Colour Fastness and Tensile Strength of Cotton Fabric Dyed with Natural Extracts of *Alkanna tinctoria* by Continuous Dyeing Technique

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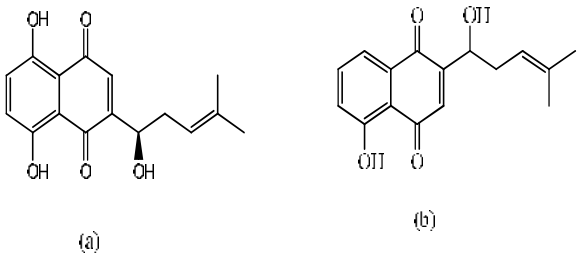
Summary: A natural dye extracted from the roots of alkanet (*Alkanna tinctoria*) was applied on cotton fabric by pad-steam dyeing technique. The study was designed to evaluate the colour fastness and tensile properties of dyed cotton after using various mordants, cationizing agents, UV absorbers and crosslinkers with this natural dye. Metallic mordants included aluminium sulphate, copper sulphate, ferric chloride, potassium dichromate and hydrated potassium aluminum sulphate or alum. Alkanet root extract produced variety of green shades with different dyeing auxiliaries. Better wash, light, crocking fastness; good colour coordinates such as chroma, hue, colour strength and increase in tensile strength was accomplished with post-mordanting of $CuSO_4$. Cationization of cotton with quaternary ammonium compound (both pre-treatment and post-treatment) and post-finishing with soft polyurethane emulsion has enhanced the fastness properties, tensile strength as well as relative colour strength (K/S) , whereas, reactive UV absorber based on oxalanilide and heterocyclic compound as UV absorber greatly increased the light fastness of alkanet dyed cotton. Crosslinkers applied with alkanet dye on cotton (methylolation product based on glyoxalmonourein, modified dimethyloldihydroxyethylene urea, modified dihydroxy ethylene urea) also improved the fastness but could not bring further development in the shade and K/S value of the dyed samples.

Key words: Colour fastness, Tensile strength, Natural dye, *Alkanna tinctoria*, Continuous dyeing, crosslinkers.

Introduction

Alkanna tinctoria is a perennial herb which belongs to borage family. It grows as wild weed and has small- sized bright blue flowers with grey-green leaves. It is also known as dyer's alkanet. Its dye is obtained from the extracts of dried roots that contain several naphthoquinone derivatives but chief of them are alkannin esters. It poses satisfactory antioxidant activity and is mostly used in the colouration of textiles, food, soap and cosmetics. It can also act as an indicator due to its varying shades in different pH values. For example, it is blue at pH 10; purple at pH 8.8; and red at pH 6.8. Its root extract also changes to blue by treatment with alkali hydroxides. The colouring component of alkanet i.e., alkannin is believed to have deep red colour in oily or greasy media and violet in alkaline media. The dye is also used as food and cosmetic colouring [1, 2]. Its molecular formula is $C_{16}H_{16}O_5$ and its chemical structure as naphthoquinone (scheme 1) was first determined in 1936 [3].

Textile dyeing processes consist of batch, continuous or semi-continuous. Batch dyeing process is also called an exhaust dyeing. In this dyeing process, temperature is the most important parameter. It is usually maintained up to 100°C for a good quality fabric. Pad-batch is a kind of semi-continuous dyeing process, which is primarily used for dyeing natural and manmade cellulosic fabrics like cotton or viscose with reactive dyes [4].



Alkannin

Scheme-1: Structure of alkannin.

Traditionally, exhaust dyeing is practiced with natural dyes. However, fastness properties and shades of comparable depth are attributed to the modifications and variety in application methods for natural dyes as compared to those obtained by traditional methods [5]. Large amounts of water is used in various wet processes by the textile industry, as a result of which great volumes of textile waste water is produced, which gets changed by chemicals and unconsumed dyes. Rubbing of crushed pigments

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into a cloth or sticking plants to fabric are some of the primitive techniques of natural dyeing [6]. These methods and other processes have gradually been improved with the passage of time and new techniques have been developed.

