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The Effect of the Acid/Dithionite/Peroxide Treatments on Reactively Dyed Cotton and Indigo Dyed Denim and the Implications for Waste Cellulosic Recycling

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The Effect of the Acid/Dithionite/Peroxide Treatments on Reactively Dyed Cotton and Indigo Dyed Denim and the Implications for Waste Cellulosic Recycling

Previous studies have established that the application of crosslinking dyes and easy care finishes to cotton can significantly reduce the dissolution of waste cotton in swelling solvents and limit potential recycling of cellulosic materials through Lyocell fibre regeneration process. In this study a sequential hydrolysis/reduction/oxidative treatment was investigated as a potential method to completely strip all types of reactive dye chromophores from cotton. It was established that the treatment could completely strip off colours from the reactively dyed fabrics and post-consumer denim jeans fabric resulting in a white, NMMO dissolvable cellulosic material, which could be used as a feedstock for Lyocell fibre regeneration. The white cellulose had an acceptable degree of polymerisation and the regenerated fibres had structural and mechanical properties similar to those of fibres regenerated from conventional wood pulp. Blending conventional wood pulp and recycled cotton pulp allowed manufacturing of regenerated Lyocell-type fibres with acceptable properties.

Keywords: Lyocell, waste cotton, Reactive dyes, Indigo, recycling, dye stripping.

1.0: Introduction

The world’s population growth together with the change in people’s lifestyle and fashion culture has led to an increased demand for textile fibres (Wang, 2006). Fuelling this growth is the increasing number of short fashion seasons in clothing retail markets, which has led to overall decreased lifespans of clothing in developed countries such as the United Kingdom. Similarly, availability of cheap clothing from retailers such as Primark, Zara and H & M has also made fashion more affordable to millions of consumers (Barnes, 2006). Accordingly, the impact on amount of waste generated has increased significantly, making the textile industry one of the most significant waste-generating sectors in the world (Morley et al., 2006; Hoornweg and Bhada-Tata, 2012).

The current disposal routes for the generated waste textile is through reuse or recycling, with up to 30% of waste being landfilled or incinerated annually (Wang, 2006; WRAP, 2012). Reuse of waste garment as second-hand clothing is associated with the decline of textile industries in developing countries due to lower cost of the imported second-hand clothing undercutting the local products (Morley, 2006). Moreover, the decreasing quality of collected waste garments resulting from the nature of fast fashion (Morley et al., 2009) suggests that the waste garments can no longer be reused and therefore require other disposal possibilities, including recycling, landfill or incineration. However, both landfill and incineration of waste textile are associated with environmental pollution, while the common mechanical recycling of waste textile back to the component fibre is also compromised by the presence of colour and mixed fibre blends which in turn results in low value non-woven products (Wang, 2006; Morley et al., 2006, 2009).

Chemical recycling of waste cotton is currently limited, with one of the technical challenges being presence of crosslinks resulting from modification of cellulose hydroxyls by reactive colorants and finishing agents. The presence of these crosslinking dyes and easy care finishes within the cellulosic structure can reduce the dissolution of the cellulose feedstock, subsequent spinning efficiency of the recycled cotton materials and ultimately affect the final properties of the "new" regenerated cellulosic fibres (Abhyankar et al., 1985, 1987; Haule et al., 2014, 2016a, 2016b). It is also worth noting that the presence of other impurities such as heavy metals present safety issues with N-Methylmorpholine N-oxide (NMMO) solvent used for Lyocell fibre regeneration (Kalt et al., 1996; Rosenau et al., 2001) and has the potential to contaminate the solvent thereby decreasing its recycling rate. Therefore, it is important to strip off any colorants, crosslinking agents and other impurities from waste garments before they can be processed into new fibres through the Lyocell process. In addition to reducing solvent dissolution, the covalently bound dyes may also adversely affect the colour of the feedstock and the resultant regenerated fibres. Therefore removal of crosslinks, derived from colorants and crease resist finishes prior to chemical recycling of waste cotton for new fibre regeneration is essential.

In a previous study (Bigambo et al., 2018), a combined acid, alkali and peroxide treatment was demonstrated to be not fully effective in stripping the anthraquinone-based reactive dyes from cotton and thereby failed to deliver a white, dissolvable cellulosic feedstock for new lyocell fibre regeneration. In this study the efficiency of an alternative combined treatment involving a sequential acid hydrolysis, alkaline sodium dithionite and hydrogen peroxide oxidative treatments was investigated as a potential method to strip reactive dyes, being the most commonly used dye class for cellulosic fibres (Kulandainathan et al., 2007) from cotton for the purpose of preparing waste cotton that could be completely dissolved in cupriethylenediamine hydroxide (CED) solvent and subsequent NMMO solvent for chemical recycling. The efficiency of each dye stripping treatment was determined with a view to maximum colour removal characterised by decreased colour strength (K/S) and increased in lightness (L*) and ISO brightness of the resultant treated cotton fabrics. In this study, we investigated the potential reuse of the stripped waste cotton materials as feedstock for producing regenerated cellulosic fibres through the Lyocell process.

2.0: Experimental

2.1: Materials

A bleached, mercerised, plain woven, 100 % cotton fabric, (135 g/m^2) was supplied by Phoenix Calico Limited, Cheshire, United Kingdom and a pair of post-consumer denim jeans was obtained from a local charity shop. C. I. Reactive Blue 19 (Blue 19) and C. I. Reactive Black 5 (Black 5) were kindly supplied by Dystar, Germany and C. I. Reactive

Red 228 (Red 228) was kindly supplied by Ciba, UK. The structures of the reactive dyes have been reported in our previous paper (Bigambo et al., 2018), but are shown in Figure 1. All other chemicals were of laboratory grade obtained from various chemical suppliers.

