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One bath cationization and dyeing of cotton fabric with Brazilwood natural dye

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ABSTRACT: Cotton fabrics were cationized with a cationic agent (Chromatech9414) then dyed with Brazilwood natural dye using ferric chloride as a mordant in one bath at three stages by exhaustion method. This process successes to impart cationic sites on cotton fabrics surface which improve its substantivity to natural dye beside save energy and water. The effect of (Chromatech9414) concentration on the nitrogen content was studied. Factors affected the dyeing stage such as dye conc., pH value, temperature and time of dyeing were investigated.The effect of cationic agent concentration and ferric chloride conc. on the colour strength of dyed cotton fabric with Brazilwood natural dye were observed. The best results were obtained at 8% Brazilwood natural dye, pH6 , 60 min., 60^{o}C for dyeing stage at 6%(Chromatech9414) and 8g/l ferric chloride. The effect of mordant, dyeing pH and cationic agent concn. on the colour hue were also investigated .The wettability and the fastness properties of dyed samples were assessed.The changes in the fiber surface, by cationization ,were evaluated using scanning electron microscopy(SEM).

KEYWORDS: Cotton fabric, *Brazilwood*, cationization, dyeing, one bath, colour strength, colour hue, colour fastness properties.

1 INTRODUCTION

Natural dyes are known for their beautiful, soft and multi-hued shades. There is a considerable current interest in the dyeing of textile fibers with natural dyes on account of their compatibility with the environment and because of their generally lower toxicity and allergic reaction. [1]

Nevertheless, dyeing with natural dyes has some problems such as low reproducibility, low dye exhaustion and poor fastness. In order to improve the dye uptake and color-fastness, most of the dyeing processes were conducted by adding metal-based mordants. There are several reports in the literature pertaining to the application of natural colorants and evaluation of their dyeing properties on various fibers using mordanting [2-9]

There are only few reports available on the chemical modifications of cotton textiles for the improvement of their dyeability with natural dyes [10]

The pre-cationization of cotton fabrics with different cationic agents was studied in many researches to enhance its substantivity to natural dyes. [11-14] The combination effects of dyeing with a vegetable mordant dyes and pretreatment with a cationic agent for deep dyeing on the cotton material were investigated. [15]

Brazilwood (often known simply as “brazil”) is a tropical hardwood of the family Leguminosae whose core yields a brilliant red pigment ideal for dyeing cloth.Brazilwood is a creamy color when first cut, but once it has been reduced to sawdust and soaked in water for several weeks, the dyestuff leeches into the solution and can be used to produce the fashionable red clothing particularly favored in the French court.

Although the name is of uncertain origin, “brazil” is thought by some to be derived from brasa, the Portuguese word for a red-hot coal. More likely the term was adopted from the common name for an East Indian dyewood called “bresel wood” which was first imported to Europe in the Middle Ages. [16]The chemical structure of brazilwood presented in **Figure (1):**

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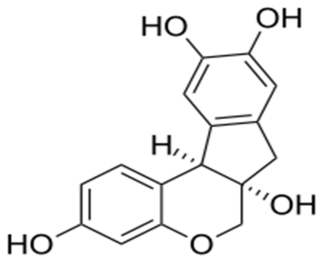


Fig. 1. C.I.Natural Red 24 (brazilin natural dye)

The driving force behind the chemical finishing of cotton during the next 10 years is anticipated to comprise several factors. Of these factors, mention is made of the following: (i) chemical finishes which maximize the added value; (ii) chemical finishes which are friendly with the environment; (iii) methods which are convenient for application, and (iv) the need for better quality and minimum use of water and energy.[17]

This work is aimed to improve the dyeability and the fastness properties of cotton fabrics dyed with brazilwood by using cationic agent (chromatech 9414) and ferric chloride as a mordant at the same bath in three stages. Using convenient dyeing method with saving water and energy by the integration of the three steps(cationization- dyeing-mordanting) in one bath.

2 EXPERIMENTAL

2.1 MATERIALS

2.1.1 FABRIC

A scoured and bleached 100% knitted cotton fabrics (260 gm/m^2) were received from Delta Textile Egypt Company, Cairo, Egypt and used throughout this study.

2.1.2 NATURAL DYE

Brazilwood natural dye used in this study is a commercial product in powder form imported from Toblamas Co.,USA.

2.1.3 CHEMICALS AND AUXILIARIES

Cationic agent: (Chromatech 9414) is a modified polymeric cationic compound produced by Chromatech Co., England.

Dispersing agent: (Ebcasperse RJL) is a solution of fatty acid ester and nonionic dispersing agent produced by Egyptian British Co., Egypt.

Mordant: Ferric chloride (Fe Cl_3) from Morgan Chemical Ind.Co., Egypt.

Non ionic detergent: (Chromatech 3QJ) supplied by Chromatech Co. England .