The methods of dye extraction of natural colourants and dyeing procedures that have been explained by the traditional dyers do not present/offer a complete picture. Therefore, a need of developing and standardizing new methods of extraction and purification of natural dyes arises. In order to have the final dye powder containing maximum dyeing colours, methods of drying of colours as well as extraction and purification of dyes have now been developed. For obtaining shades with acceptable light, wash and rubbing fastness, cotton fabrics can be padded with low concentration of mordant and natural dyes [5]. Every mordant-dye combination presents a unique feature on account of the optimum amount of mordant needed for the same amount of dye. Commonly used continuous dyeing methods include: pad-steam, pad-pad-steam (wet-on-wet), pad-dry-pad-steam and pad-dry-cure. Among all these, pad-dry-pad-steam is conventionally used for 100% cotton fabrics where dye is applied on the first pad and then the fabric is dried [7].

Pad dyeing usually gives good dye penetration and leveling, low tailing risk and excellent washing off as well as wet fastness. The advantages of pad-dye pad-steam process includes high colour yield, cost-effectiveness for large production runs, neat attractive appearance of the dyed fabric, better reproducibility and no detrimental influence on chlorine and light fastness [8]. Tailing is minimized at low temperature of the formulation in padder, while at high temperature wetting is promoted within a short span of time till the fabric is in the pad formation. For dyeing long runs of a particular shade, continuous dye range provides the most efficient and economical process. Padding technologies are particularly beneficial for dye application with products exhibiting low affinity. In case of this process, the dye's affinity to fibre is unnecessary in the phase of dye deposition [9].

Material and Methods

Extraction of Dye

The roots of Alkanet were acquired from Pride International, Karachi. To isolate colour from the roots, a solvent extraction procedure was performed with soxhlet apparatus, using ethanol as an organic solvent. Rotary evaporator was used to evaporate the solvent. The roots were chopped manually and then the dried and chopped root material of plant was refluxed with ethanol. The extract was evaporated to get a powder form.

Preparation of Fabric

Light-weight; 100 % cotton; plain woven fabric with thread count of 62 ends and 60 picks per inch and weight per unit area or GSM of 70 g/m^2) was desized by industrial scale pad-batch method. Scouring and bleaching was carried out by pad-steam method. Formulation for desizing involved 2 g/L of Bactosol MTN (bacterial amylase, by Clariant Ltd) treated under pH 6-6.5 at 60 °C for 1 hour. Recipe for scouring comprised 15 g/L of NaOH; 1 g/L of wetting agent, 2g/L of sequestering agent (Polyron by Clariant Ltd) and 1 g/L of detergent. All the ingredients were processed at 80-90 °C for 1 hour.

Bleaching was carried out by adding 10 g/L of hydrogen peroxide (H_2O_2) in the formulation. Other substances were: 2 g/L of NaOH (pH 10-10.5), 2 g/L of stabilizer (Pentex GP, by Clariant Ltd) and 1 g/L sequestering agent all managed at 80-90 °C for 1 hour. Eventually, the desized, scoured and bleached fabric was cut into small pieces of 12×18 inches each for the application of various dyeing recipes.

Preparation of Dyeing Recipes

Dye bath for control (untreated) sample was prepared by adding 30 g/L of dye together with 1 g/L of wetting agent, i.e., Albaflow Conti (Table-1) and 1 g/L of migration inhibitor. Dye formulation of pre-treatment and post-treatment included 20 g/L of a specific mordant or 30 g/L of UV absorbers, Dicrylan and Fixative finishes or 50 g/L of crosslinkers.

