Tanzania Journal of Engineering and Technology 2025, **44**(1):137-152
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Websites: https://ajol.org/tjet; https://tjet.udsm.ac.tz

ISSN 1821-536X (**print**); ISSN 2619-8789 (**electronic**)
https://doi.org/10.52339/tjet.v44i1.921

Regular Research Manuscript

Cellulose Recovery from Waste Denim Fabrics through Indigo Vat Dye Reduction and Spandex Dissolution

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ABSTRACT

This study addresses environmental conservation by tackling end-of-life management for post-consumer denim garments through the recycling of cotton fibres from waste denim. The purification process involved dithionite reduction of vat dyes in the presence of an alkali followed by selective dissolution of spandex using N,N-dimethylformamide (DMF). Optimal conditions for dye removal were determined at 90°C for 120 minutes with sodium hydroxide at 25 g/L, sodium dithionite at 6 g/L and PVP at 4.5 g/L, while spandex extraction was achieved using a 5% DMF solution at 70°C for 4 hours. Ultraviolet (UV)-vis spectrophotometric analysis indicated a significant increase in whiteness (DL). ATR-FTIR and TGA confirmed the purity and structural integrity of the recovered cellulose, comparable to pure cotton. This research demonstrates effective removal of vat dyes and spandex, supporting potential applications for the recycled cotton.*

ARTICLE INFO
Submitted: **Jul. 4, 2023**
Revised: **Nov. 19, 2024**
Accepted: **Feb. 20, 2025**
Published: **Apr. 2025**

Keywords: The denim, Vat dye, Cellulose, Stripping-off, Waste-garment, Spandex, Recycling.

INTRODUCTION

The re-use of second-hand garments has been a well-known practice for many years. This is because, apart from wearing of clothing being one of fundamental human requirements, the second-hand garments are cheap relative to new ones (Bartl, 2014).

Although majority of people express ethical concerns about how to dispose garments, many people in developing nations favour the idea of re-using second-hand garments. Apart from second hand garments being cheap relative to the new ones, one of the major triggers for the increase in second hand garment is the so called "Fast Fashion" (Nunziata, 2021). The term refers to as the mass manufacture of inexpensive, highly profitable apparel. As a result, there is accumulation of used garments especially in developed countries, which makes the possibility of transporting them to offshores to developing countries as second-hand clothing.

However, according to the OXYFAM report in 2005, the second-hand clothing has shorter life span of less than 5 years (Baden and Barber 2005). Consequently, the second-hand garments have to be disposed in landfills, open dumps or must be incinerated. These disposal options can cause various forms of pollution to the environment such as increased littering and pollution of solids on land as well as pollution of dye products and chemical finishes in the environment and water bodies.

Some of the previous approaches which have been taken to recycle post-consumer garments include recycling for re-use as second hand clothing (Becker-Leifhold and Iran 2018) and "conventional" technical recycling to reclaim the fibres and converted them into other physical products. The most common technical recycling process for post- consumer garments involves shredding up the raw materials or pulling into fibrous form called 'shoddy' (from knits) or 'mungo' (from woven garments). The applications of the reclaimed fibres include industrial filling materials, for mattresses and upholstery, sound insulation panel and carpet underlay (Ball and Hance 1994).

Denim recycling techniques involve the applications of reclaimed fibres for use in geo-textiles (Morley, Bartlett, and McGill 2009), conventional spinning of reclaimed fibres into new yarns by blending the reclaimed with virgin fibres (Hawley 2006) and the use of waste denim deconstructed fibres in composite making (Zhong *et al*., 2020; Meng *et al*., 2020, 2021). However, one of the limitations to such recycling approaches is the complication of handling dyes and non-cellulosic fibre blends during re-processing of the waste denim garments as part of end-of-life waste management. There is still limited information on attempts to recycle denim fabrics through cellulose purification process that involve removal of the vat dyes and non-cellulosic fibre blends that are non-degradable such as spandex.

Indigo is one of the world's oldest known textile dyes used for dyeing of cellulose. It is one of the world's most important textile chemical, with annual global usage of indigo and associated vat dyes estimated to be around 33 million kilogrammes (Roessler and Jin 2003). Indigo is identified as CI Vat Blue 1 and is also known as 2- (1, 3-dihydro-3-oxo-2H-indazol-2-ylidene)-1, 2-dihydro-3H-indol-3-oneis, a vat dye that seems to be practically insoluble in water in its solid blue pigment state and it has no substantivity for cellulosic fibre.

In an attempt to strip-off indigo dye fixed in the textile fibres, indigo dye is reduced by sodium dithionite ($\mathrm{Na_2H_2SO_4}$) into soluble leucoindigo (Figure 1) in alkaline environments (Achwal and Vaidya 1969; Sheth and Bhattacharya 1987; Wambuguh and Chianelli 2008; Blackburn, Bechtold, and John 2009; Turcanu and Bechtold 2011; Abebe and Gebino Gelebo 2019). The process is carried out in absence of air so as to avoid oxidation back to insoluble indigo dye. Sodium dithionite is very easily oxidised by atmospheric oxygen and its stability in aqueous alkaline solution declines very rapidly with increasing temperatures, even in the absence of oxygen. Therefore, it is necessary to use an excess of sodium hydrosulphite (Aydin *et al*., 2006). In some cases, the highly reductive power of sodium hydrosulphite may lead to excessive reduction and destruction of the dye.

Spandex belongs to the generic classification of man-made fibres and it is described in chemical terms as segmented polyurethane (PU). It is composed of soft, or flexible, segments bonded together with hard, or rigid segments. The soft section is commonly made up of an aliphatic polyether or polyester urethane block, whereas the hard segment is made up of polyurea (Nakano *et al*., 1997).

The dominant functional groups in the PU structure are $\mathrm{N-H}$ and $\mathrm{C=O}$ end groups in the $\mathrm{-CON-}$ part of the backbone. In the solid state, there are numerous types of hydrogen bonds between the hard and hard segments, as well as the hard and soft segments, with $\mathrm{N-H}$ and $\mathrm{C=O}$ groups forming the majority of hydrogen bonds. The soft segment domains which are regarded as physical cross-linking locations play a crucial role in the elastic characteristics of PU materials and generate strong hydrogen bonds. It is this molecular structure which endows the fibre with its in-built capacity to stretch and recover (Yin *et al*., 2014).

