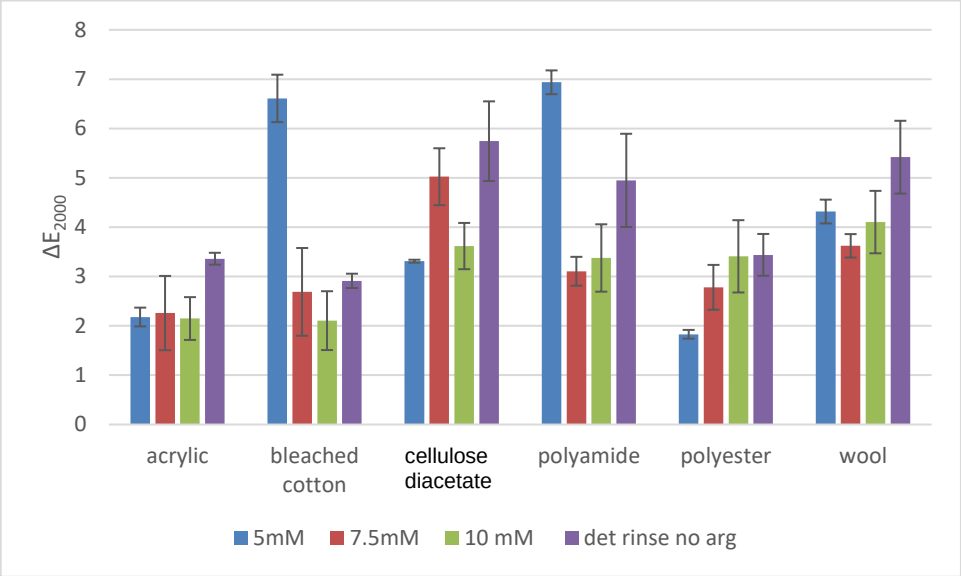


Figure 4.2: Dye transfer from denim with detergent with different concentrations of Arginine in wash solution. 5 mM arginine (blue), 7.5 mM arginine (red), 10 mM arginine (green), no arginine (purple). Error bars show ± standard deviation of three repetitions.

Figure 4.2 shows that there was no one optimum concentration for all fibre types present. Reasons for this may include the kind of complex that is formed with different stoichiometry of arginine to the staining species. Lower concentrations of arginine may produce complexes in which areas of the staining species are exposed such as a 1:1 ratio complex (Figure 4.3).

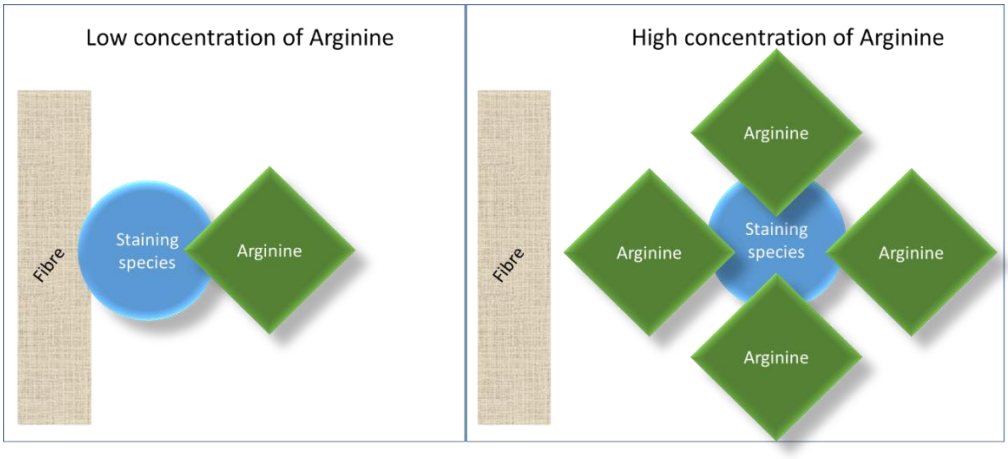


Figure 4.3: Schematic of how concentration of arginine may affect staining species coming into contact with acceptor fibres.

As discussed in Chapter 3.4.1, arginine likely interacts with the staining species through its side group, a guanidinium functionality. In a higher concentration of arginine, where multiple arginine molecules can form supramolecular interactions with the same staining species particle, the negative charges of the amino acid COO^- groups of the arginine molecules, facing away from the staining species and towards the outside of the complex, will be repelled by fibres that are anionic in aqueous media.

Therefore, the staining species can still be attracted to certain fibre types, for example through hydrogen bonding. Bleached cotton and polyamide are capable of acting as hydrogen bond donors, meaning they provide the covalently bonded hydrogen atom which forms the intermolecular bond (Figure 4.4).

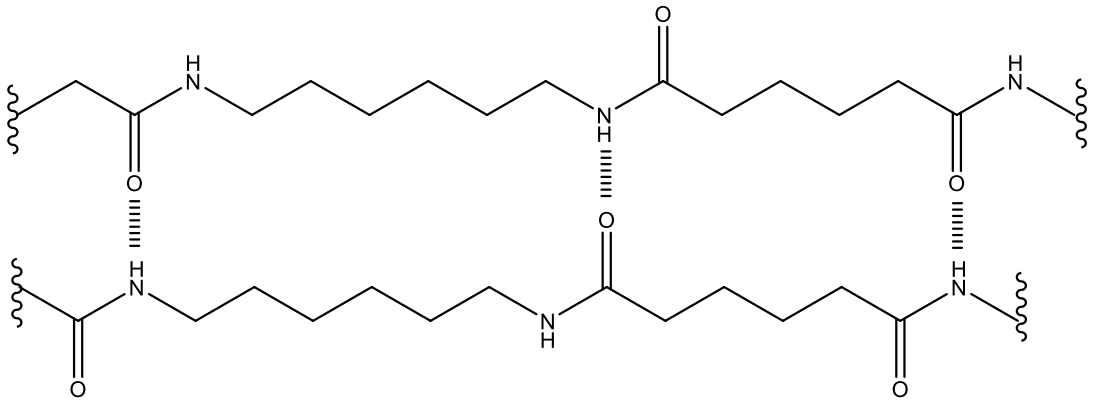


Figure 4.4: Example of hydrogen-bonding (dashed line) between nylon-6,6 polymer chains.