Fabric Dyeing

A continuous dyeing or pad-steam dyeing procedure (two-bath-two-stage) with a 3-dip-3-nip treatment and a wet pick up of 80% was carried out following drying for 3 minutes at 120^{0}C and then steaming the sample for 10 minutes at 100^{0}C. Dyeing was accomplished by heavy duty padding mangle machine. For the pre-treatment of auxiliaries, the sequence of experiment was:

Pad (treatment) → Dry (air) → Steam → Pad (dye) → Dry (120^{0}C) → Steam

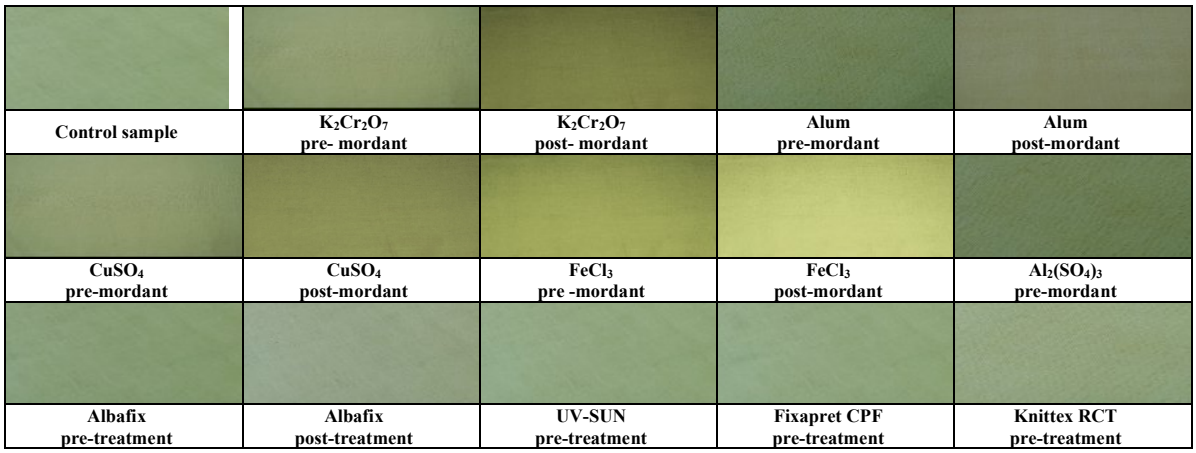

Fig 1: Shades produced by cotton samples dyed with alkanet under different conditions.

Table-1: Dyeing auxiliaries used in this study for the colouration of cotton [10].

Commercial Name	Function	Chemical constitution	Supplier
Thermacol MP	Migration Inhibitor	Aqueous solution of a poly-acrylic acid derivatives	Huntsman Textile Effects
Albaflow Conti	Penetration Accelerant	Preparation based on fatty alcohol ethoxylate and alkyl phosphoric acid	Huntsman Textile Effects
Albafix WFF	Cationizing Agent	Aqueous preparation of a polymeric, quaternary ammonium compound	Huntsman Textile Effects
Dicrylan	Finishing Agent	Multipurpose polymer/polyurethane emulsion	Huntsman Textile Effects
UV- SUN	UV Absorbers	Reactive UV absorber based on an oxalanilide	Huntsman Textile Effects
Rayosan C		Fibre-reactive UV absorbers/ heterocyclic compound	Clariant Pakistan Ltd.
Fixapret CPF		Methylolation product based on glyoxalmonourein	BASF Pakistan (pvt) Ltd
Fixapret F-ECO	Crosslinking Agents	Modified dimethyloldihydroxyethylene urea	BASF Pakistan (pvt) Ltd
Knittex RCT		Modified dihydroxy ethylene urea	Huntsman Textile Effects

In the post-treatment procedure, the sample was dyed first and then padded the dyed sample with a specific dyeing auxiliary.

Fabric Testing

Colour characteristics of dyed fabrics were measured to check the effect of various dyeing auxiliaries on colour fastness properties fabric dyed with Alkanet root extract. Standard methods of ISO such as ISO 105-C06 [11] for wash fastness, ISO 105X-12 [12] for crocking fastness and ISO 105 BO2 [13] for light fastness have been employed. Samples were checked through CIE La*b* and CIE LC*ho system using spectrophotometer SF 600 [14]. Tensile strength of all the samples was tested using electronic tensile tester, Testometric 220 D, according to standard procedure of testing [15].

Results and Discussion

Data related to the colour fastness, colour strength (K/S) and tensile strength of alkanet dyed cotton samples with various pre and post-padding of auxiliaries are included in Tables 2 & 3 and displayed through Figs 1- 3.