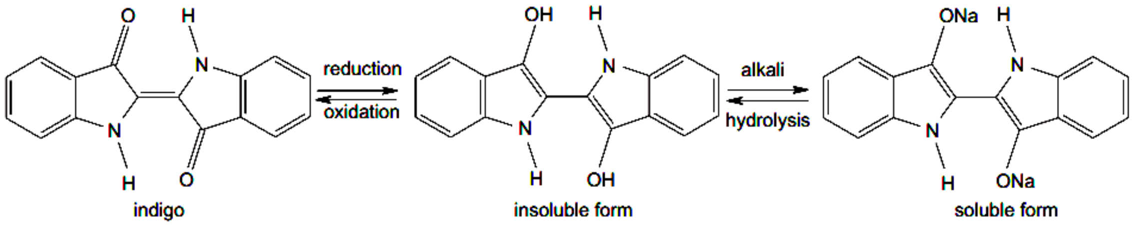

Figure 1: The reversible reduction to leuco-indigo and oxidation to back insoluble indigo structure.

Among the methods of separating spandex from fibre blends is the process of dissolution of spandex fibres in an appropriate solvent without affecting the target fibre. The chemical (DMF) has been used as successfully dissolved spandex from polymers such as Nylon (Yin et al. 2014). Spandex can be separated from cotton by using the solvent N, N-dimethylformamide (DMF) by selective dissolution process whereby; cotton cannot be dissolved in DMF. This study aimed at extracting cotton fibres from post-consumer denims for value addition as an alternative route of providing proper end-of-life management of the post-consumer denim garments. Cotton in denim fabric was purified through the processes of removing vat dyes by dithionite reduction in alkaline environment and removal of spandex fibres by selective dissolution of spandex using dimethylformamide (DMF) solution. The effectiveness of vat dye removal was investigated by assessing the degree of whiteness and colour removal by colorimetric method using visual appearances and UV-vis spectrophotometer. The FTIR analysis was used to study the molecular structure of the vat stripped-off denim fibres in comparison with the pure cotton fibres. Thermogravimetric analysis (TGA) was used study the thermal stability of purified cellulose, as an indirect method for studying the level of impurities removal in denim as cotton purification process.

MATERIALS AND METHODS

Materials

Second-hand denim garments (trousers) were obtained through sorting at local market in Dar es Salaam, the business capital of Tanzania. The sorted denim garments consisted a blend of cellulose fibres 90% and spandex 10%. Chemicals that were used in this study include sodium hydroxide (NaOH), sodium dithionite ($Na_2H_2SO_4$) polyvinypyrorridone (PVP) and acetic acid obtained from Sigma Aldrich. Other chemicals used were N, N-dimethylformamide (DMF) and ethanol obtained from LOBA CHEMIE PVT LTD. All the chemicals were of analytical grade. Persil pro-clean stain fighter (liquid and powder) laundry detergent was obtained from domestic stores in Dar es Salaam.

Equipment

Equipment used in the study include infra-red dyeing machine (Mathis Labomat BFA-12), electric blender (ES-2255 Europe), analytical balance (Wintech, JA203P, (Wintech) and oven drier box (Zuk-OV23A, China). Also, magnetic stirrer with hot plate (MS-7 H-550-Pro, Biobase, China) and pH meter were accessed at University of Dar es Salaam and X-Rite i5 Ultraviolet-visible (UV-vis) spectrophotometer assessed at INSIGNIA company in Dar es Salaam. Analytical equipment used included Thermogravimetric Analyzer (TGA) machine Q500, TA Instruments, USA) and Attenuated Total Reflectance - Fourier Transform Infra-Red microscope (ATR-FTIR) - (Brucker Optics, Germany) from the University of Dar es Salaam.

Methods

Determination of optimum condition for Vat Dye Stripping-Off

Stripping off indigo vat dye involved dithionite reduction of the dye under alkaline environment using sodium dithionite together with the sodium hydroxide. Polyvinylpyrrolidone with trade name Albgen A60 (PVP) was used as stripping agent. The role of PVP was to form complex compounds within the dye by-products and hence hindering the re-solubilisation of the vat dye and preventing the fabrics to be re-dyed. It also insures proper levelling during vat dye stripping process. The range of chemical concentrations for the solution is as follows (Park and Shore 2004).

Sodium hydroxide ($\mathrm{NaOH} = 20\ \mathrm{g/l} - 30\ \mathrm{g/l}$)

Sodium dithionite ($Na_2S_2O_4$) = (5g/l - 6 g/l)

Polyvinylpyrrolidone (PVP) = (4.0 g/l – 5.0 g/l).

The temperature range was from $80\ ^{0}\mathrm{C}$ to $100^{0}\mathrm{C}$ and treatment time in a range from 60 to 150 minutes.

The higher the concentration of reducing agent, the more the rapidly reducing takes place (Shore 1995). Therefore, the upper value of dithionite concentration (6 g/L) was used in the stripping-off process. In addition to that, sodium dithionite is easily oxidised by atmospheric oxygen and its stability in aqueous alkaline solution declines very rapidly with increasing temperatures, even in the absence of oxygen. This could result in products such as sodium thiosulphate and sodium sulphite (Park and Shore 2004).

The stripping-off recipes were prepared first by measuring three portions of 20, 25 and 30 g/L of sodium hydroxide stock solutions. Then to each of the sodium hydroxide concentration 6 grams of sodium dithionite were added. 4.5 g PVP was further added to each solution containing hydroxide and dithionite. The scoured waste denim fabric samples were weighed and mixed with the recipes at the liquor ratio of 1:20. For each portion, the temperatures were varied from $80\ ^{o}\mathrm{C}$ to $100\ ^{o}\mathrm{C}$ in interval of $10\ ^{o}\mathrm{C}$ and treatment the time varied from 60 to 150 minutes in interval of 30 minutes.