Hydrogen bonding is directional and so the H-bond donor and H-bond acceptor need to have correct geometry to one another to form this kind of bond.[128] If, when the concentration of arginine is increased, the complex between the staining species and the arginine reduced the number of H-bond forming sites available on the staining species, then these interactions between the staining species and the acceptor fibres will be reduced. This could explain why for bleached cotton and polyamide, lower concentrations of arginine produce higher dye transfer. However, it can be seen that with the exception of bleached cotton and polyamide, the addition of arginine does reduce dye transfer across acceptor fibre types with little difference between the concentrations of arginine.

4.3.1.3. Glutamic acid concentration investigation

Glutamic acid also reduced the level of dye transfer in these initial wash tests. Different concentrations of glutamic acid were investigated to find an optimum concentration. It was found that for most acceptor fibres, 5mM of glutamic acid in the wash produced the lower ΔE_{2000} values; however there wasn't much difference when concentration of glutamic acid was increased (Figure 4.5).

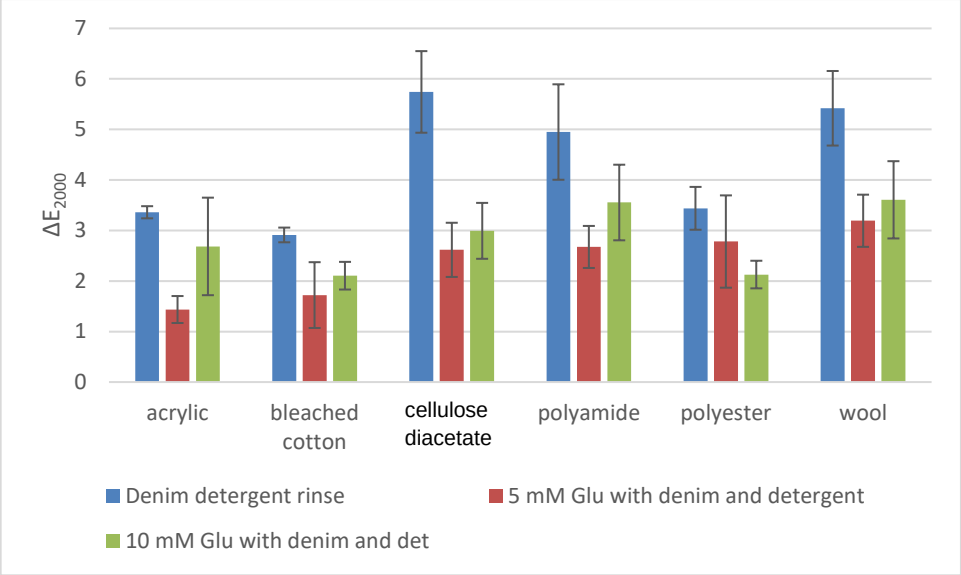


Figure 4.5: Dye transfer from denim with detergent with different concentrations of glutamic acid in wash solution. No glutamic acid (blue), 5 mM glutamic acid (red), 10 mM glutamic acid (green). Error bars show ± standard deviation of three repetitions.

Experimentation in a nil-detergent wash found that the addition of glutamic acid actually increased dye transfer to a higher extent that control conditions. Figure 4.6 shows the large difference between dye transfer from denim with glutamic acid, depending on whether detergent is present or not (red bars vs blue bars respectively).

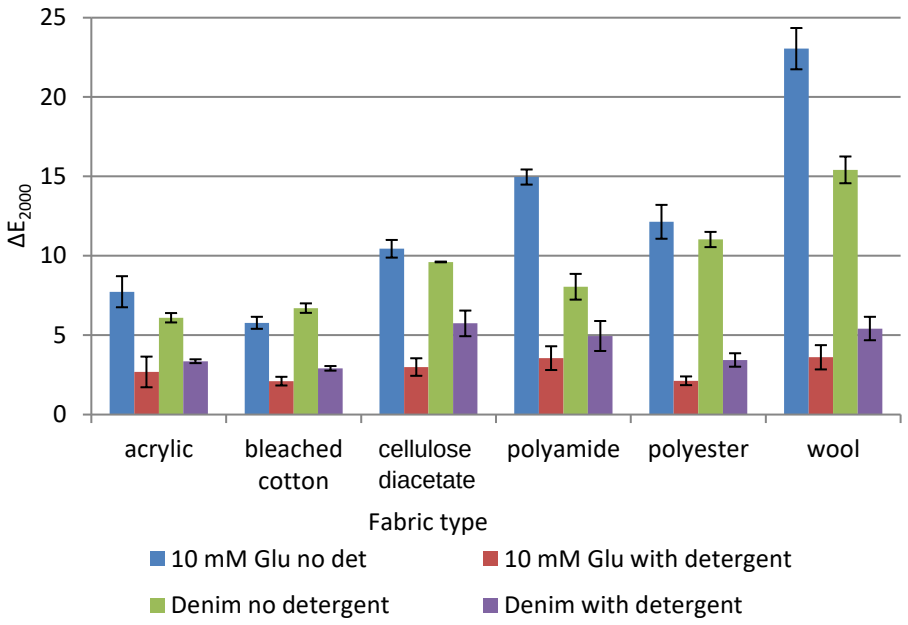


Figure 4.6: ΔE_{2000} values for denim washed with and without glutamic acid (10 mM) in detergent and nil-detergent conditions. 10 mM glutamic acid nil detergent (blue), 10 mM glutamic acid with detergent (red), denim nil glutamic acid nil detergent (green), denim nil glutamic acid with detergent (purple). Error bars show ± standard deviation of three repetitions.

