FTIR ANALYSIS OF COTTON FABRIC DYED WITH NATURAL DYES

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Abstract

The application of synthetic dyes has been questioned due to the associated negative impact of the chemicals used during dye manufacturing of the dyes. Scientists are searching for an alternative source of textile dyes whose sustainability is potentially better that the traditional synthetic dyes. Dyes from plants are have previously been researched and a dominant category of such dyes is the indigo dyes mainly used for dyeing of denim jeans. In Tanzania some entrepreneurs have successfully managed to extract dyes form dry leaves of certain plants and such dyes are used for the "tie –and dye" of cotton fabrics. While the chemical nature of such dyes remains the secret of the inventor, the chemical environment of the dye when applied in cotton fabric is yet established. In this paper the surface of cotton fabric dyed with locally manufactured dye were characterised by the use of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) in order to understand the performance of the locally manufactured natural dyes.

Key words: cotton, natural dye, FTIR,

1 Introduction

Natural dyes have been used for colouring of textiles from ancient times but started to decline after the investigation of synthetic dyes (Saxena and Raja 2014). Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer (Gupta *et al* 2004). Research shows that, natural dyes can be used for dyeing almost all types of natural fibres and some synthetic fibres. Due to the environmental and health problems associated with synthetic dyes, in recent years, there is an increase of dyeing of textile fabrics using natural dyes extracted from plants, insects and shellfish (Sutlović et al 2011).

The identification of unknown dyes in textiles is a challenging task. The major barriers to characterize unknown dyes on dyed textiles are: the relatively small quantity of samples available, the low concentration of chromophores in the textiles, the presence of possible degradation products, and the lack of information on the origin of the dye (Ahn, and Obendorf 2004, Nowik *et al* 2005). Natural dyes are usually not a single chemical entity but a mixture of closely related compounds. Absorption spectroscopy has been successfully used for measuring the dye content of synthetic dyes but has limited applicability for natural dyes because there are no clearly defined absorption maxima (Saxena and Raja 2004). Literature shows that the earliest attempts to characterize the natural dyes were made in the context of identifying the dyes present on historical textiles kept in museums or those found in archaeological excavations (Osman *et al* 2014, Kramell *et al* 2015). This was done by first extracting the dyes from the textiles but was a big challenge due to the small amount of samples available. Various spectrometric and chromatographic methods includes high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), high-performance thin-layer chromatography (HPTLC), UV visible, infrared spectroscopy (IR), FTIR, and mass spectroscopy have been used (Gillard *et al* 1994, Trojanowicz *et al* 2004, Deveoglu *et al* 2012, Samanta and Agarwal 2009).

Researchers now put more effort on analytical techniques based on direct mass spectrometry to avoid wet sample preparation, minimum sample requirement, less contamination as well as reducing sample lost. Such techniques include direct exposure mass spectrometry (DE-MS), laser desorption/ionization mass spectrometry (LDI-MS), matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) (Wyplosz et al 1998, Van Elslande 2008, Lee 2008). (Lee *et al* 2013). Lee et al (2013) used FTIR technique to detect natural dyes in silk fabric to avoid extraction and to use minimum amount of sample. FTIR identifies the unknown fibre constitution and as well as the organic and inorganic dyes present in the fibre (Garside and Wyeth 2003). The unknown compound can be identified by comparing with the library of known material (Smith 1996). The interaction between fibres and dyestuff plays important role on stability of dyed fibres. The molecular structure change induced by natural dye can be identified by FTIR due to the vibration mode modification of the molecules involved. This study aimed on identifying and characterizing the structural changes of a cotton fabric dyed with natural dyes of by using FTIR.

2 Methodology

2.1 *Material*

Scoured and bleached plain woven cotton fabric was supplied by URAFIKI textile mills. Natural dyes of unknown commercial name were supplied *by Said Natural products.*

2.2 *Preparation of Material*

The dyeing process was done by *Said Natural products* within Small Industries Development Organization (SIDO). Prior to dyeing the fabric was rinsed in clean water in order to remove any surface impurities. The dyes used were of two types in terms of colour appearance, which are purple dye and brown dye. Both of these dyes were in solution form and claimed to be natural dyes from the dry leaves of the plants. Unfortunately, for commercial purposes the names of such plants, process of extraction of these dyes and concentration of these dyes are unknown.