INSERT FIGURE 1

2.2: Methods

2.2.1: Reactive Dyeing of Cotton

Cotton fabric was dyed in a Mathis Labomat dyeing machine with 4% on mass of fabric (o.m.f.) of the specified dye and at a liquor to goods ratio of 15:1 following commercial conditions recommended by the dye manufacturers. For Black 5 and Blue 19, fabrics were initially immersed in a liquor containing the dye and 50 g/L sodium chloride before raising the temperature to 40°C and further running the machine at this temperature for 15 minutes. 5 g/L sodium carbonate was then added and the dyebath maintained at 40ºC for a further 30 minutes. 2 g/L of sodium hydroxide was then added and the dyeing continued for another 60 minutes. The fabrics were then removed from the dyebath and rinsed thoroughly in deionised water prior to after-soaping, final rinsing and air drying.

For Red 228, fabrics were introduced in a bath containing the dye and 50g/L sodium chloride before raising the temperature to 60°C and further running the machine for 30 minutes. 20 g/L sodium carbonate was then added and dyeing process continued for a further 60 minutes. The dyebath temperature was then dropped and the fabric rinsed thoroughly in deionised water prior to soaping, final rinsing and air-drying.

2.2.2: Washing-off

All dyed fabrics were after-soaped for 10 minutes at 60°C in a solution containing 2 mL/L of aqueous non-ionic detergent to remove any unfixed and hydrolysed dyes from the fabrics. Washed fabrics were rinsed in warm and then cold water prior to air drying.

2.2.3: Stripping of Reactive Dyes from Coloured Cotton

Stripping of reactive dyes from cotton fabrics was based on using the combined effects of acid hydrolysis, sodium dithionite reduction and hydrogen peroxide oxidative treatments. All treatments were done using a Pyrotec Infra-red laboratory scale dyeing machine and 275 mL dyeing pots.

2.2.3.1: Acid treatment of the reactively dyed cotton

The acid stripping treatment was based on a previously reported method (Abhyankar et al., 1985, 1987). Dyed fabrics were initially soaked for 2 hours in 10 mL/L sulphuric acid at room temperature, liquor: goods ratio of 30:1, before raising the liquor temperature to 60°C and further treating the fabrics for 1 hour. Treated samples were then divided in two equal portions where one portion was warm rinsed and neutralised in 0.2 mL/L NaOH followed by warm rinsing in water and air dried (Acid Treated Cotton). The other portion was further treated in an alkaline sodium dithionite solution.

2.2.3.2: Alkaline dithionite treatment of the reactively dyed fabrics

Sodium dithionite was chosen as the reducing agent due to its widespread use in both laboratory and industrial scale reduction and decolorisation processing. A dye scavenging agent, polyvinylpyrrolidone (PVP), was also added to the stripping liquor to prevent redeposition of dyes on the fabrics (Walles, 1963). During treatment, the acid treated cotton was immersed in an alkaline dithionite liquor containing 30 g/L sodium dithionite, 40 g/L sodium hydroxide, 2.5 g/L PVP and 2 mL/L non-ionic detergent at a 30:1 liquor to goods ratio. The bath temperature was raised to 80°C and fabrics were treated at this temperature for 30 minutes, before raising the temperature to 100°C and further treating for 1 hour. The treatment bath was then cooled to 50°C and the stripped fabrics were rinsed in hot water for 5 minutes. The dithionite treated sample was then neutralised in 0.2 mL/L acetic acid prior to warm rinsing and air drying (Acid/Dithionite treated fabric).

2.2.3.3: Peroxide treatment of the reactively dyed fabrics

The acid/dithionite treated fabric was further treated for 60 minutes at 85°C in a bath containing 1M hydrogen peroxide (35%Vols), 1.2 g/L sodium hydroxide, 1.8 g/L sodium carbonate and 7 g/L sodium silicate, at a liquor to goods ratio of 30:1, followed by water rinsing and air drying (Acid/Dithionite/Peroxide treated fabric).

2.2.4: Colorimetric Analysis

The K/S values of fabrics were calculated from the Kubelka-Munk equation, which relates the reflectance of the dyed fabric to its absorbance and scattering at a specific wavelength. The K/S and CIE L*a*b* values were calculated from the mean of four reflectance measurements produced by a Datacolor Spectroflash 600 spectrophotometer. The CIE L*a*b* coordinates were calculated under illuminant D65 using a 10° standard observer while the K/S values were calculated at the λmax of the treated fabrics. Each fabric sample was folded twice in order to achieve opacity. The ISO brightness values, defined as the intrinsic reflectance factor measured at a specific wavelength of 457 nm and a half bandwidth of 44 nm (British Standards, 2009), were also determined due to it being the main colorimetric parameter used to evaluate the brightness of a cellulosic pulps (Biermann, 1996). In this study the ISO brightness of the stripped and unstripped fabrics were measured at 460 nm wavelength using a Datacolor SF600 spectrophotometer.