The visual assessment was used for quick study of an optimum a range of vat dye stripping-off conditions. The samples which were observed to have relatively larger colour changes (whiter) compared to untreated waste denim sample were further considered for objective analysis using UV-vis- spectrophotometer.

Colorimetric Analysis using UV-vis-spectrophotometer

The effectiveness of vat dye stripping-off was assesses by using UV-vis spectrophotometer within the visible light wavelength. The analysis was carried on the best treated samples based on visual appearances (photos) in comparison with originally untreated denim fabric. Colorimetric analysis of each dithionite vat dye reduced sample was carried out using the UV-visible x-rite i5 spectrophotometer using D65 illuminant. The viewing angle was set to be 10^{o} with aperture size 6 mm specular included. Then the colorimetric data were taken in comparison with the reference standard white fabric.

The CIELAB (CIE L*a*b*) colour data were obtained from the spectrometer and the colour strength at 420 nm wavelength was calculated using Kubelka and Munk equation for colour depth $\frac{K}{S} = \frac{(1-R)^2}{2R}$. where; R is the reflectance of the dyed fabric, K is the sorption coefficient and S is the scattering coefficient. The samples were coded with two numbers separated by a “dash” whereby, the first number is the treatment temperature (^{o}C) and the second number being treatment time (minutes) except for sample OG, which was untreated denim fabric sample.

Purification of Cotton Cellulose from Denim

Cellulose was purified by selective dissolution of spandex (polyurethane) from optimal vat-stripped-off denim samples, which were coded as DENF-90. The mechanism of purification involves selective dissolution of spandex fibres with the use of N, N-dimethylformamide (DMF).

DENF-90 samples were shredded into approximately less than 1 cm pieces, which were further reduced into fibrous forms by the use of ES-2255 Europe blender with distilled water. The fibre samples were then oven-dried for 24 hours at $50\ ^{\mathrm{o}}\mathrm{C}$.

The mixture containing 5% g/mL concentration of the fibre blend in DMF solvent was stirred using BIOBASE Magnetic stirrer model MS7-H550-Pro, for 4 hours at 70 °C in order to dissolve spandex. Then, the solution of spandex and DMF was separated from the mixture by filtration using whatman filter paper No. 1. The residue fibres were oven dried at $50\ ^{\mathrm{o}}\mathrm{C}$ for 24 hours.

Structural Examination of Extracted Cellulose by FTIR-Analysis

The examination of the quality of extracted cellulose from the waste denim was carried out using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) – spectrometer (BRUCKER). In this study the structural change of vat dye stripped-off sample DENF-90 was analysed and compared to untreated denim sample DENF-OG. The structure of purified denim sample DENF-90-PR was analysed in order to compare with that of the previously vat dye stripped-off denim sample DENF-90. Further, the structure of purified denim sample DENF-90-PR was compared to that of pure cotton fibre. Each sample was run in duplicate and the results presented are the average of two runs. The samples were dried at $51 \pm 0.5\ ^{\circ}\mathrm{C}$ for 24 hours before the analysis.

The analysis involved scanning of the samples at the wave number ranging from $4000\ \mathrm{to}\ 400\ \mathrm{cm}^{-1}$. Then data were processed using Origin Pro 8.5 SR3 application software. Similar analysis was used for studying the structure of electrospun fibrous web.

Examination of Thermal Stability of Derived Cellulose

Thermal stability measurements of the purified cellulose were carried out between 30°C and 550°C at a heating rate of 5°C per minute in an oxygen atmosphere with a flow rate of 50 ml/min using a TGA machine (Model: Q500, TA Instruments, USA). For the Thermogravimetric Analysis (TGA), approximately 10 mg samples of each of the DENF-90-PR, DENF-90, and DENF-OG samples were maintained within a weight range of 10.0±0.5 mg. The samples were initially dried for 24 hours before analysis. Data on mass change and mass change per temperature increment were recorded for further analysis.

RESULTS AND DISCUSSION

Visual Assessment of Vat Dye Stripped-off Denim

It was observed that upon treatments, the concentrations of the stripping chemicals caused great variation for effectiveness. Visual colour changes were observed at different effective stripping conditions and sample shade photos indicated in Figure 3. Samples treated using lower value of sodium hydroxide showed ineffective removal of vat dye with very little colour change as the solution becomes less alkaline. On the other end, the higher concentration of sodium hydroxide apparently caused yellowing of the sample which implied that the cellulose has greatly been degraded. Moreover, this possibly resulted in increased alkalinity in the stripping liquor and destabilized sodium dithionite and the stripping-off the vat dyes was not effective. The intermediate value of $25\ \mathrm{g/L\ NaOH}$ indicated effectiveness in stripping off vat dyes.

Low concentration of PVP (4.0 g/L) gave no effective stripping-off. This could be attributed to insufficient amount of PVP to complex with the reduced dyes hence as a result the dye molecules were re-oxidized back easily during rinsing in water. Meanwhile, larger concentration resulted in excess of PVP which agglomerates and segregates on the surface of the fabric as spots and the stripping-off process appeared unlevelled as shown in Figure 2.

The optimum concentrations were obtained to be; $\mathrm{NaOH} = 25\ \mathrm{g/L}$, $\mathrm{Na_2S_2O_4} = 6\ \mathrm{g/L}$ and $\mathrm{PVP} = 4.5\ \mathrm{g/L}$ for all cases. It was from these concentrations; the effect of temperature and treatment time was studied with regards to the prescribed range of values (levels).

The effectiveness of vat dye stripping-off denim fabric was assessed by using UV-vis spectrophotometer. This was carried out on the best treated samples by visual appearances (photos) at different temperature and treatment time based on the photos taken in comparison using spectrophotometers, reference to standard white fabric as shown in Figure 4. For the optimum liquor concentrations, the samples that resulted in best whiteness change as compared to originally untreated denim are the ones treated at the temperatures of $90\ ^{o}\mathrm{C}$ and $100\ ^{o}\mathrm{C}$, and at different treatment time of 60, 90, 120 and 150 minutes.