Shades Obtained with Alkanet Root Extracts

Dyeing of cotton fabric with natural extracts of alkanet by twenty-five different dyeing recipes produced greenish (inclined towards grey) colour samples. On the basis of intensity and shades, samples were grouped as medium greenish-grey, greenish-brown and yellowish-brown. The most greenish, smooth and level dyed sample was yielded by the recipe of post-mordanting potassium dichromate (Fig-1). This was followed by a coloured sample obtained from the post-mordanting of copper sulphate. Medium greyish-green samples were resulted from the pre-treatments of aluminium sulphate, Fixapret CPF, Knittex, and both pre and post-treatment of Rayosan C. These samples were exactly similar in shade to the control sample. These findings support the earlier work of [16] who reported a range of colours produced by various mordants with natural dyes.

Colour Fastness of Alkanet Dyed Cotton

Table-2 contains data related to the wash, crocking and light fastness of cotton dyed with various dyeing formulas of alkanet. Recipes having $FeCl_3$ as pre-mordant, $Al_2(SO_4)_3$ as post-mordant, $K_2Cr_2O_7$ as post-mordant and Dicrylan as post-finish yielded good (4 GS) wash fastness. Most of the auxiliaries produced samples with dry rubbing equal to 4-5 on Grey-scale, thereby, representing very good fastness performance of dyed articles. Maximum light fastness of 5 Blue Wool Standard was exhibited by alkanet dyed sample with a combination of pre-mordanting potassium dichromate; post-mordanting ferric chloride; and post-treated Albafix WFF, Dicrylan, UV-SUN and Rayosan.

Table-2: Colour fastness properties of alkanet dyed cotton fabric samples using various auxiliaries.

Type of Auxiliary	Method	Wash fastness (Grey-scale)		Crocking fastness (Grey-scale)		Light Fastness (Blue Wool standard)
		change in shade	staining on fabric	dry rubbing	wet rubbing	
$Al_2(SO_4)_3$	Pre-mordanting	3-4	4-5	4	3	4
	Post-mordanting	4	4	4-5	3	4
$CuSO_4$	Pre-mordanting	3-4	4	3-4	2-3	4
	Post-mordanting	2-3*	4-5	4-5	2-3	4
$FeCl_3$	Pre-mordanting	4	4-5	2	3	4
	Post-mordanting	3-4	3	4-5	4-5	5
$K_2Cr_2O_7$	Pre-mordanting	3	4-5	3	3	5
	Post-mordanting	4	4	4-5	3	4
$KAl(SO_4)_2{\cdot}12H_2O$	Pre-mordanting	3	4	3-4	2-3	4
	Post-mordanting	2*	3-4	4	3-4	4
Albafix WFF	Pre cationizing	3	3	4	4-5	4
	Post cationizing	3	4-5	4	3	5
Dicrylan	Pre finishing	3	4	4	3	4
	Post finishing	4	2-3	3-4	4	5
UV-SUN	Pre-treatment	3	4	3-4	2-3	4
	Post-treatment	3	4	3-4	2-3	5
Rayosan C	Pre-treatment	3-4	4	4-5	3-4	4
	Post-treatment	2-3	4	4-5	3	5
Fixapret CPF	Pre-treatment	3	4	4-5	3	4
	Post-treatment	3	4-5	4	3	5
Fixapret F-ECO	Pre-treatment	3	4	4-5	3	4
	Post-treatment	3	4	4-5	3	5
Knittex RCT	Pre-treatment	3	3-4	4-5	3-4	4
	Post-treatment	3	4-5	4-5	3	4
Control sample	Untreated	2-3	4	4-5	3-4	3

- shade became darker than original during testing.