In order to understand what is happening in this multi-component system with detergent and glutamic acid, each component was investigated alone. Glutamic acid was found to decrease the detergent wash solution to pH 3. Therefore, it was necessary to investigate whether the glutamic acid molecules themselves were responsible for the decrease in dye transfer or whether it was the pH effect that the glutamic acid had on the detergent in the wash. The pH of the detergent in solution was pH 8. Denim and multifibre were washed with glutamic acid at the usual detergent pH of pH 8, with nil detergent. Denim and multifibre were also washed with detergent at pH 3 with no glutamic acid. The pKa of the side group of glutamic acid is 4.25. Therefore, by increasing the pH to pH 8 in the nil detergent study, this would deprotonate this carboxyl group to a carboxylate anion which may slightly alter interactions between glutamic acid and other species as it gains a formal negative charge.

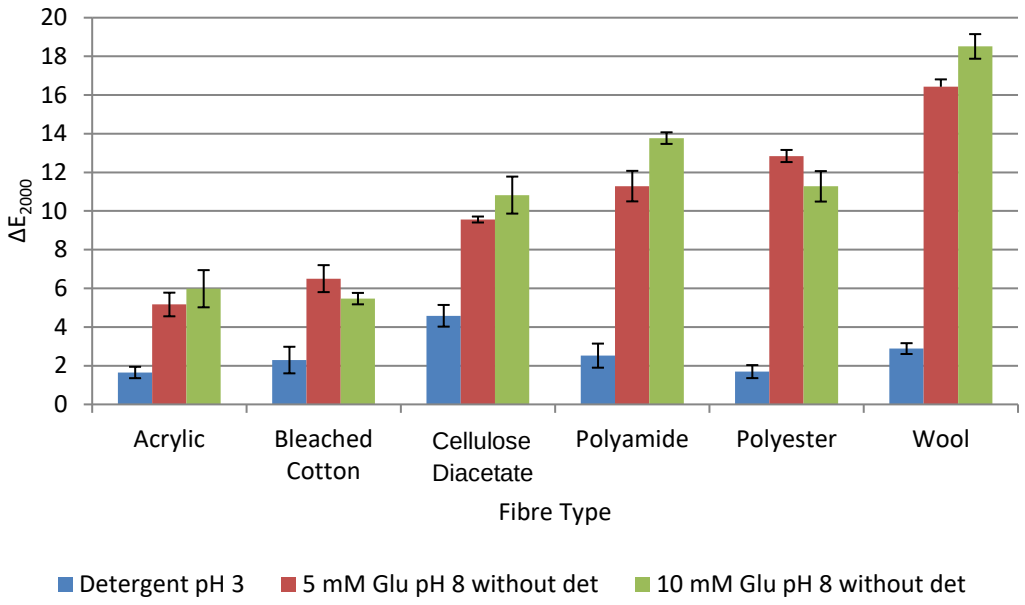


Figure 4.7: ΔE_{2000} values for denim washed with pH adjusted detergent (blue), and pH adjusted glutamic acid at concentrations 5 mM (red) and 10 mM (green). Error bars show ± standard deviation of three repetitions.

It was found that the glutamic acid alone was not causing the reduction in dye transfer; however, the low pH detergent condition did produce a significant reduction in dye transfer from the denim (Figure 4.7). This suggests that the reduction in dye transfer from glutamic acid was a result of the amino acid lowering the pH of the detergent in the wash system.

4.3.1.4. Low pH

As it was discovered that glutamic acid was having a pH effect on the detergent system which in turn reduced dye transfer from denim, pH was investigated further to identify the optimum pH for reducing dye transfer in the wash step.

Low pH detergents have been produced before, one purpose being that they interfere less with the skin's natural, more acidic pH and so may be better suited to those with sensitive skin.[129] Lactic acid has been added to detergent bar compositions to enable this lower pH.

However, alkaline detergents are typically used as they have enhanced soil removal.[130] In dishwashing, the disadvantages of using alkaline detergent, such as etchings on glass items and formations of films were not present when acidic detergents were used, and good cleaning was achieved. Laundry detergents may function similarly in that, while it is known in the literature that alkaline detergents can remove soils, acidic detergents may also work well.[131]