Photos for each experimental vat-dye-stripped-off sample were taken using the UV-visible x-rite i5 spectrophotometer using D65 illuminant at viewing angle 10^{o} with aperture size 6 mm specular included and presented in Figure 4.

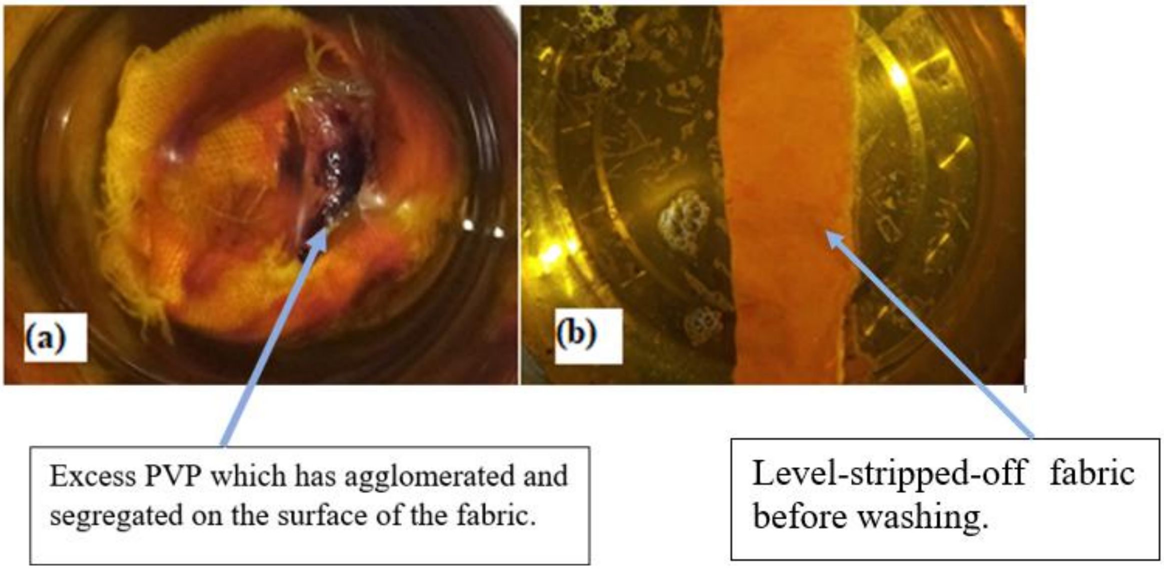

Figure 2: Effect of stripping agent as seen before rinsing in water (a) un-levelled stripping and (b) Levelled stripping, whereby the PVP was just enough to complex the vat dyes.

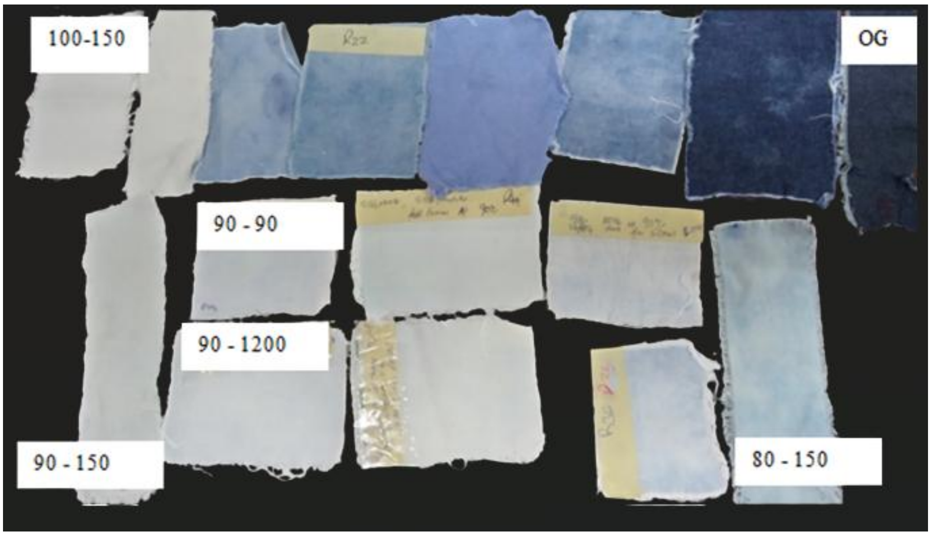

Figure 3: Some selected photos during removal of vat dye from denim. Colorimetric Analysis of Vat Dye Stripped-off Denim.

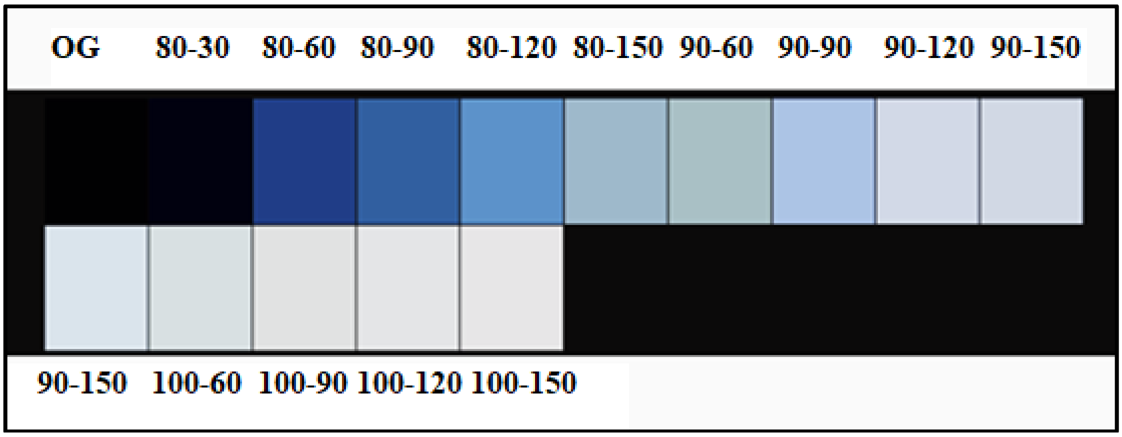

Figure 4: UV-vis spectrophotometer images.