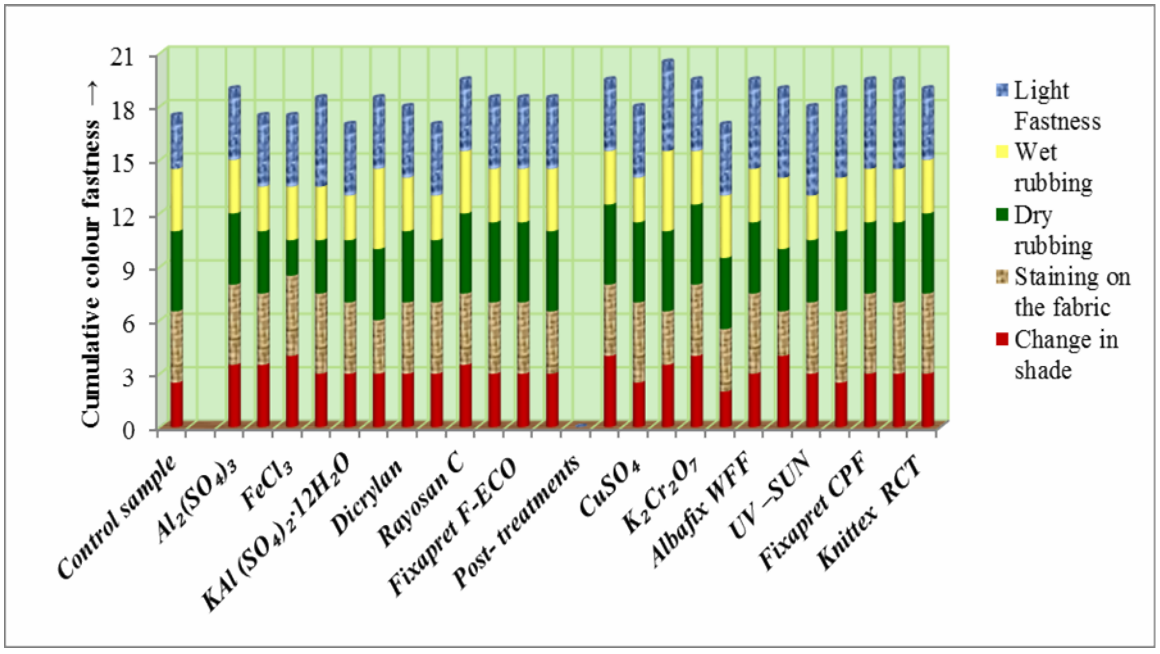

Fig. 2: Cumulative colour fastness of cotton dyed with various dye formulations of alkanet.

Analysis of Cumulative Colour Fastness: T-Test

Cumulative colour fastness (wash, crock and light fastness) of cotton samples dyed with alkanet root extracts with the help of various dyeing auxiliaries has been displayed in Fig-2. A paired-sample t-test showed significant difference in the scores (rating) of pre and post-treatments of the dyeing auxiliaries. These results suggest that post-treatment procedure was a better option. Significant difference was found between the fastness of control and pre-treated samples as well as between the control and post-treated fabric samples by applying t-test. Mordants have played their useful role in improving the light fastness properties of the cotton samples with natural dye. In an earlier work [17] it

was reported that dyed fabrics without metal mordant had poor resistance to the UV rays. Furthermore, for improving colourfastness properties from poor to good, Iron as pre and post mordant with 4 % solution has also been suggested in one study [18].

Colour Properties of Alkanet Dyed Cotton Fabric

The data related to the colour yield or lightness (L*) of cotton samples dyed with alkanet (Table-3), ranged from 46.59 to 59.74. Greater colour yield was found in the sample which was pre-mordanted with ferric chloride. The values of chroma (C*) ranged from 2.06 to 8.47. Maximum K/S value (7.94) among this group was registered by post-mordanting of $CuSO_4$. Zarkogianni et al. [1] studied the colour and fastness of natural dyes on cotton and wool and found the process of mordanting as playing significant role in increasing K/S for cotton samples. In case of un-mordanted cotton samples they have reported a value of 1.5 from Alkana (*Alkanna tinctoria*).

Employing similar natural dye and mordant, the comparatively higher values of K/S in the present study (1.92) clearly indicate that dyeing procedure was the only factor responsible for this greater colour yield. As pad-steam dyeing procedure was adopted in the current study, which boosted the dye uptake and resulted in greater colour yield (K/S). It is very important not only to select proper mordants but the adoption of suitable dyeing procedure is also a crucial step in optimizing the fastness properties of natural dyes.