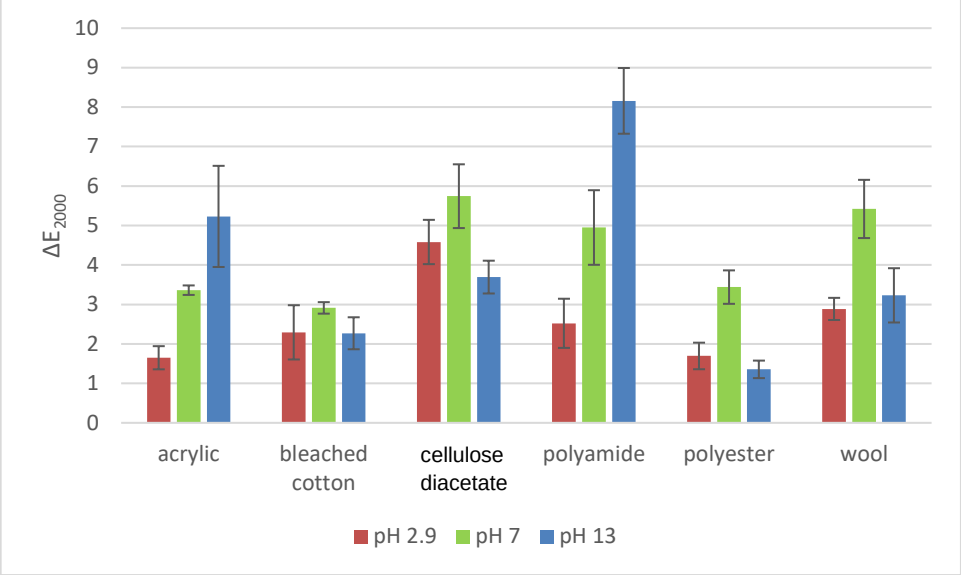


Figure 4.8: Denim washed with detergent at pH 3 (red), pH 7 (green) and pH 13 (blue). Error bars show ± standard deviation of three repetitions.

Figure 4.8 indicates that washes with detergent at both high and low pH have good effects on reducing dye transfer, with the exception of acrylic and polyamide whereby dye transfer was exacerbated at a high pH.

In Chapter 3, the effects of pH on dye transfer from denim in a nil detergent system were investigated. It was found that while high pH gave lower dye transfer, as observed in this detergent system, low pH gave high level of dye transfer. This suggests that the detergent interacts differently with the staining species at low pH.

At low pH, the staining species will become protonated and so, will be more attracted to anionic surfactants in the detergent which encapsulate the

staining species thus inhibiting dye transfer. An anionic surfactant present in the detergent is sodium dodecyl sulfate, which has a pKa of 1.9 and so will still be anionic at pH 3.[132] As was the case for the nil detergent system, at high pH, the staining species will be deprotonated and so, will be repelled by fibres which are also anionic in alkaline medium. The fibres which do not repel the anionic staining species as strongly, acrylic and polyamide, experience a higher level of dye transfer as there are more dyestuff molecules available in the volume of the wash canister than when all acceptor fibres are available for redeposition of dyestuffs. The pH of typical liquid detergent is around pH 8 and so this may be worsening dye transfer in current washing; pH 3 provides the overall significant lowest ΔE_{2000}.

4.3.2. Reduction of dye transfer from model wash load

4.3.2.1. Addition of arginine to wash

After some significant reduction in dye transfer from denim when arginine was added to the wash, arginine was subsequently investigated as an additive to reduce dye transfer from the model wash load.

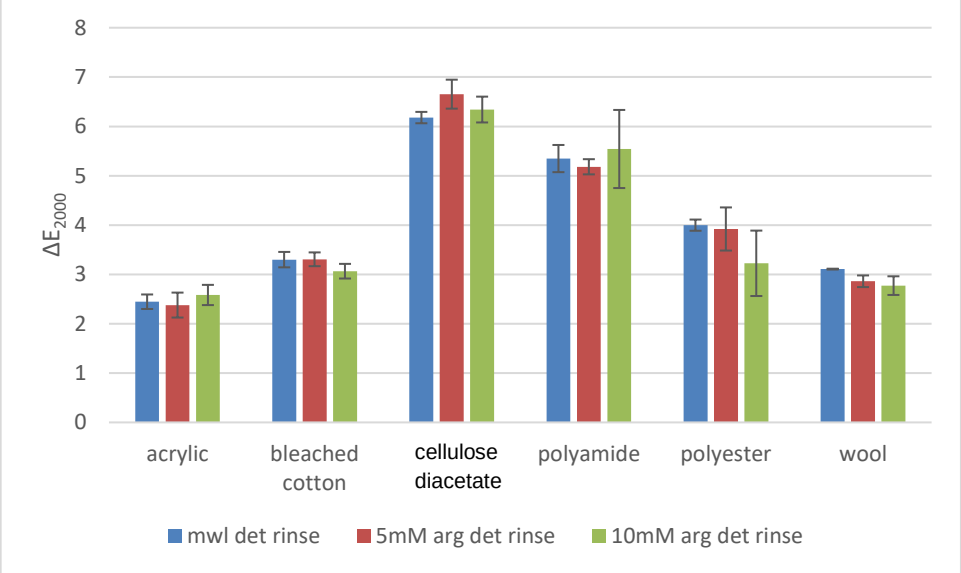


Figure 4.9: The effect of different concentrations of arginine on dye transfer from the model wash load. Detergent rinse (blue), detergent rinse with 5 mM arginine (red), detergent rinse with 10 mM arginine (green). Error bars show ± standard deviation of three repetitions.

However, there was no significant decrease in dye transfer when arginine was added to the detergent wash system (Figure 4.9). The reason for the lack of reduction in dye transfer from the model wash load is likely due to weak interactions between arginine and the larger reactive dyes and disperse dyes found in this load. This suggests that the mechanism for arginine-induced dye transfer reduction is the complexation of the staining species with the arginine, removing it from solution. The other possible mechanism is if the arginine was blocking dye binding sites on acceptor fibres. However, this would produce reduction in ΔE_{2000} regardless of the dye types present and so a reduction would be expected for the model wash load also, therefore this cannot be the mechanism by which arginine reduces dye transfer from denim.