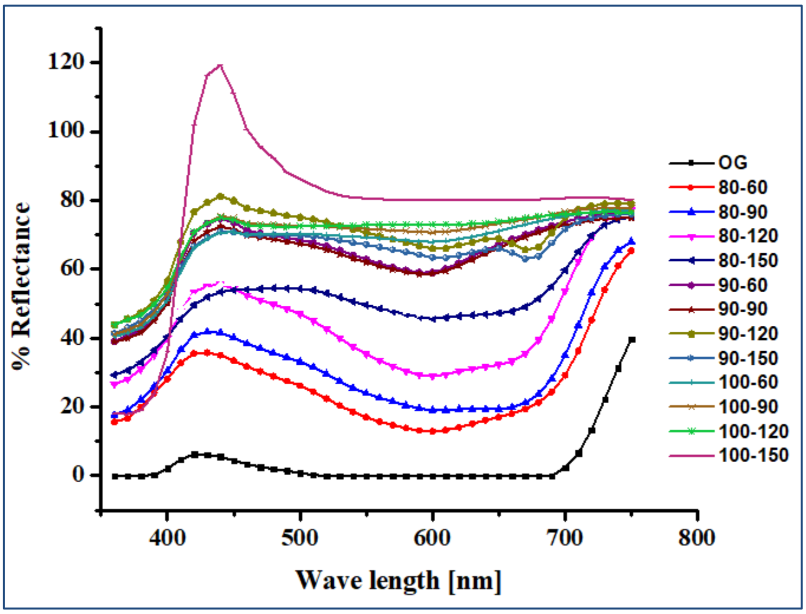

Figure 5: Reflectance values measured using UV -vis spectrophotometer.

Calorimetric reflectance data for each sample, as measured by spectrophotometer were re-coded and the curves plotted in Figure 5. The curves indicate that the peak for untreated sample OG is at approximately wavelength close to 420 nm which reflects the blue colour wavelength in the visible spectrum. The peaks shift to higher wavelength as treatment time and temperature increases which indicates shift from blue spectrum peak toward to the white appearance.

Reflectance values of the samples were compared at 420 nm wavelength as indicated in Figure 6 and the values for the samples were higher as the treatment temperature increases to 90 °C and above at different treatment time. It was observed that reflectance (%) with respect to reference white fabric, and colour strength (K/S) increases with decrease in the amount of vat dyes in the samples as indicated in Figure 6. Samples treated at higher temperatures (above 90 °C and higher treatment time (90 minutes and above) indicated to have relatively higher colour strength (K/S) and reflectance values. This implies that the vat dye was largely removed. The overall highest reflectance and K/S values were for the samples treated at 90 °C for 150 minutes.

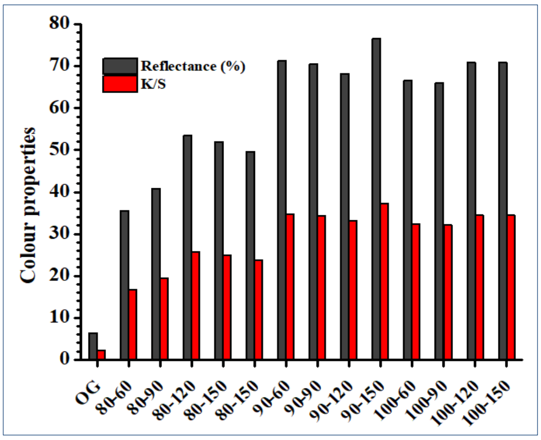

Figure 6: Colour strength (K/S) and Reflectance value for denim samples treated at different conditions.

CIE L*a*b* data values were obtained through measuring the reflectance values and then auto-calculated using the i5X-rite software of the uv-vis spectrophotometer. The DL*and Db* values of the samples with respect to standard white fabric were graphically presented.

As observed in Figure 7 for DL*, the whiteness of the sample increases with increase in temperature. The most effective whiteness started at the temperature of 90 °C for the whole treatment times and largest difference in contrast was observed for samples treated at 100 °C mainly for treatment time greater than 60 minutes. The whiteness values for these samples closely matched to that white reference fabric with their DL* absolute value being very low.

It was further observed that lower temperatures (< 90 °C) resulted into inefficient removal of vat dyes whose spectrophotometric data indicated that the samples treated at lower temperature of 80 °C (samples 80-60, 80-90,80-120 and 80-150) have their whiteness highly deviated from that of reference white fabric which is indicated by large DL* absolute values.

The samples that were treated at 90 °C and treatment time of ≥ 90 minutes closely matched to that of reference white fabric, were chosen for further investigation on purification of cotton in the denim fabric. This was due to reason that the whiteness of the samples was close to that of reference white fabric. In order to avoid premature oxidation of cellulose due to prolonged exposure of cellulose to high temperature, only samples treated at 90 °C for 90 minutes were selected for further purification process. The samples were generally coded DENF-90.

Structural Examination of Extracted Cellulose by FTIR-Analysis

The FTIR spectra for the three samples; original denim (DENF-OG), vat stripped-off denim (DENF-90) and purified cellulose fibres (DENF-90-PR) were analysed. The FTIR results indicated that there was initial sharp transmittance peak from around 1632 to 1660 cm^{-1} for DENF-OG sample which corresponds to the presence of the stretching $C = C$ bond (Yin et al. 2014) and

$\mathrm{C=O}$ groups in the denim fabric (Coates 2004). These groups are attributed to the presence of vat dye and spandex compound in the denim fabric structure. It was observed that vat stripped of samples DENF-90 indicate that there was a significant decrease in the spectra peak intensity for transmittance frequencies due to vibrating the $\mathrm{C=C}$ and $\mathrm{C=O}$ as shown in Figures 8 and 9 as compare to untreated denim sample DENF-OG. This peak diminished significantly in the purified sample DENF-90-PR.