The percentage of dye stripped from the fabric was calculated by relating the K/S values of treated fabrics and that of untreated dyed fabrics using Equation 1.

$$\%\,Stripping = \frac{K/S_{\text{unstripped fabric}} - K/S_{\text{stripped fabric}}}{K/S_{\text{unstripped fabric}}} \text{ x } 100 \qquad \text{(Equation 1)}$$

2.2.5: *Pulp preparation*

Cotton pulps were prepared by first stripping-off the dyes from the reactively dyed cotton fabrics and the post-consumer denim jeans using the optimised acid/dithionite/peroxide stripping treatment. Although the dyes used had no traces of heavy metals, a 2 g/L of diethylenetriamine pentaacetic acid (DTPA) chelating agent was added in each stripping bath to assist the removal of any heavy metals present in the cotton materials as a result of the potential heavy metal sources sush as in processing water or equipment such as the dyeing pots. DTPA was chosen due to its ability to offer best chelating properties when used under high pH conditions and in the presence of oxidizing agents such as peroxides (Shore, 2002).

The stripped fabrics were then disintegrated to form a cotton pulp by using a food blender. Fabrics were first cut into small pieces of 10 x 10 cm before being agitated in a 500W Breville blender (with stainless steel blades, using medium speed setting) until the complete disintegration of the fabric pieces was achieved. A 2 g/L of the chelating agent was again added to the disintegration equipment to prevent possible contamination of the pulp with metals from either the processing water or equipment. After disintegration, pulps were washed in distilled water, air dried and were then stored in re-sealable plastic bags.

2.2.6: *Pulp characterisation*

The solubility of cotton was assessed by dissolving the material in 0.5M CED solvent as per BS ISO 5351:2010 method (British Standards, 2010), following a procedure previously described (Haule et al., 2014). The solubility of cotton was then determined by a ‘filtration and oven-drying’ method using a Whatman Glass microfiber-GF/C where, the CED-cellulose solution was filtered onto a pre-weighed glass filter which was then oven dried for 4 hours before being cooled for 2 hours in a desiccator containing phosphorus pentoxide. The cooled glass filter was then weighed and the percentage of cellulose dissolved in CED solution was calculated as per Equation 2 below:

$$\%\,Solubility = \frac{X-(F_a - F_b)}{X} \times 100 \qquad \text{(Equation 2)}$$

where X is the oven dry (OD) weight of the sample before dissolution in grams, and F_a and F_b are the OD weights in grams of the glass filter after and before filtration, respectively.

The limiting viscosity of recycled cotton pulp was calculated by relating the efflux times of the cellulose-CED solutions measured through a capillary tube viscometer at 25°C and the corresponding values of viscosity ratio obtained from a standard table (British Standards, 2010). However, the degree of polymerization (DP) was obtained from the calculated values of limiting viscosity using equations reported by Marx-Figini (1978). Both limiting viscosity and DP are important factors required for the quality of the spinning dope for fibre spinning (Fink et al., 2001).

2.2.7: Fibre spinning

The spinning solution (spinning dope) was prepared by mixing 49.6%v/v NMMO hydrate solution with the cotton pulp and propyl 3,4,5-trihydroxybenzoate (propyl gallate ester) in a suitable ratio using a Lenzing knitter mixer. The dissolution process was achieved by mixing the materials at increasing temperature and pressure starting from room temperature and 250 mbar to 110°C and 400 mbar, respectively. The final spinning solution had 9% cellulose concentration, 78% NMMO and 13% water.

Fibres were spun in a laboratory scale spinning machine at Lenzing AG, Austria using a spinneret with a single hole of 100µm in size. The dope throughput was 0.03 g/min and the air gap conditions were set at 20 mm, with temperature and relative humidity adjusted to fit the required fibre output. The winding speed was 26 m/min and water was used for fibre precipitation and regeneration of the cellulose. The spun fibres were then oven-dried overnight at 60°C temperature.

The Lyocell-type fibres were regenerated from the wood pulp, cotton pulps and blends thereof as detailed in Table 1.

INSERT TABLE 1

The linear density (L, in dtex) of regenerated fibres was calculated by relating the winding speed (Ws, in m/min), percent cellulose in the spinning dope (cellulose) and the rate of extrusion of the dope (Ds, in g/min) as per Equation 3:

$$\boldsymbol{L = 121 \times \frac{D_s}{W_s} \times \mathbf{cellulose}} \qquad \text{(Equation 3)}$$

2.2.8: Characterisation of the regenerated fibres

The surface morphology of fibres regenerated from recycled cotton pulps were analysed using a Hitachi S-2600N SEM instrument and were compared with standard Lyocell fibres from wood pulp. Microscopic images were taken at 2000x magnifications, using 5kV accelerating voltage and an average working distance of 5.3 mm.

The structural properties of regenerated fibres were assessed using an Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) technique. The IR spectra of the fibres were obtained using a Perkin Elmer Spectrometer BX FT-IR which recorded at a frequency range of 400 to 4000 cm^{-1}, 16.0 cm^{-1} resolution and the presented were the average of 32 scans. The data obtained was used to determine the IR crystallinity of fibres regenerated from recycled cotton pulp and those made from wood pulp using a method proposed by Nelson and O'Connor (1964a and b), who defined Total Crystallinity Index (TCI) and Lateral Order Index (LOI) as the ratios of the FTIR 1372/2900cm^{-1} and 1420/893cm^{-1} absorptivity peak intensities, respectively.

The mechanical properties of regenerated fibres including tenacity and elongation at break were determined by using an Instron tensile tester.