4.3.2.2. pH investigation

It was found that pH 3 produced the lowest levels of dye transfer from both denim and the model wash load in a detergent system (Figure 4.10). As with for denim, this is likely because at this low pH, the dyestuff will be protonated and may be more likely to be encapsulated by anionic surfactants. For example, the pKa values of Reactive Black 5, known to be present in this wash load, are 3.8 and 6.9 and so this dyestuff would be protonated at pH 3.[133]

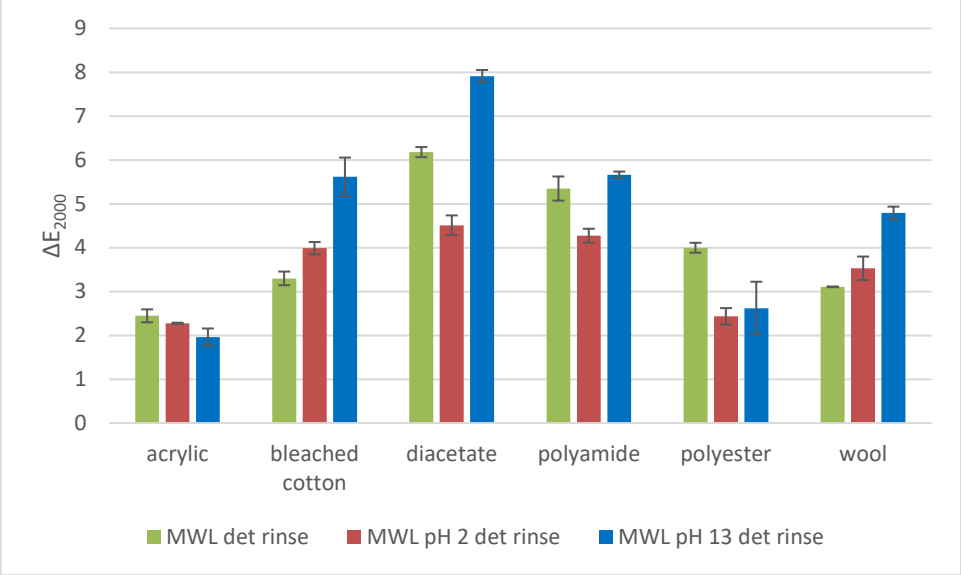


Figure 4.10: Model wash load washed with detergent at pH 7 (green), pH 3 (red) and pH 13 (blue). Error bars show ± standard deviation of three repetitions.

4.3.2.3. Full scale wash testing of Model wash load.

The model represents a full consumer wash load and so, it can provide meaningful insights into the relationship between full scale washing and dye transfer. It is reported that 97.1% of British households have access to a washing machine and that these machines have changeable settings allowing for an optimum wash condition to be utilised.[14,25]

Parameters that consumers can easily alter in their washing machines are the temperature of a wash and also the length of time of a wash. Previously there have been messages conveyed to consumers to use lower temperatures for their laundry washes, from advertisements as well as on product packaging. This was to reduce the energy and water spent during the wash.[14] However, there has been little mention of the length of wash in which a consumer should use.

As can be seen in Figure 4.11a, the effect of temperature on dye transfer is small across all tracer fabrics. There seem to be some benefit of using colder temperature but there is not a large decrease in dye transfer, and for some fabrics there actually is not a decrease at all. However, when the

difference in time is considered, as seen in Figure 4.11 b, there is a large difference between the Automatic (78 minutes) time setting and the Express (30 minutes), both at 40 °C. When considering the average dye transfer for each condition, moving from Automatic 40 °C to Cold Express produces a decrease in ΔE_{2000} by 42%. Mean ΔE_{2000} values across all tracer fabrics decreased in the following order Automatic at 40 °C > Automatic cold >> Express at 40 °C > Express cold.

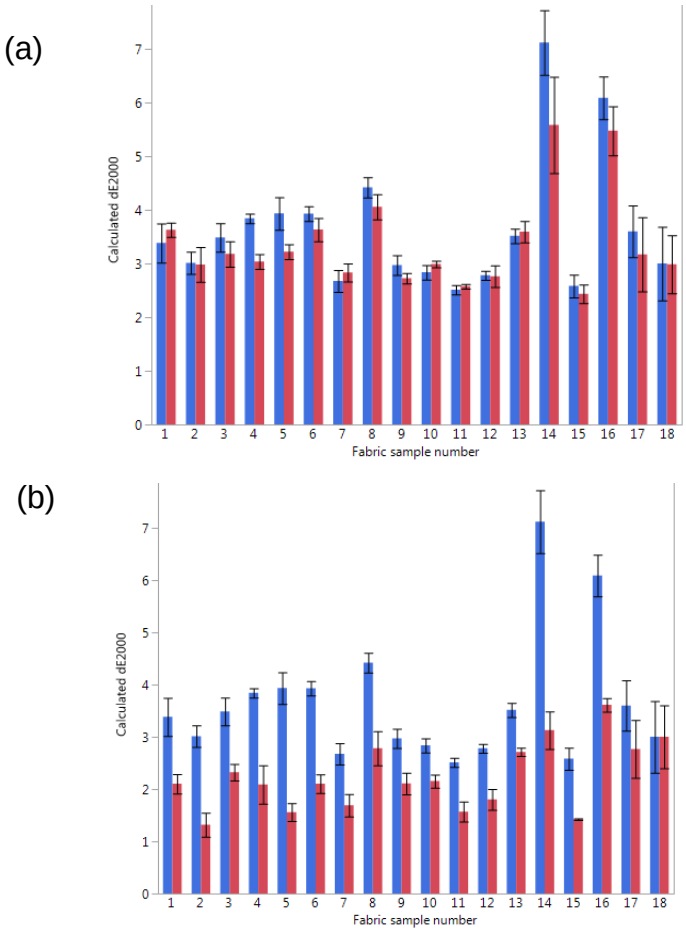


Figure 4.11: Mean ΔE_{2000} values for fabric tracer samples washed on (a) Automatic setting at 40 °C (blue) or at cold (red), and (b) mean ΔE_{2000} values for fabric tracer samples washed at 40 °C on either 'Automatic' (blue) or 'Express' (red) setting. Error bars show ± standard deviation of 3 repetitions.