2.3 *Dyeing of cotton fabrics*

The dyeing process of the fabric was done using a method called “tie and dye” method and the method is described hereunder.

1. The fabric was folded according to the patterns designed to appear on the fabric surface
2. The fabric was tied at its edges using a thin ropes
3. The dyes were applied according to the given instructions in order to achieve a desired patterns
4. The fabric was left for about ten minutes in order to allow absorption of the dyes into the fabric

5. The fabric was washed using normal cold water in order to clear residue dyes on the fabric surface

6. The fabric was dried in area with low sunlight. It was cautioned that the dye fastness is affected if it is sun cried.

2.4 *Wash fastness test*

In order to test for wash fastness of the cotton fabrics dyed with natural dye, the fabric was washed in a machine by following the ISO6330-2012 test method using washing procedure number 3N. The wash chemical used was non phosphate detergent with enzymes. A polyester ballast fabric was included in the washing in order to get the required machine load during washing.

Both washed and unwashed dyed cotton fabrics were subjected to the wash fastness test using a standard grey scale. The standard *grey scales* used in assessment had grades between 1 and 5 are given in half steps, with 1 being low and 5 highest fastness. The fastness assessment was done with clean grey scales using masks and under standardized lighting conditions in a dark room. During the assessment the specimen were observed in terms of c*hange in shade*; loss in colour and self-staining if any relative to the original unwashed specimen.

2.5 *Rub Fastness Test*

The wet and dry rub fastness tests were done on the dyed cotton fabrics using Tanzanian standards, TZS138:1981 and briefly described hereunder;

Two pieces of specimen each not less than 14cm X 5cm were prepared. One specimen of each pair had the long direction parallel to warp yarns or wales of the fabric, the other parallel to the weft yarns or courses. Since the fabric had two different colour shades, each colour shade was tested. The test procedure is as described hereunder;

1. White test cloth was put on to the grating and stag by steel wire

2. The sample was run twenty times automatically for ten seconds and the rubbing fastness was accessed

3. For the wet rub fastness test, the rubbing cloth was soaked in water and squeezed prior to testing. The wet rubbing cloth was placed on the grating and held by stainless-steel wire and running ten times automatically

4. Finally change of shade of sample was measured with grey scale and degree of staining of white test cloth was measured by recording the staining scale

The grey scale for assessing rubbing fastness consists of four parts labelled by numbers: 3,3/4,4,4/5 and 5. These parts are arranged in order of increasing rub fastness properties, i.e. part number 3 means lowest (poor) rubbing fastness and part number 5 means highest(excellent) rubbing fastness, other parts means intermediate fastness.

2.6 *Tensile Tests*

The tensile test of the dyed cotton fabrics was done in accordance to Tanzanian standard TZS 22:1979. Prior to testing the specimen were conditioned to moisture equilibrium in the standard atmosphere of 65±2% and 27±2ºC. Ten replicates were done and the mean breaking load and extension were recorded.

In this work, fabric washing, fastness tests and tensile tests were conducted in the Tanzania Bureau of Standards (TBS) textile laboratory.

2.7 *ATR-FTIR analysis of the dyed cotton fabrics*

The ATR-FTIR spectra were collected on an Alpha Bruker Optic GmbH 2011 instrument with a diamond crystal available in Chemistry Department, UDSM. Scanning was performed from 4000 to 600 cm^{-1} with 25 scan repetitions and a resolution of 4 cm^{-1}. For consistency and reproducibility all spectra were normalized against the C-O-C asymmetric stretching vibration at 1155 cm^{-1}.

The ATR-FTIR data were processed using Origin Pro 8.1 SR3 application software

3 Results and Discussions

3.1 *Dyeing of the cotton fabric*

The dyed cotton fabric appeared as in figure 1. From the figure it can be observed that with the “tie and dye” method, limited patterns can be produced in the fabric due to limitations on the number of folds that the fabric can respond to. If a better dye technology is developed or made available, the Small and Medium Enterprises (SMEs) dealing with supply of tie and dye products will have improved product fashion varieties.