The present findings also support the earlier postulates [9] which mentioned that both natural dyeing and mordant dyeing can coexist if padding technologies are utilized for natural dyes which will particularly be advantageous for those products of dyeing which have low affinity. The current results confirm the earlier opinion of Mughal et al. [19] who stated that cationization before dyeing can prove more beneficial method for improving the affinity of dye by the fibre.

Tensile Strength of Cotton Dyed with Alkanet

Most of the dyeing formulas in respect of natural extracts of Alkanna tinctoria extracts lowered the tensile strength of dyed cotton samples. However, an increase in strength was also noticed from some of the dye formulas. The most prominent among them were 16 and 12 percent increase from the post-mordanting of potassium dichromate and post-treatment of UV- SUN, respectively (Fig- 3). Maximum decrease in strength of 28 percent was demonstrated by pre-mordanting of potassium dichromate. Loss in strength of 25 percent occurred due to the treatment of pre-mordanting ferric chloride.

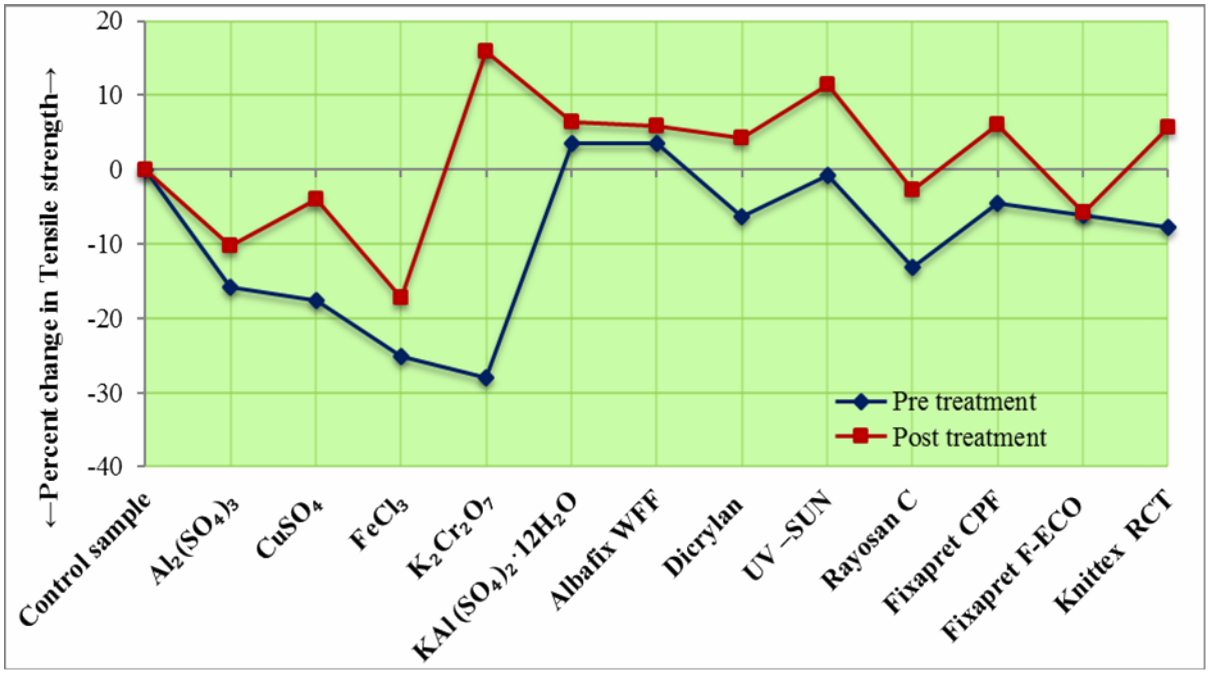

Fig. 3: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with root extracts of alkanet.

Table-3: Colour coordinate values (properties) of alkanet dyed cotton samples using various auxiliaries.