Broad transmittance peak intensity for wave number $3330\text{ to }3345\ \mathrm{cm^{-1}}$, which is attributed to stretching $-\mathrm{OH}$ intermolecular hydrogen bond increased slightly in vat stripped sample DENF-90 as compared to the untreated denim sample DENF-OG. This increase is attributed to less transmission of the infra-red energy due to removal of vat dye from the denim cellulose structure which resulted into increase in exposed $-\mathrm{OH}$ groups of cellulose in the denim fabric. The remained peak corresponding to $1660-1632\mathrm{cm^{-1}}$ is due to presence of $-\mathrm{OH}$ groups of water absorbed in cellulose as indicated in Figures 8 and 9. The peak sharpness decreased and shifted to $1635\ \mathrm{cm^{-1}}$ wave number for OH of water absorbed from cellulose, which is a typical wavenumber for cotton fibres spectrum (Carrillo et al. 2004).

The peak at the wave number $3222\text{ to }3255\ \mathrm{cm^{-1}}$ assigned to $\mathrm{N-H}$ bond in present in untreated denim sample DENF-OG did not disappear completely in vat dye stripped-off sample DENF-90. The remained portion is attributed to the unremoved $\mathrm{N-H}$ groups of spandex fibre in the denim. It was late observed that the previously observed transmission peak at the wave number $3222\text{ to }3255\ \mathrm{cm^{-1}}$ assigned to $\mathrm{N-H}$ bond disappeared in purified denim sample DENF-90-PR as indicated in Figures 8 and 9.

The FTIR spectra indicated that the observed peak in untreated sample DENF-OG at wave number $2875\ \mathrm{cm^{-1}}$ for $-\mathrm{CON}-$ particularly $\mathrm{C-N}$ bonding remained during removal of vat dye in sample DENF-90. The peak diminished and was not observed in purified sample DENF-90-PR after purification of cotton cellulose.

It was observed that FTIR spectrum for sample DENF-90-PR had the peak at position $2900\ \mathrm{cm^{-1}}$ which corresponds for CH stretching bond is clearly observed to match that of cotton as indicated in Figures 8 and 9. The matching of the two peaks implied that the spandex fibre was removed from the denim fibre blends. It was further observed that there was no obvious shift of the peak at wave number $1160\ \mathrm{cm^{-1}}$ corresponding to asymmetric stretching of $\mathrm{C-O-C}$ glycosidic bond as indicated in Figure 10, which is similar to previous studies in a range of $1157-1160\ \mathrm{cm^{-1}}$ (Nelson and O'Connor 1964). This implied that there was no alkali hydrolysis of β-glycosidic linkage in cotton cellulose and that the cellulose structure was not significantly changed (Coates 2004; Garside, Paul and Wyeth 2014). It was also observed that the broad transmission peak between wave number 3330 and $3345\ \mathrm{cm^{-1}}$ corresponding to OH stretching intermolecular bond in purified sample DENF-90-PR was found to match that of pure cotton cellulose as indicated in Figure 9.

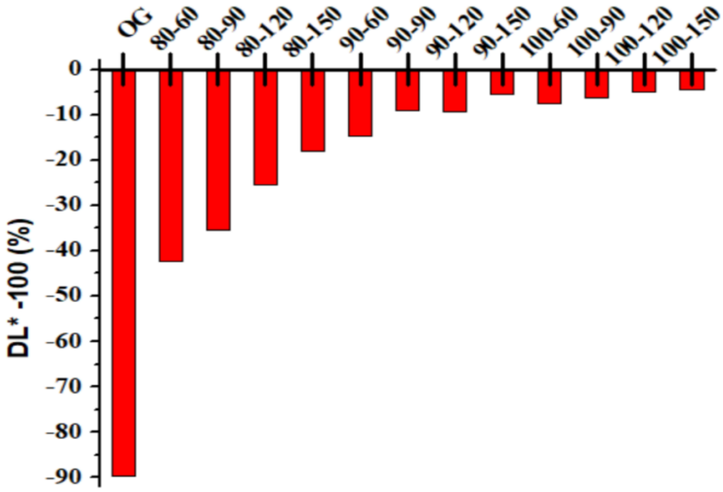

Figure 7: DL* values measured by UV-vis. Spectrophotometer.

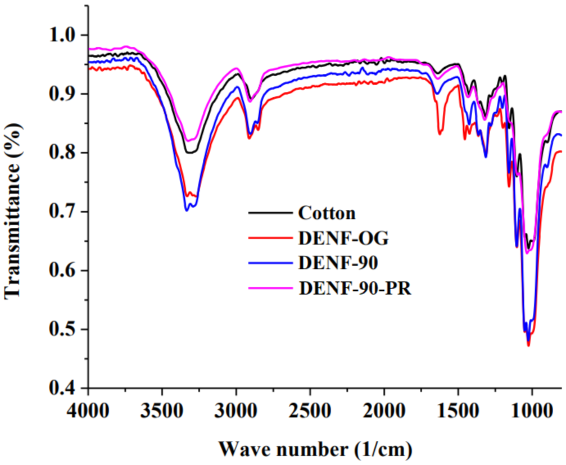

Figure 8: The ATR-FTIR Spectra for denim purification process samples.

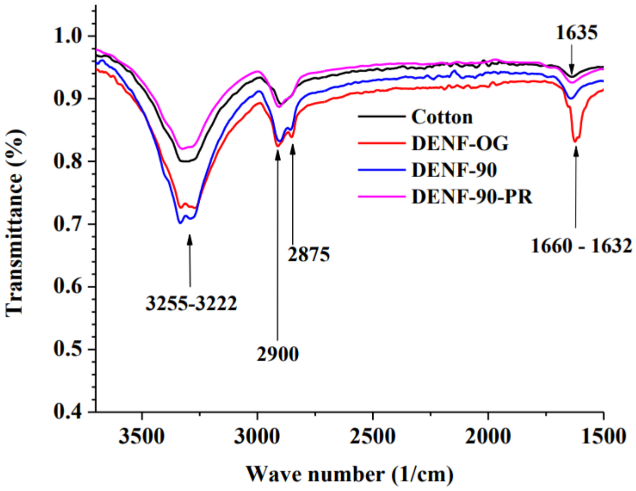

Figure 9: The ATR-FTIR Spectra for denim purification process in a range of $(3700 - 1500\ \mathrm{cm}^{-1})$ wave number.