4.4. Conclusions

Experimental data from Chapter 3, such as UV/vis measurements (Figure 3.38), Dynamic Light Scattering (Table 3.3), and IR spectroscopy (Figure 3.52, Figure 3.53, Figure 3.54, and Figure 3.55) demonstrated that the denim staining species interacted with amino acids and PHMB to differing extents. Addition of the same amino acids and PHMB to the wash liquor samples found that arginine was effective at reducing dye transfer from denim. It was not effective at reducing dye transfer from the model wash load, suggesting that it is the arginine-denim staining species complex formation which drives this reduction in ΔE_{2000} by removing the staining species from solution and immobilising it. Arginine may be a good detergent additive to consider for reduction in dye transfer in a bespoke denim detergent product.

The complex formation between the denim staining species and arginine was still strong in a multicomponent system (with detergent). This implies that the side group of arginine, a biguanide unit, is the most complementary in terms of geometry and supramolecular bond formation to the denim staining species.

While PHMB also has a biguanide moiety, it was not found to reduce dye transfer from denim in a wash setting; it actually increased the level of dye transfer. The PHMB polymer may disrupt existing DTI technologies within the detergent for example, by forming multiple intermolecular bonds with DTI polymers, reducing their ability to bind to dyestuffs. In Chapter 3.4.3, data suggests that phenylalanine did not have a strong interaction with the denim staining species. Because of the lack of interaction, phenylalanine was not able to perform as a dye transfer inhibitor in the wash system. While the aromatic amino acid did act as a blocking molecule for some acceptor fibres, it did not for polar fibres cotton and polyamide and so worsened dye transfer onto these fibres.

Glutamic acid was found to reduce dye transfer in the presence of detergent but greatly increased dye transfer in a nil-detergent environment. Further investigation of this found that the glutamic acid was decreasing ΔE_{2000} values by reducing the pH of the detergent system to around pH 3, instead

of forming any complexation with the staining species. When detergent is present, this low pH helps its performance of dye transfer inhibitors. However, when detergent is not present, the low pH system increases dye desorption, as seen in Chapters 2 and 3 for the model wash load and denim, respectively.

The model wash load represented a full scale consumer wash load. It was therefore investigated how different wash settings, that are easily tuneable on most washing machines, affected dye transfer. Two wash cycles were chosen, an ‘Automatic’ wash and an ‘Express’ wash. Both cycles were trialled at different temperature, 40°C and inlet, ‘cold’ temperature, approximately 25 °C.

A change from a moderate temperature, 40 °C, to a cool temperature, Cold (~25 °C), was found to have a maximum decrease on ΔE_{2000} of 7%. However, a shift from a moderate wash time, Automatic setting: 1 hour 15 minutes, to an Express wash time: 30 minutes, led to a much larger decrease in dye transfer. A maximum decrease in ΔE_{2000} of 39% was recorded for different wash times at the same temperature. While there is only a small benefit from shifting to a cooler wash temperature, the total decrease in ΔE_{2000} between Automatic 40 °C to Cold Express was 42%. This indicates that Cold Express may be the most beneficial wash condition to prevent dye transfer and so, reduce the impact of domestic laundering on the environment.

There are several environmental implications of this finding. Firstly, a reduced wash time as well as reduced wash temperature will use less energy per wash. As well as this, fewer dyestuffs will migrate out of the dye donor materials meaning fewer dyestuffs enter wastewater systems. Also, less dye transfer and colour fading will occur and so the longevity of garments could be potentially prolonged, and textiles are less likely to end up in landfill waste.

Once in use, washing and laundering of clothes has a large contribution to the energy expenditure of a clothing product.[14] Previous research has assessed the use of cooler wash temperatures as a means for reducing this energy.[14] While this present research has not found any significant benefit in

terms of reducing dye transfer when shifting to a cooler temperature, it has also not found any disadvantage. However, the benefits shown by reducing wash time may have a significant reduction of the carbon footprint of clothing.

Reduction of dye transfer is only one function of a detergent. Others include stain and soil removal and perfuming. If a short wash time and lower temperature is required to reduce dye transfer, it must be ensured that the other functions of a detergent can be carried out in these conditions. It is currently thought that bleaching agents do not perform well at temperatures lower than 30°C.[19] Therefore there is scope for future detergent product development to address this issue so that bleaching agents may be incorporated into detergents designed for cooler washes.

Chapter 5- Conclusions and future recommendations

Chapter 2 investigated a model wash load, which was developed and validated against real consumer wash loads using ΔE_{2000} and L*, a*, b* analysis. There was a similar trend of discoloration across acceptor fibres from the model as from consumer loads. There were higher levels of dye transfer from the model wash load than the average consumer wash loads, but this is because the garments were new, and leach more dye in the first few washes. It was found that mostly darker colours from the wash load such as navy, black and purples caused dye transfer. This validated model may be used to test and compare future dye transfer inhibitor technologies. This model may be more beneficial for consumer insight than technical materials, as it is composed of commercially available items which have the same level of treatment as garments on sale and have not been produced to the high standard that technical test materials are, which may affect how much dye is released from the technical test material. The finding that new garments exhibit a higher level of dye transfer has implications for the fast fashion trend. Increased purchasing and therefore washing of newer garments increases the amount of dye leached during each wash. Therefore, along with higher production levels and earlier disposal of clothing, this is another reason why fast-fashion should be reduced. Methods of reducing fast fashion as a business model and as a buying behaviour of consumers should be investigated.