Figure 1. The dyed cotton fabric

The "tie and dye" technique is not new in the textile craft industry in Tanzania. Other technique used by the Tanzanian textile crafts SMEs is the wax technology. The wax technology works on the principles of transfer printing which can be positive or negative transfer printing. In both techniques, there is no formal dye equipment; the dye man uses any equipment which is available in their locality. Some use plastic buckets, some uses steel bowls and some uses sinks/troughs made from cement concretes to mix up the dye liquor. The current dye equipment cannot used by SMEs cannot optimise the dyeing process, due to lack of control of the dyeing conditions such as temperature, pH etc. therefore under such technologies it is difficult to control and manage the amount of effluent from the dyeing process. Most of the SMEs dye the textile crafts using reactive dyes with highest degree of reactivity so as to allow dyeing at room conditions. The amount of effluents from such high reactivity level can pose serious environmental effects if the technology is not improved.

However, the effects of dye effluents in the environment can be minimized if the reactive dyes are replaced by natural dyes and the dyeing technology/ dyeing process optimised. The challenge with the dyes used in the current study is that the method of extraction of the dyes from plants is not known, the chemical nature and the nature of interaction of the dye with cellulose polymers is also not known. For instance if the chemical nature of the dye is known, one can easily forge the interaction between the dye and the fibres so as to improve the dyeing efficiency. For instance the dye man could not provide reason why the fastness properties of the dye are improved by not exposing the wet dyed fabric after dyeing under sunlight. It is speculated that under wet state the natural dye is affected by light of certain wavelength such as Ultraviolet light. During this study no comparison were made between the fabric dried under sunlight and that dyed in the absence of the sunlight and this could be an avenue for further study.

3.2 *Wet and Rub Fastness of the Cotton Fabrics Dyed with Natural Dyes*

The gray scale results for the wash fastness tests indicated that both brown and purple dyed fabrics scored a scale of 4. This implies that both brown and purple dyes had similar and very good wash fastness properties.

The results on the rub fastness properties of the cotton fabrics dyed with natural dyes indicated that the dyed cotton fabrics had a rub fastness which is below excellent (5) and above poor (3). The fastness results of the dyed cotton fabrics indicated a marginal lower wet rub fastness than the dry rub fastness properties Table 1. The differences in rub fastness properties in dry and wet state may mean that the natural dye is not stable to rubbing under wet environment. A typical wet and dry rub fastness results for a brown dyed cotton fabric is indicated in figure 2. From the figure it can be observed that the level of staining of the wet fabric is higher that the dry fabric.

Table 1. rub fastness results for the cotton fabrics dyed with natural dyes

Weft		**Warp**	
Brown dyed cotton fabric			
DRY	WET	DRY	WET
4/5	3/4	4/5	3/4
Grey dyed cotton fabric			
4/5	3/4	4/5	3/4

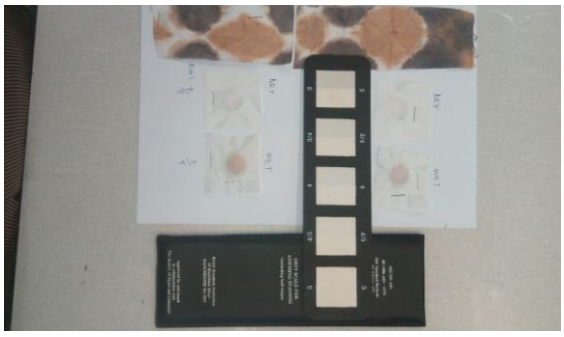


Figure 2: rub fastness results for the cotton fabric dyed with a brown natural dye

Examination of the tensile properties of the fabrics before and after dyeing indicated that the dyes do not cause any strength loss to the fabric. The fabric mean strength increased from 167.1N to 177.6N

after dyeing. The strength increase may be caused by stress relaxation of the fabrics under aqueous treatments (Haule, 2016).

Table 2: tensile strength of cotton fabrics dyed with natural dyes

	Tensile strength [N]	**strain (Extension) at Tensile strength [mm/mm**	**Tensile strength [N]**	**strain (Extension) at Tensile strength [m/mm]**
	Control cotton fabric		dyed cotton fabric	
Mean	167.1	0.32	177.6	0.32
Max	185.2	0.33	192.2	0.33
Min.	150.6	0.30	153.4	0.30
S.D	20.1	0.02	15.2	0.01

3.3 *ATR-FTIR spectral analysis*

The FTIR spectra of the plain untreated cotton fabric, and fabrics dyed with natural dyes is presented on figure 3. From the figure it can be observed that the untreated cotton fabric presents a spectrum which is typical cellulose I structure. The cellulose I spectral features are discussed somewhere else (Haule, et al., 2016) and summarized in table 4 for comparison purpose. The comparison is done in the 2000 cm^{-1} to 800cm^{-1} wave numbers because this is the area where most of the chemical changes take place during modification of cellulose polymer.