3.0: Results and Discussion

In this study three reactively dyed cotton fabrics and post-consumer denim jeans were treated in a stripping process involving sequential acid hydrolysis, sodium dithionite reduction and hydrogen peroxide oxidative treatments in order to strip colour and any associated crosslinking introduced by the dyes in the fabrics.

3.1: Effect of sequential acid/dithionite/peroxide treatments on the colour of dyed cotton

Figure 2 presents the colour strength of the reactively dyed fabrics and denim fabrics treated in sequential acid/dithionite/peroxide treatments. Acid treatment of the reactively dyed fabrics resulted in a minimal decrease in colour strength of all treated materials, indicating the stability of the dye chromophores present in the three reactive dyes, and their covalent linkage to cellulose, to acidic hydrolysis. The treatment also slightly decreased the colour strength of the denim fabric. However subsequent alkaline dithionite treatment significantly decreased the colour strength of all cottons resulting in a K/S value of 0.1 on both bifunctional Black 5 and monofunctional Blue 19 dyed fabrics, while K/S values of 0.6 and 0.8 were obtained on the trifunctional Red 228 dyed and denim cotton, respectively, compared to the original K/S values of 29.7, 22.9, 26.0 and 20.6, for Black 5, Blue 19, Red 228 dyed fabrics and denim, respectively. The high reducing potential of alkaline sodium dithionite [-850mV at 50°C] (Shore 2002) together with the dye binding capacity of polyvinylpyrrolidone (PVP) scavenging polymer (Sheth 1985; Boardman and Jarvis, 2000) added to the dithionite stripping liquor are thought to have caused the high level of dye removal. PVP polymer can combine with the stripped dye, forming a dye-polymer complex, which is then washed out during subsequent washing.

INSERT FIGURE 2

Further oxidative peroxide bleaching treatment resulted in an additional decrease in K/S values to 0.02, 0.03, 0.1 and 0.2 on Black 5, Blue 19, Red 228 dyed fabrics and denim jeans, respectively. The slightly lower treatment effect observed on Red 228 dyed cotton is thought to be due to multiple crosslinking nature of the C. I. Reactive Red 228 dye. The dye has three functional groups (two vinylsulphones and one monochlorotriazine) (Taylor, 2000) thereby forming three possible bonds with the hydroxyl groups of the cellulose. It is therefore possible that the treatment could only destroy one or two of the dye-fibre bonds, leaving the other bonds still attached to cellulose fibre and restricting accessibility of degradative chemicals to the chromophore (Matsui et al., 1998). However the lower treatment effect on denim was thought to be due to higher warp yarn twist used in making denim yarns (Shaw, n.d.), which could have limited their accessibility to water and chemicals.

The ISO brightness of treated fabrics, Figure 3, increased significantly after sequential acid/dithionite/peroxide treatment resulting in brightness values approaching that of 90% recommended for dissolving pulp (Biermann, 1996). Visual analysis of the treated and untreated fabrics, Figure 4, further confirmed the effectiveness of sequential acid/dithionite/peroxide treatments on the three reactively dyed cotton fabrics and on denim jeans, with the appearance of the fabrics treated in a complete acid/dithionite/peroxide treatment being similar to that of the original undyed cotton.

INSERT FIGURE 3 AND FIGURE 4

Figure 5 compares the stripping efficiency of the combined acid/dithionite/peroxide treatments to the previously reported acid/alkali/peroxide treatments (Bigambo et al. 2018) and it is clear that the two methods had similar effects on the azo-based Black 5 and Red 228 dyed fabrics, stripping up to 99.8% of dyes from the cotton. However the effect of combined acid/alkali/peroxide treatments was lower on the chemically resistant Blue 19 dyed fabric and the indigo dyed fabric stripping only up to 81% of the dyes. In contrast the stripping efficiency of the combined acid/dithionite/peroxide treatments was higher an all dyed fabrics stripping more than 99.1% of the dyes from all fabrics, including the highly chemical resistant anthraquinone-based Blue 19 dye and the indigo dyed fabric. This indicates that the combined acid/dithionite/peroxide treatments could be an effective commercial treatment for producing a white cellulosic feedstock for Lyocell fibre regeneration.

INSERT FIGURE 5

3.2: Analysis of solubility of the chemically treated cotton pulp

The purpose of the sequential acid/dithionite/peroxide treatment was not only to strip colorants but to also break any chemical bonds formed between the dyes or finishing agents and cellulosic hydroxyl molecules, thereby, providing a white cotton material with a significant reduction in crosslinking and therefore increased solubility in swelling solvents.

Analysis of solubility of the materials, Table 2, indicated that although the original undyed cotton fabric could be dissolved completely in 0.5M CED solution, the Black 5 dye decreased the solubility of dyed cotton to about 66%, while the minimum level of acceptable pulp solubility was 99%. This reduction could be attributed to the limited swelling ability of the dyed cotton cellulose due to the strong dye-fibre covalent bonds formed as a result of two functional groups present in the C. I. Reactive Black 5 dye (Matsui et al., 1998). For solvent to dissolve the cellulosic polymer, it must form hydrogen bonds with hydroxyl groups of the amorphous region of the cellulose, swell the material and finally disrupt the crystalline region of cellulose to form a polymer solution (Krässig, 1993). However following the sequential acid/dithionite/peroxide treatments, the solubility of cellulose increased to 100%. This solubility increase was due to the increased accessibility of solvent to the amorphous and crystalline cellulose regions and the associated increased cellulose surface area following crosslink scission.