Type of auxiliary	Method	Colour properties					
		L*	a*	b*	C*	h°	K/S
$Al_2(SO_4)_3$	Pre-mordanting	54.06	0.04	5.13	5.13	89.56	2.83
	Post-mordanting	50.61	0.23	7.20	7.21	88.16	1.28
$CuSO_4$	Pre-mordanting	46.59	2.48	12.02	12.27	78.33	3.92
	Post-mordanting	51.12	-1.14	8.39	8.47	97.75	7.94
$FeCl_3$	Pre-mordanting	49.31	-0.43	3.00	3.03	98.14	7.80
	Post-mordanting	59.74	1.85	5.25	5.56	70.58	5.18
$K_2Cr_2O_7$	Pre-mordanting	59.69	-2.89	12.78	13.10	102.73	4.49
	Post-mordanting	58.19	2.43	12.71	12.94	79.17	2.30
$KAl(SO_4)_2 \cdot 12H_2O$	Pre-mordanting	57.94	-1.81	4.26	4.63	113.02	3.26
	Post-mordanting	59.39	1.95	5.62	5.95	70.84	1.80
Albafix WFF	Pre cationizing	45.90	1.40	5.10	5.30	75.00	4.46
	Post cationizing	59.30	-0.20	2.40	2.40	94.00	1.28
Dicrylan	Pre finishing	56.50	-0.10	3.70	3.70	92.10	3.49
	Post finishing	57.90	-0.90	1.20	1.80	118.90	3.36
UV –SUN	Pre-treatment	56.20	-0.50	2.10	2.20	103.90	20.6
	Post-treatment	54.10	-0.30	2.80	2.80	95.80	2.42
Rayosan C	Pre-treatment	58.80	-0.40	1.30	1.40	105.80	1.27
	Post-treatment	59.90	0.70	1.80	2.00	70.00	1.38
Fixapret CPF	Pre-treatment	58.22	0.02	3.24	3.24	89.60	1.82
	Post-treatment	58.30	-0.86	1.85	2.04	114.99	1.61
Fixapret F-ECO	Pre-treatment	58.78	-0.32	2.67	26.9	96.90	1.74
	Post-treatment	58.93	-0.72	1.93	2.06	110.56	1.24
Knittex RCT	Pre-treatment	57.94	0.40	4.30	4.32	84.63	2.04
	Post-treatment	59.75	-0.54	1.25	1.64	109.05	1.44
Control sample	Untreated	58.77	0.41	4.32	4.34	84.55	1.92

Paired samples t- test between pre-treated and post-treated samples revealed significant result at 5% level of significance. Mean strength value due to post-treatments was higher than the pre-treatments. From the significance testing (t-test) of the tensile strength of alkanet dyed cotton fabric, the results showed significant difference between the strength of control and pre-treated samples. While the difference between the control and post-treated fabric samples were insignificant.

Conclusion

If cotton is to be dyed in any shade of green, a solvent extracted dye from alkanet root should be applied through pad-steam dyeing procedure. A mordant copper sulphate has been successful in acquiring better fastness to wash, light, rub (dry only); colour coordinates such as chroma, hue and colour strength; soft, smooth and leveled dyed fabric as well as maintained/improved tensile strength, with this dye through post-mordanting procedures. The use of potassium dichromate is not recommended for the dyeing of cotton with alkanet as it has not only affected the shade of the dyed sample but its pre-mordanting has severely damaged the fabric in terms of its tensile strength. Cationization of cotton with quaternary ammonium compound has been capable of yielding good colour strength and offering potential for environmental friendly dyeing operation. Reactive UV absorber based on oxalanilide (UV-SUN) and heterocyclic compound as UV absorber (Rayosan C) should be used as post-padding with alkanet dye on cotton. Similarly, Soft polyurethane emulsion (Dicrylan) proved useful as post-treatment for improving light and wash fastness as well as maintaining the tensile strength of cotton dyed with alkanet root extracts. Crosslinkers are not required to be applied with alkanet dye on cotton if greater K/S value of the dyed is article required.

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