Raman spectroscopy was found to be a successful method of identifying dyes and dye functional groups, along with UV/vis spectroscopy. Building libraries of dyes analysed by these methods would be beneficial for future identification of dyes present on textiles. It was found that predominantly reactive dyes were present in the wash load over other dye types, though disperse dyes were also identified. The implication of this is that previous research detailing methods of reducing dye transfer for other dye groups such as direct dyes should be assessed for their applicability (in UK wash systems). Also, future research and technologies to tackle dye transfer should focus on the chemistry of reactive dyes and wastewater treatment plants may be able to focus more on degradation of this dye group and

removal of toxic species produced during the degradation of reactive dyes. In particular, hydrolysed reactive dyes should be focused on, as reactive dyes are known to have good wash fastness and so, it is likely that the dye transfer occurs from hydrolysed dyestuffs that wash not fully washed off the textile during manufacture. Therefore, there is also an opportunity for manufacturers to improve their wash off and finishing procedures to reduce the presence of hydrolysed reactive dyes on finished garments. More dyestuffs were found to be released from cotton than from polyester, as would be expected due to hydrophobic disperse dyes being used to colour polyester. Future research could develop a cotton finishing technique which prevents so much dye being released during laundering.

In a nil detergent condition, increased time of wash and higher temperature of wash increases dye particle desorption from donor textiles in the model wash load as well as dye re-adsorption into donor textiles. This is because the higher temperature gives more energy into the wash liquor allowing the molecules to have higher kinetic energy and diffuse more. At low pH and high ionic strength, less dye particle desorption occurred from donor textiles but there was higher dye adsorption onto the acceptor fibres. This is because low pH and high ionic strength increased substantivity of dye for fibre by reducing the repulsion between anionic dye particles and fibres that experience a negative charge in aqueous media. Implications of this are that shorter washes and cooler temperatures are beneficial for reducing dye transfer, so detergent products should be developed to provide all other functions, such as soil removal and perfuming, in these wash conditions. By tailoring pH and ionic strength of a detergent, less dyes and dyestuffs will enter wash solution and therefore wastewater systems. However, this needs to be further investigated to find an optimum condition. Any dye that is released would have stronger association an acceptor textile which would increase visible dye transfer.

Denim was investigated in Chapter 3 for its contribution to dye transfer and for the elucidation of the staining species it releases upon washing. Technical denim dyed with only indigo was validated against shop bought denim samples and showed similar trends of dye transfer to acceptor fibres and similar $\lambda_{max\text{-}vis}$ values on UV/vis spectra. This allowed for a uniform

denim sample to be used which was not affected by any aesthetic modifications such as dye fading, in which different samples would contain significantly different dye concentrations. This technical denim could be used for future experiments to replicate UK denim samples.

The blue species that causes dye transfer from denim is not indigo alone. This was suspected after a perceived higher solubility of the blue species in water, which indigo in its parent blue form, does not have apart from trace amounts. The larger solids that were filtered out of the wash liquor, such as dyed cotton fibres, were found not responsible for any substantial level of dye transfer. Different HPLC chromatograms and NMR Spectra to those recorded for indigo in the literature further confirmed this finding. However, UV/vis of commercial indigo's sparing solubility in water did show that the staining species has the same $\lambda_{max\text{-}vis}$ and so, possibly the same chromophore. In comparison, the UV/vis of indigo carmine, was significantly different to that of the staining species and so was not a match. FT-IR indicated that both indigo and cellulose were present in the freeze-dried staining species sample. It was theorised that there was some supramolecular interaction between indigo dye and cellulose oligomers, which led to unique DLS, LC-MS and TGA results that did not match existing literature for indigo or cellulose oligomers. Particle sizing (DLS) suggested that the staining species existed as a colloid in the wash water. However, the refractive index had to be estimated for this measurement and so the data may not be correct, but it is likely to be similar to the true sample as the refractive index for cellulose is similar. The PDI values were also very broad which suggested particles of many different sizes were present. As the PDI values of all measured species were of the same magnitude, a reasonable comparison of size between samples could be made. The sample must have some solubility in order perform analysis techniques that require a solution, such as UV/vis spectroscopy and liquid chromatography.

Crystallisation of the denim staining species in different solvents was attempted but was unsuccessful. Future research could investigate whether there are other methods to crystallise the staining species, or more suitable

NMR solvents/conditions, to elucidate its structure present in the wash liquid (as a colloid or suspension).

In wash tests with multifibre acceptor fabric, the staining species was found to have high affinity for wool, polyamide, diacetate and polyester both with and without detergent. The level of dye that transferred to each different acceptor fibre was not even, suggesting that the characteristics of the acceptor fibre are the factors which drive dye attraction, as there is no blanket dye transfer for all different fibre types. Wool, polyamide, cellulose diacetate and polyester contain hydrophobic regions and so the staining species could interact with these species through hydrophobic interactions, such as through aromatic rings which were confirmed to be present by FT-IR and NMR. However, these fibres are also capable of hydrogen bonding and could interact with different parts of the staining species by forming strong intermolecular bonds. FT-IR also showed the presence of –OH and –NH groups in the staining species, which can act as hydrogen bond donors.

Further wash tests showed that in a nil detergent system, dye transfer increased as pH decreased, due to acidic protons shielding repulsive interactions between dye and fibres. It was also found that increased temperature and increased agitation led to increased dye transfer in a nil detergent system. This is due to particles having more energy to move around the wash solution and come into contact with other items in the wash canister, such as the multifibre.