Higher solubility results were also observed on the Blue 19 dyed cotton with solubility of up to 100% obtained after the acid/dithionite/peroxide treatments. These findings are thought to be due to availability of only one functional group present on the C.I. Reactive Blue 19 dye offering a single dye-fibre bonding option which is more readily to be disrupted by the solvent hence the slightly higher solubility levels observed on the Blue 19 cotton. The slightly lower solubility observed with the denim could be due to the coarser warp yarns and the high degree of twist used for making denim yarns (Shaw, n.d.). The higher warp yarn twist holds the fibres together, thereby reducing the interspace between fibres which in turn reduce the capillary action in the yarn and limit their accessibility to water and chemicals (Hollies et.al, 1957).

It is interesting to note that while the multi-functional Red 228 modified cotton was resistant to decolorisation using the degradative treatments, it was surprisingly highly soluble in CED solvent. This effect was probably due to alkalinity of the CED solvent and the crosslinks of this tri-functional reactive dye being susceptible to alkaline hydrolysis and hence being soluble in the swelling solvent.

INSERT TABLE 2

In this study the CED solubility of the cellulosic materials chemically stripped in presence of DTPA was also assessed and it was found that as previously observed the undyed cotton could be dissolved completely in the solvent, Table 2. However for the Black

5 material the cotton solubility decreased to 44% probably due to the absence of heavy metals which could catalyse the degradation of the cellulose and easier solubilisation. Subsequent acid treatment of the Black 5 dyed cotton increased the solubility to 70.7%, and further degradative dithionite and peroxide treatments destroyed more of the crosslinking bonds and chromophores resulting in solubility values reaching approximately 100% with all dyed samples.

3.3: Analysis of limiting viscosity and DP of the chemically treated cotton pulp

The sequential acid/dithionite/peroxide treatment reduced significantly the limiting viscosity and degree of polymerisation (DP) of the treated cottons, Table 3. This decrease was thought to be due to degradation of the cotton cellulose by scission of the glucosidic linkages of the cellulose polymer (Howitt, 1956) resulting from acid hydrolysis and subsequent alkaline dithionite treatment of the materials. Although the dithionite reducing agent alone is unable to chemically modify the cellulose (Howitt, 1956) the presence of a strong alkali in the dithionite stripping liquor in conjunction with the acid pre-treatment of the materials could have assisted in the alkali hydrolysis of the glucosidic linkages of the cellulose polymer (Clibbens, 1954), resulting in a further decreased limiting viscosity and the subsequent DP. In addition, the hydrogen peroxide is known to oxidise the alcohol groups of the cellulose resulting in the formation of the reducing and acidic oxycelluloses which cause weakening or scission of the glucosidic linkages and subsequent decrease in limiting viscosity and DP (Davidson, 1934; Howitt, 1956). Furthermore, the presence of alkali in the peroxide treatment solution could have also contributed to the decreased viscosity and DP due to alkali hydrolysis. It is interesting to note that the post-consumer denim material had significantly higher limiting viscosity and DP values than the reactively dyed fabrics which could reflect the nature of its original dyeing method and/or the proportion of undyed cotton weft yarns in the fabric.

INSERT TABLE 3

The obtained parameters for ISO brightness, degree of solubility, limiting viscosity and DP of the acid/dithionite/peroxide treated cotton substrates indicated that the resultant cotton pulps could be used as feedstock for regenerating cellulosic fibres through the Lyocell process.

3.4: SEM analysis of the regenerated cellulosic fibres

Analysis of the surface morphologies of the fibres (not presented) showed no significant variations between the surface topography of fibres regenerated from wood pulp to those regenerated from the recycled cotton pulps. The slight roughness observed on fibres regenerated from cotton pulps was presumed to be due to contaminants resulting from fibre processing and uneven washing of the fibre.

3.5: Infrared crystallinity of the regenerated cellulosic fibres

Comparison of Total Crystallinity Indices (TCI) and Lateral Order Indices (LOI) of fibres regenerated from recycled cotton pulps and those regenerated from conventional wood pulp indicated the Lyocell fibres produced in this study had comparable IR crystallinity and LOIs to those regenerated fibres reported previously by Haule, 2016a, Table 4. This was thought to be due to the broadly similar degree of polymerisation of the processed cotton cellulose compared to that of traditional Lyocell wood pulp feedstock, which typically has a DP range of 400 – 1000 units (White, 2001). Similarly fibres derived from recycled cotton pulp had comparable Total Crystallinity Indices (TCI) values to the conventional Lyocell fibres. Furthermore it would be expected that in a commercial operation there would be blending of recycled cotton pulp with wood pulp and this would result in a more uniform product closer to 100% wood pulp derived Lyocell fibres.

INSERT TABLE 4

Conventional Lyocell fibres have previously been reported to have TCI and LOI of 0.76 and 0.35, respectively (Colom, 2002; Carrillo, 2004) which is lower than those obtained in our previous study and in this study. These variations could be due to different spinning conditions used, including the solution state and its composition, air gap length, spinning speed, take off tension, draw ratio, temperature, humidity and the precipitation, drying and post-treatment conditions as previously reported in the literature (Fink et al., 2001).

3.6: Mechanical properties of the regenerated fibres

Analysis of mechanical properties of the regenerated fibres (Lyocell-1 to Lyocell-5) indicated that fibres regenerated from recycled cotton pulps had similar properties to those regenerated fibres reported previously (Haule, 2016b), where there was higher tensile strength and lower elongation at break compared to those regenerated from wood pulp, Table 5. The higher tenacity and lower degree of extension of the fibres is thought to be due to higher DP of the cotton cellulose and the lower cellulose concentration (9%) in the spinning dope, respectively.