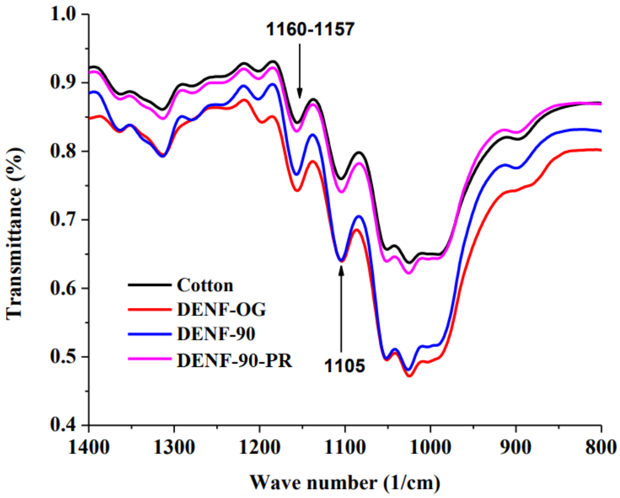

Figure 10: The ATR-FTIR Spectra for denim purification process in a range of $(1400-800\ \mathrm{cm}^{-1})$ wave number showing the peak for glycosidic bond between $1157-1160\ \mathrm{cm}^{-1}$.

Examination of Thermal Stability of Derived Cellulose

The TGA thermograms for the three samples; original denim (DENF-OG), vat stripped-off denim (DENF-90) and purified cellulose fibres (DENF-90-PR) were compared and results related to previous researches on degradation of pure cotton. Both samples indicated nearly the same behaviour at the temperature interval of 50 °C to 150 °C as indicated in Figure 11. This range of temperatures was basically due to rapid depolymerization and primary thermal decomposition release of more volatile substances such as NO_2, CO_2, H_2O and/or CO for denim materials for the case of sample DENF-OG (Abidi, Hequet, and Ethridge 2006; Huntley et al. 2015).

Purified cellulose sample DENF-90-PR indicated higher large decomposition onset temperature at 250 °C compared to DENF-OG and DENF-90 which both have the same on set temperature ≤ 220 °C as indicated in Figure 11. The relatively lower onset temperature for the other two samples before purification were due to presence of dyes and spandex for the case of DENF-OG and spandex polymer for the case of DENF-90. This was attributed to the decrease primary decomposition temperature with lower rate of decomposition.

The TGA thermograms for the fibres from DENF-90-PR shown in Figures 12 and 13 for weight change per temperature indicated that there were three peaks with two major distinct peaks and one minor (gentle) peak. Whereas the other two samples; DENF-OG and DENF-90 exhibited only two peaks, one of them being major and the other being minor.

One of the major peaks in DENF-90-PR was between 250 °C and 350 °C corresponds to relaxation of the broken chains in previous lower temperature range and dehydration, decarboxylation, or decarbonylation of anhydroglucose units followed by evolution of major volatile units of polymer pyrolysis. This is the range of temperature at which the cellulose based polymers are considered to undergo major decompose. This trend is similar to previous finding on the decomposition of cotton fabrics in inert and oxygen environment (Moltó et al. 2006). The second major peak for DENF-90-PR sample was observed at temperature between 380 °C and 430 °C as indicated in Figure 12 and 13. This is basically the temperature range at which the hydrocellulose forms chars with the evolution of other volatile gases such as CO_2, in presence of. This peak mainly distinguishes the purified cellulose sample DENF-90-PR from the other two which do not have such thermal decomposition peak (Moltó et al. 2006).

The degradation temperature of DENF-90-PR was observed to be around 305 °C while stripped denim sample - DENF-90 had intermediate decomposition temperature of around 315 °C, and the cellulose fibres for DENF-OG showed a degradation temperature of approximately 319 °C as indicated in Figures 12 and 13.

The untreated denim fabric sample DENF-OG and the vat stripped-off sample DENF-90 had their major decomposition peak temperature region shifted to higher values and the range was narrowed, as shown in Figure 13. The peak value for major decomposition of DENF-OG sample was observed to be in the range from 270 °C to 330 °C . Nearly the same value was observed for DENF-90 vat stripped-off denim sample. The shift was attributed to the presence of additional materials which act as impurities to the cellulose cotton in the denim. The presence of foreign substances in cotton cellulose masks the second degradation peak for cotton cellulose substances. For this case, vat dyes and spandex in DENF-OG and spandex in sample DENF-90 were regarded as foreign substances (Bourmaud and Baley 2010).

The degradation temperature of purified denim (DENF-90-PR) fibres was 305 °C which was within the range of degradation temperature of pure cotton cellulose in a range 300 to 310 °C, depending on the type and maturity of cotton fibres (Abidi, Hequet, and Ethridge 2006).

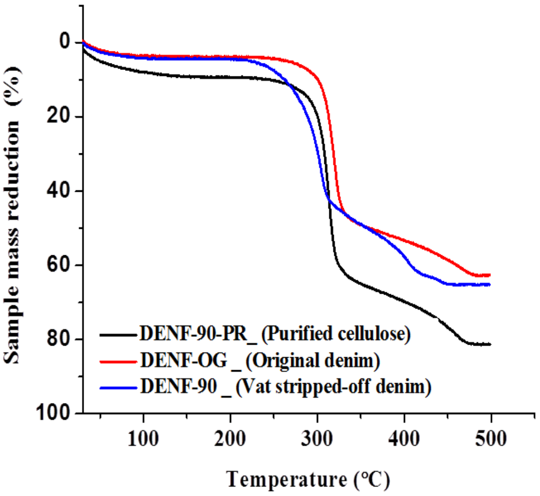

Figure 11: TGA thermograms (% mass change) for purification of denim fabric.