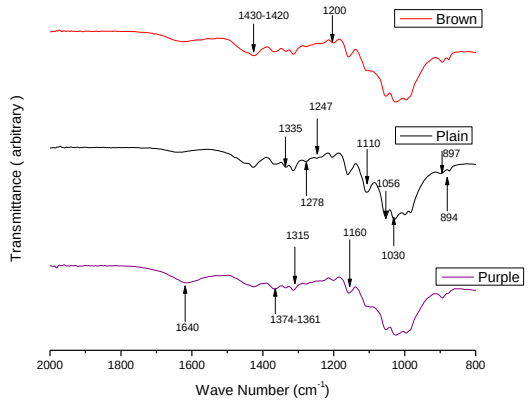


Figure 3: FTIR spectra of cotton fabrics-(a) plain, untreated cotton, (b) Brown, dyed with brown dye and (c) purple, dyed with purple dye.

Frequency (cm^{-1})	**Vibrational Assignments**	**References***
1635	OH of water absorbed from cellulose	(Carrillo, et al., 2004; Široký, et al., 2010)
1455	OH in plane bending	(Carrillo, et al., 2004)
1420	CH_2 scissoring at C(6)	(Carrillo, et al., 2002; Nelson & O'Connor, 1964a, b; Široký, et al., 2010)
1374	CH bending	(Carrillo, et al., 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, et al., 2010)
1335	OH in plane bending	(Carrillo, et al., 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, et al., 2010)
1315	CH_2 wagging	(Carrillo, et al., 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, et al., 2010)
1278	CH bending	(Carrillo, et. al, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a; Široký, et. al., 2010)
1247	OH in plane bending	Nelson & O'Connor, 1964a; Široký, et. al., 2010)
1200	OH in plane bending	(Carrillo, et.al., 2004; Široký, et al., 2010)
1160	C-O-C asymmetric stretching	(Carrillo, et al., 2004; Široký, et al., 2010)
1110	C-O stretching	(Carrillo, et.al., 2004)
1056	C-O stretching	(Carrillo, et.al., 2004)
897	C-O valence vibration – cellulose I	(Široký,et al., 2010)

Frequency (cm^{-1})	Vibrational Assignments	References*
894	C-O-C valence vibration II	(Carrillo,et al., 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, et al., 2010)

**For references, please refer to (Haule et. al, 2016)*

From figure 3, unique feature at 1640cm^{-1} wave number appears for the brown dyed and purple dyed fabrics. These feature is unique, does not appear in the plain, un-dyed cotton fabrics. Peak at 1247 cm^{-1} on the untreated cotton fabric has weaker intensity after the dyeing process and the peaks at 1200 cm^{-1} for the case of the dyed fabrics remains. Peak at 1160cm^{-1} of the untreated cotton fabric disappear after dyeing and is reduced to 1157cm^{-1}. Peak at 1107cm^{-1} as seen on the untreated cotton fabric, disappears after the dyeing of the cotton fabrics. Peak at 1030 cm^{-1} of the untreated cotton fabric is reduced to 1025cm^{-1} after dyeing of the cotton fabrics.

From the spectrum, it can be speculated that the chemical functional bonding of the dyes and cellulose takes place in the 1640 cm^{-1}- 1600cm^{-1}. Further analysis is required to elucidate the functional groups involved in the chemical interaction between the dye and cotton cellulose.

4 Conclusion

The locally manufactured natural dye was applied in a cotton fabric. The rub fastness of the dyed cotton fabrics indicated that the natural dyes is more stable to dry rubbing than wet rubbing conditions. The tensile strength results indicated that the natural dyes do not cause any strength loss to the dyed cotton fabrics. FTIR analysis could not establish dye chemical groups involved in the interaction with cellulose but unique feature appears in the 1600cm^{-1} wave number of the FTIR spectrum of the dyed cotton fabric. More studies are required in order to understand the nature of the dyes and its interaction with cellulose in order to optimise the dyeing conditions and performance of the dyes.

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