INSERT TABLE 5

4.0: Conclusions

This study has demonstrated that a combined acid/dithionite/peroxide treatment could be used as a robust treatment to strip covalently bound reactive dyes from cotton fibres. The treatments removed virtually all colorants from dyed fabrics with even the cotton dyed with the chemically resistant anthraquinone-based, C. I. Reactive Blue 19 dye, being decolourised and producing a white dissolvable cellulose feedstock suitable for producing new cellulosic fibres through the Lyocell fibre regeneration process. This was thought to be due to high reduction potential of the alkaline sodium dithionite which could reduce both azo and anthraquinone dye chromophores. Analysis of the solubility of cellulosic materials in CED solution also indicated that after the complete acid/dithionite/peroxide treatment the cotton could be dissolved completely in the swelling solvent.

The recycled waste cotton garments were successfully deconstructed and used to generate Lyocell fibres from both 100% recycled cotton pulp and a blend of recycled cotton pulp (20%) and wood pulp (80%). The structural and mechanical properties of the new regenerated fibres were comparable to those of conventional Lyocell fibres.

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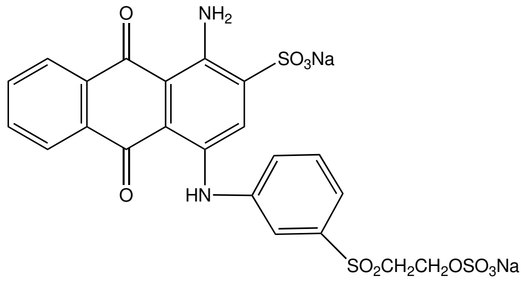
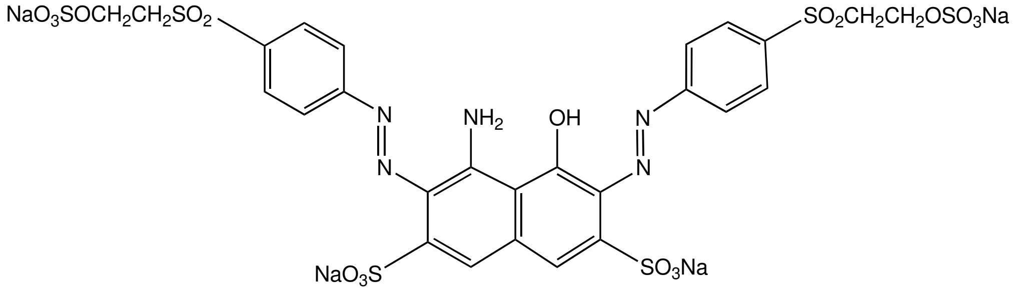
Fibre Type	***Pulp Feedstock Composition***
Lyocell - 0	100% wood pulp
Lyocell - 1	100% Reactive Black 5 cotton pulp
Lyocell - 2	100% Reactive Blue 19 cotton pulp
Lyocell - 3	100% denim pulp
Lyocell - 4	20% Reactive Black 5 cotton pulp & 80% wood pulp
Lyocell - 5	20% recycled denim pulp & 80% wood pulp

Table 1. Lyocell pulp compositions and fibre-type assignments.



C. I. Reactive Blue 19



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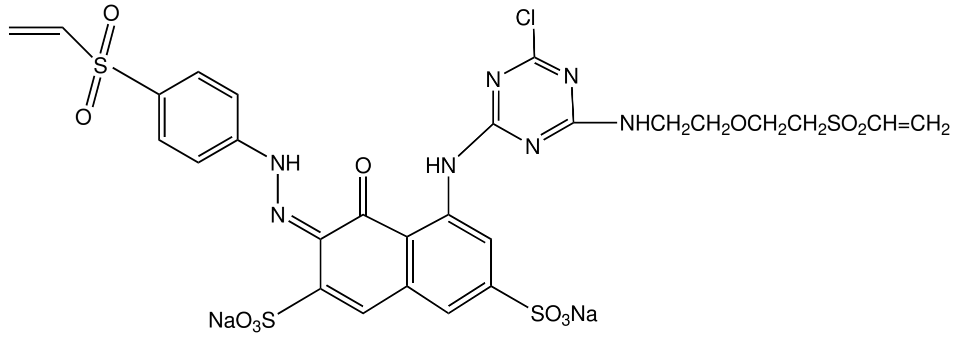
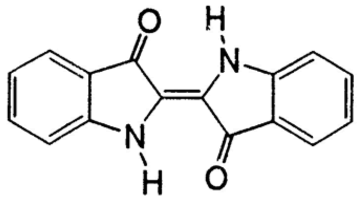