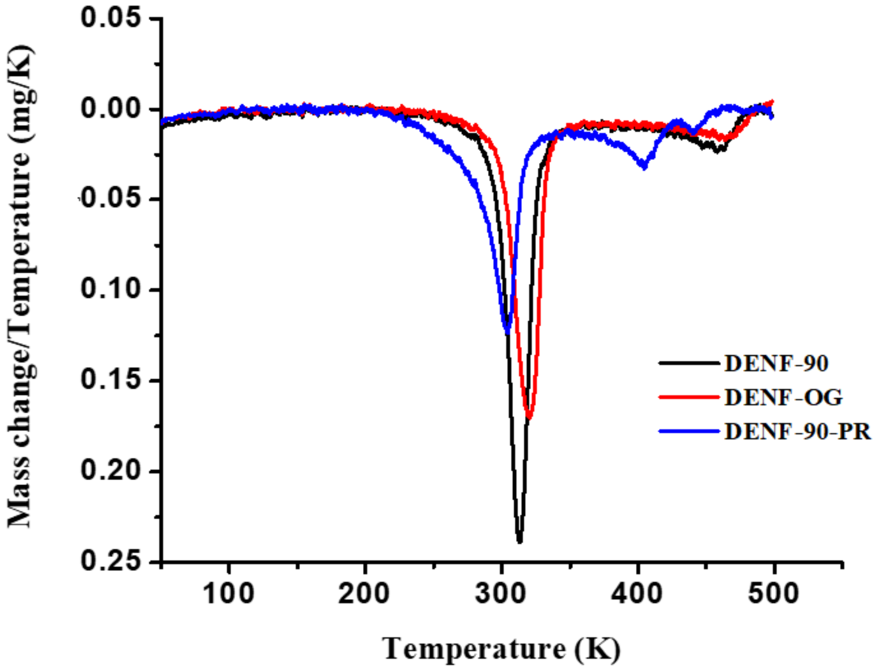

Figure 12: TGA thermograms (Delta m/Temperature) for purification of denim fabric.

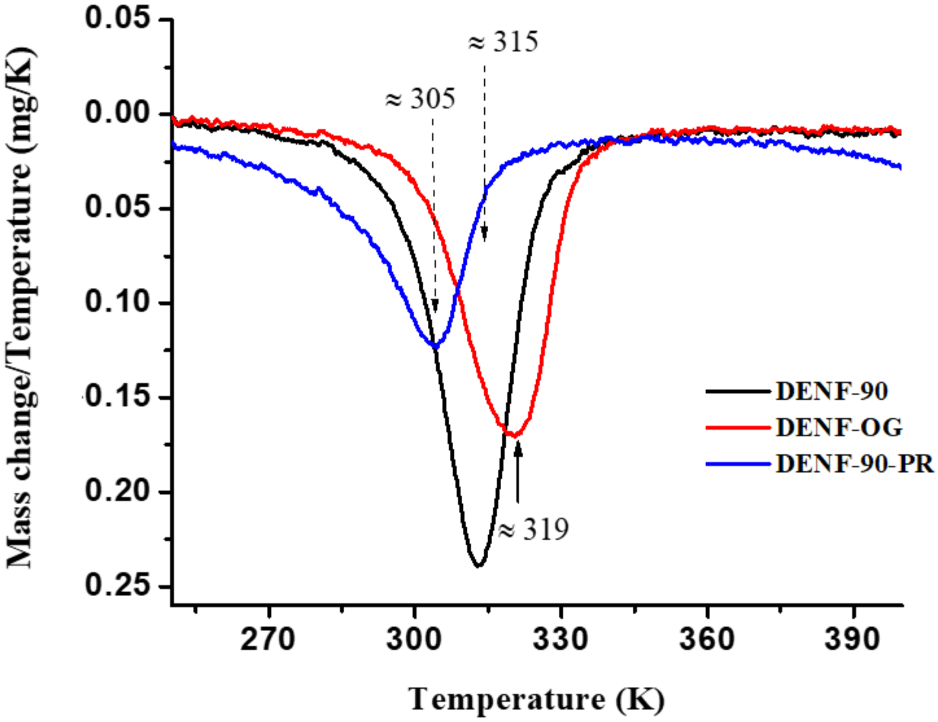

Figure 13: TGA thermograms (Delta m/Temperature) for purification of denim fabric samples showing degradation temperatures.

CONCLUSIONS

This study successfully recovered cellulose from waste denim fabrics by removing vat dyes through alkali dithionite reduction, which converted the dyes into water-soluble leuco products that dissolved easily. Reflectance spectra revealed that at temperatures of 90°C and higher, the colour shifted from blue to white, indicating effective dye removal. Increased reflectance and K/S values at elevated treatment temperatures showed a significant reduction in the blue vat dye, confirming the effectiveness of the process. The optimal conditions for dye stripping were established through visual assessment and UV-vis spectrophotometric analysis, using sodium hydroxide at 25 g/L, sodium dithionite at 6 g/L, and PVP at 4.5 g/L. Treatments were carried out at temperatures exceeding 90°C for more than 90 minutes. Additionally, spandex fibres were efficiently extracted from the vat-stripped denim via selective dissolution in a 5% DMF solution at 70°C for 4 hours. Infrared analysis of the purified cellulose fibres from sample DENF-90-PR showed a close similarity to pure cotton, particularly in regions associated with O-H and C-H bonds, confirming the effective removal of vat dyes and spandex. Thermogravimetric analysis indicated a maximum degradation temperature of approximately 305°C for the purified cellulose, which is lower than the 319°C for untreated denim, highlighting the impact of spandex on thermal stability. This research offers significant potential for enhancing the recycling of post-consumer denim garments, contributing to sustainable waste management and encouraging further studies into cellulose regeneration for textile and allied industrial applications.

Acknowledgments

This work was supported by the University of Dar es Salaam through PhD research fund.

Conflicts of interest

No conflict of interest declared by authors.

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