Owing to the interaction between two amide containing fibres, wool and polyamide, with the denim staining species, amino acids investigated for their affinity for staining species to act as a competitive inhibitor against acceptor fibres. Arginine, Glutamic acid and Phenylalanine were investigated as they represent a range of side group properties. It was found that arginine seemed to form an amorphous complex with the staining species when added to denim wash liquor. When added into the wash in Chapter 4, arginine was also successful at reducing dye transfer both with and without detergent present in the system because arginine was able to complex with the staining species through its biguanide side group, which was not disrupted by the presence of detergent. Phenylalanine was not successful,

possibly due to hindrance and a preference for self-assembly. Glutamic acid was successful at reducing dye transfer in the presence of detergent but greatly increased dye transfer without detergent present. It was found that it was a pH effect that glutamic acid was having, reducing the pH of the detergent system to around pH 3. Without detergent present, the wash system was reduced to pH 3, which increased affinity for protonated dyestuffs to anionic fibres. Further washes confirmed that in conjunction with detergent, a low pH was beneficial for low dye transfer. Dye transfer from the model wash load was also reduced by low pH. This is likely because of how the detergent interacts with the dyestuffs at low pH, for example, with increased anionic surfactant encapsulation of protonated dyestuffs. This may have implications for the pH of detergents. Currently, detergents have a pH of around 8 or higher to remove acidic soils. If soil removal was possible a lower pH, then acidic detergents could be developed. Arginine was not successful at reducing dye transfer from the model wash load due to different dye groups being present. Therefore, an arginine additive to a detergent may best suit a bespoke denim product. As it is a naturally occurring biomolecule, arginine entering into waterways shouldn’t have a significant negative impact on the environment. Future research could investigate, alongside elucidation of staining species structure, whether the complex formed with arginine could be elucidated. This would allow for supramolecular studies such a Job plot and NMR titrations to be undertaken which help understand the ideal ratio between two species in a supramolecular complex.

Future research could also investigate whether other amino acids or small biomolecules could have an even better effect on decreasing dye transfer. For example, Lysine is an amino acid which is found in many foodstuffs, and has an amine group in its side chain, similar to arginine and so could be worth investigation.

The model wash load was also investigated in Chapter 4 in full scale wash tests using parameters that most consumers can easily alter at home no matter what model and make their washing machine. It was found that a quicker wash time and a cooler wash temperature were both separately beneficial for reducing dye transfer and when combined produced the lowest

dye transfer observed. Implications of this finding are to communicate to consumers to use shorter and cooler wash settings which may be done through advertisement and notices on laundry products. This change in consumer washing behaviour should be easy to adopt and practice, especially if consumers are given confidence to do so by detergent manufacturers. Dye transfer is only one function of a detergent and so, the other functions such as stain removal and perfuming should also be able to occur in a shorter wash time window.

There are limitations to this research that must be considered when drawing conclusions.

The model wash load was only composed of t-shirts made of cotton and polyester. While this was chosen to represent the consumer loads that had been received (n= 28), across a wider sample of consumers other fibres types would have been present which may have been coloured with different dye groups. This wash load was also only validated against consumer wash loads from the UK, but the validation method could be extended to incorporate other countries wash loads. Should the dye landscape change again, a new representative wash load would need to be assembled, validated and measured for the dyes that they are coloured with.

The technical denim that was used did not have any other dye on it such as C.I. Sulfur Black 1, which is often used as a shading dye on top to create darker denim. Although it was validated against commercially available denim jean material, which likely had other dyes and finishes present, it was only validated against three samples which were all medium blue to dark blue. Therefore, further research should be conducted to ascertain whether a broader range of commercially available denims- with shading dyes and chemical finishes- behave in the same way as the technical denim particularly in the conditions found to reduce dye transfer.

The finding that arginine could be added to detergent to produce a bespoke denim detergent may increase the number of wash loads from a household, if a consumer has to separate their denim which they may have included in other wash loads before. This potentially would increase water and electricity usage per household as well as packaging. Further research should be

conducted to see if arginine would be compatible in a non-bespoke detergent to perform this function for denim in a mixed wash, so that extra wash loads do not need to be generated. Initial wash tests of the model wash load with arginine seemed to suggest that there was not a marked negative effect of the addition of arginine to a non-denim wash.

One critical point is that, if less migrant dyestuffs are being adsorbed by textiles within a wash, there will be possibly more of these toxic dyestuffs entering the waterways with the potential to harm flora and fauna. Therefore, while this research has investigated ways to stop re-deposition of dyestuffs, it has also provided the fundamental mechanisms by how dye might be released from both a model wash load and denim. Future research must focus on preventing dye release from garments if this problem is to be effectively solved.

List of Abbreviations

ARG	Arginine
BOD	Biochemical Oxygen Demand
C.I.	Colour Index
CMC	Carboxymethylcellulose
COD	Chemical Oxygen Demand
DLS	Dynamic Light Scattering
DTI	Dye Transfer Inhibitor
DWL	Denim Wash Liquor
DWL-ARG	Denim Wash Liquor mixed with Arginine
DWL-GLU	Denim Wash Liquor mixed with Glutamic Acid
DWL-PHE	Denim Wash Liquor mixed with Phenylalanine
DWL-PHMB	Denim Wash Liquor mixed with Poly(hexamethylene biguanide) Hydrochloride
EDTA	Ethylenediaminetetreaacetic acid
ESI	Electrospray Ionisation
FTIR	Fourier Transmission Infrared spectroscopy
GLU	Glutamic Acid
HPLC	High Performance Liquid Chromatography
LCMS	Liquid Chromatography Mass Spectroscopy
M_w	Molecular weight
NMR	Nuclear Magnetic Resonance spectroscopy
PDI	Polydispersity Index
PHE	Phenylalanine
PHMB	Poly(hexamethylene biguanide) Hydrochloride
PVP	Polyvinylpyrrolidone

SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
UV/vis	Ultraviolet/visible light spectroscopy

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