C. I. Reactive Red 228



C. I. Vat Blue 1

Figure 1. Structures of Dyes used in Study

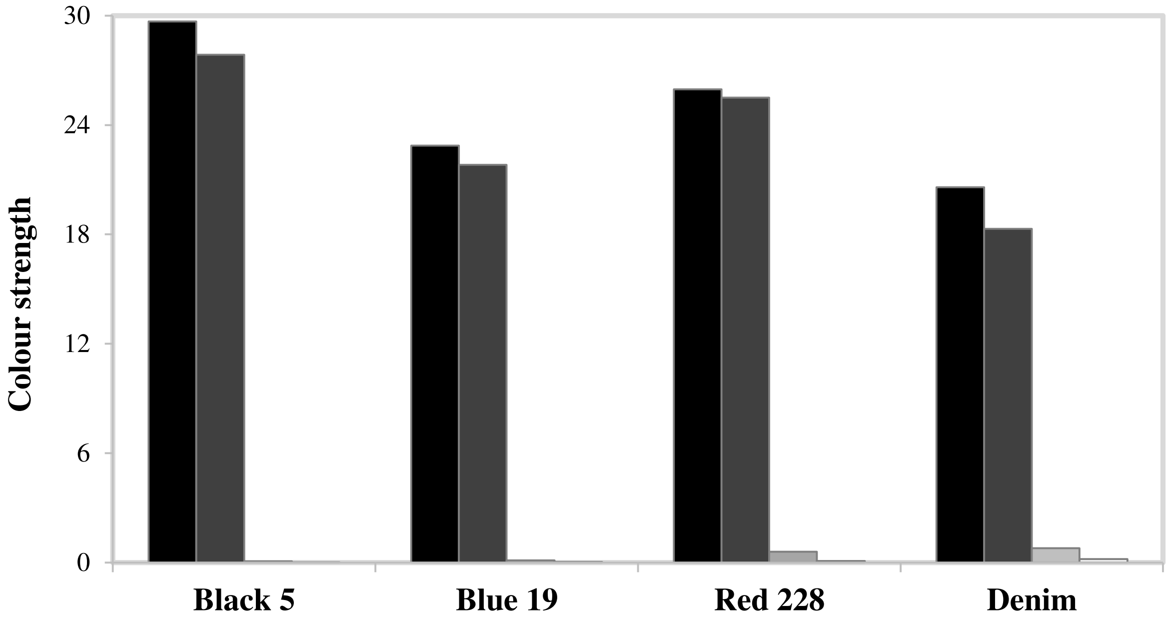


Figure 2. Colour Strength, K/S, of Reactively Dyed (4% o.m.f.) Cotton Fabrics and Indigo Dyed Denim Treated with Sequential Acid/Dithionite/Peroxide Treatments. ■ Original Dyed Fabric; ■ Acid Treated Fabric; □ Acid/Dithionite Treated Fabric; □ Acid/Dithionite/Peroxide Treated Fabric.

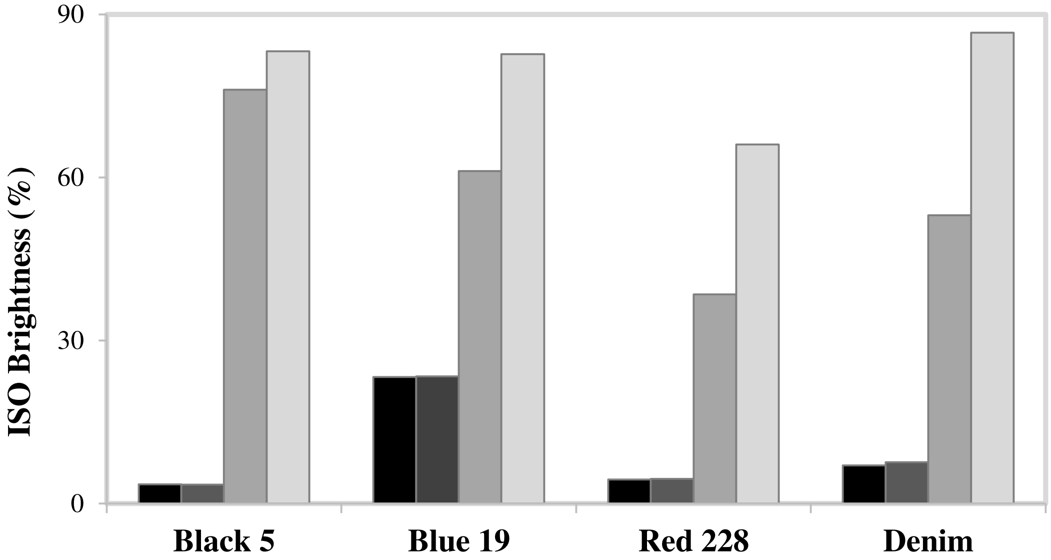


Figure 3. ISO Brightness Values for Reactively Dyed (4% o.m.f.) Cotton Fabric and Indigo Dyed Denim Treated with Sequential Acid/Dithionite/Peroxide Treatments. ■ Original dyed fabric; ▨ Acid Treated Fabric; ☐ Acid/Dithionite Treated Fabric; ☐ Acid/Dithionite/Peroxide Treated Fabric.

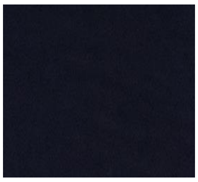
Colorant	Dyed fabric	Acid treated	Acid/Dithionite treated	Acid/Dithionite/ Peroxide	Undyed fabric
Black 5					
Blue 19					
Red 228					
Denim					

Figure 4. Visual Appearance of Reactively Dyed Cotton and Indigo Dyed Denim Fabrics Stripped by Sequential Acid/Dithionite/Peroxide treatment.

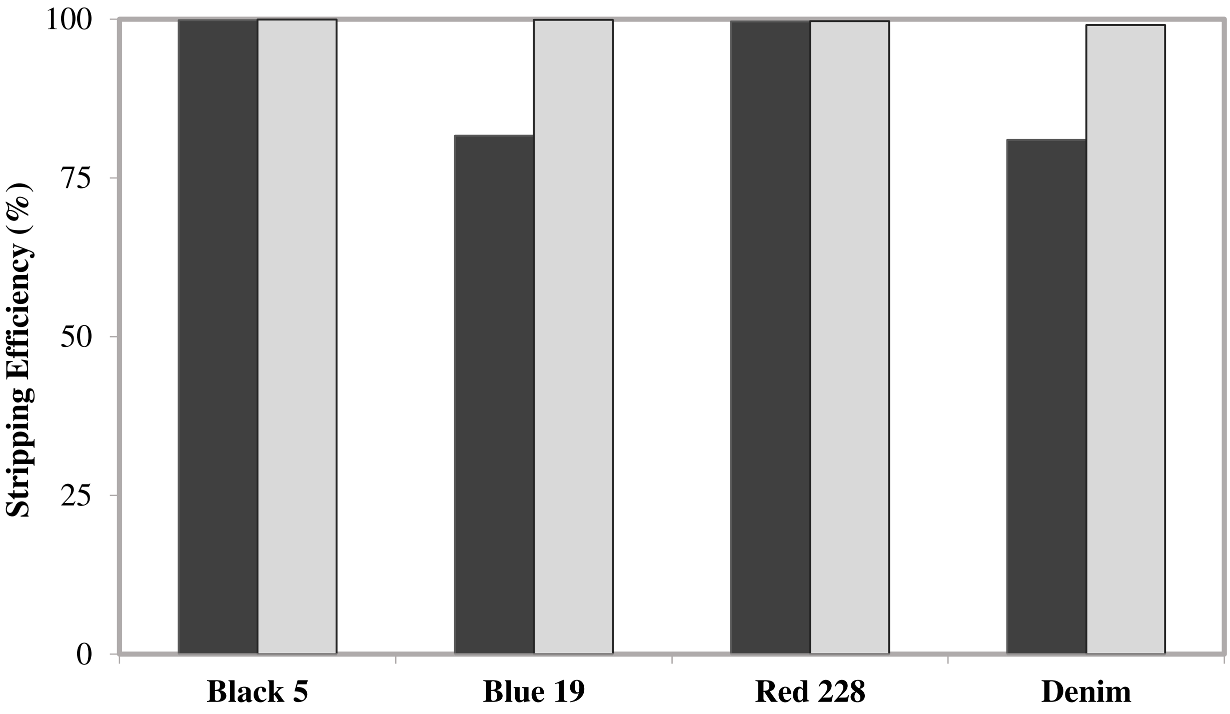


Figure 5. Effect of Sequential Acid/Alkali/Peroxide Treatments and Sequential Acid/Dithionite/Peroxide Treatments on Colour Stripping Efficiency for Reactively Dyed Cotton Fabric and post-consumer denim jeans. ■ Acid/Alkali/Peroxide Treated Fabric; ☐ Acid/Dithionite/Peroxide Treated Fabric.

Reactive Dyed Cotton (4% o.w.f.)	Solubility in CED Solvent			
	Untreated Dyed	Acid Treated	Acid/Dithionite Treated	Acid/Dithionite/ Peroxide Treated
C. I. Black 5	66.2	91.4	98.9	99.9
C. I. Blue 19	93.9	98.5	100.0	100.0
C. I. Red 228	99.6	100.0	100.0	100.0
Denim	88.6	91.1	92.4	99.6
Processed with 2 g/L of DTPA Chelating Agent				
C. I. Black 5	43.8	70.7	97.9	100.0
C. I. Blue 19	94.4	99.3	100.0	100.0
Denim	86.4	88.1	97.7	99.0

Table 2. Solubility of Chemically Treated Dyed Cotton in CED Solvent. Undyed Cotton had 100% Solubility in CED.

Fabric	Limiting Viscosity (mL/g)	Degree of Polymerisation (DP)
Undyed Cotton	1513.0 ± 37.7	5186.5 ± 169.0
Reactive Black 5 Dyed Cotton	474.0 ± 131.5	1120.3 ± 269.0
Reactive Blue 19 Dyed Cotton	480.6 ± 128.0	1152.3 ± 283.0
Post-consumer Denim	590.5 ± 104.4	1512.5 ± 346.0
Wood Pulp	170 - 435	400 – 1000 (White, 2001)

Table 3. Limiting Viscosity and Degree of Polymerisation of Cellulose Derived from the acid/dithionite/peroxide treated Cotton.

Fibre Type	TCI[a] (1368/2892 cm^{-1})		LOI[b] (1420/894 cm^{-1})	
	Mean	SD	Mean	SD
Lyocell*	1.10	0.02	0.42	0.04
ReCell- Denim*	1.33	0.08	0.48	0.09

Table 4. IR Total Crystallinity Index (TCI) and Lateral Order Index (LOI) for the regenerated Lyocell fibres.

*Original data presented in Carbohydrate Polymers, 2016, 144, 131-139 (Haule 2016b).

Fibre Type	Linear Density (dtex)		Tenacity (cN/tex)		Elongation (%)	
	Mean	SD	Mean	SD	Mean	SD
Lyocell*	1.3	9.4	34.7	9.6	11.2	14.1
ReCell-Denim*	1.3	9.1	42.5	8.4	9.7	13.4

Table 5. Mechanical Properties for regenerated Lyocell fibres.

*Original data presented in Journal of Cleaner Production, 2016, 112, 4445-4451 (Haule 2016a).