2.2 METHODS

2.2.1 DYEING PROCESS

Exhaust dyeing method was used in this study by using laboratory-beaker dyeing machine- Rapide- China. Cotton fabrics were dyed with Brazilwood natural dye after cationizing with (chromatech 9414) and then were mordanted with ferric chloride in one bath through three sequence stages as follows:

First stage (cationization): cotton fabrics were introduced into the bath which contained (chromatech 9414) 0-10% o.w.f at L R 1:50, the pH was adjusted at 6.The treatment was started at 40^{O}C where the temperature was gradually raised to 60^{o}C within 10 minutes. The cationization stage was continued for 30 min.

Second stage (dyeing): the Brazilwood natural dye (2-10% o.w.f) and the 2g/l dispersing agent were added to the bath at pH (6-9), temperature (60-90^{o}C) and the dyeing process was continued for (30-90min.)

Third stage (mordanting):ferric chloride was added to the bath at different conc. (2-10 g/l) at pH6 after which, the dyeing was continued for another 30min. at 60°C.

After dyeing the samples were removed and soaped at 50 °C , for 15 min with 1g/l non-ionic detergent. Further, the samples were rinsed with hot and cold water and air dried.

The three stages (cationization- dyeing – mordanting) were carried out according to process presented in **Figure (2)**.

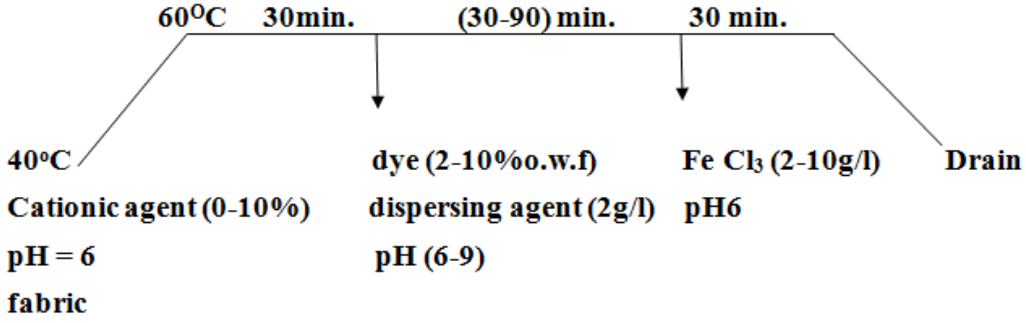


Fig. 2.

2.3 MEASUREMENTS AND TESTING

2.3.1 COLOUR MEASUREMENTS

The colour strength of dyed cotton samples were measured by using reflectance spectrophtometer model Datacolor Spectrophotometer SF600+Datacolor Company, U.S.A.

The colour strength expressed as K/S values was assessed by applying the Kubelka Munk equation: [18]

$$K/S = (1- R)^2/2R$$

Where K and S are the absorption and scattering coefficient respectively, and R is the reflectance of the dyed fabric.

2.3.2 DETERMINATION OF NITROGEN CONTENT PERCENTAGE

Nitrogen content of the cationized fabrics was determined according to kjeldahl method[19].

2.3.3 DETERMINATION OF WETTABILITY OF COTTON FABRICS

This test was intended for use in determining the effect of cationic agent conc. on the rate of absorption of cotton fabric. This test was carried out by putting drop of water on the fabric surface and calculating the passed time until the fabric absorbed the water drop.

2.3.4 SCANNING ELECTRON MICROSCOPE ANALYSIS

Fibers samples previously coated with gold in vacuum coating unit were viewed under scanning electron microscope (JE 100 s), at different magnification .Control fabric was also examined for comparison.

2.3.5 COLOUR FASTNESS

Fastness properties of dyed samples were tested according to ISO standard methods. The specific tests were: ISO-X12(1987), colour fastness to washing; and ISO 105-E04, colour fastness to perspiration. The dyed samples were subjected to tests, for fastness to light by AATCC test method 16-1993.

3 RESULTS AND DISCUSSION

3.1 EFFECT OF CATIONIC AGENT CONCENTRATION ON NITROGEN CONTENTS

To obtain the effect of cationic agent concentration on the nitrogen contents of cotton fabric , tests were carried out for samples cationizedwith different concentrations of cationic agent ranging from (zero to10% o.w.f) .The results obtained were cited in **Table(1)**. It was found from the results that the nitrogen content was gradually increased as the concentration of cationic agent increased resulting in the formation of cationic sites on the surface of cotton fabrics which fit directly proportional with the cationic agent concentration .The increase in the nitrogen content of the fiber was accompanied with an appreciable increase in colour strength of dyed fabric.

Table 1. Effect of cationic agent concentrations on the nitrogen content

Cationic agent conc. %(o.w.f)	Nitrogen content
zero	Zero
2%	0.05
4%	0.07
6%	0.25
8%	0.26
10%	0.21

3.2 EFFECT OF CATIONIC AGENT CONCENTERATION ON COLOUR STRENGTH

To evaluate the effect of (Chromatech 9414) concentration on the colour strength(K/S) of dyed cotton fabric with Brazilwood natural dye, three stages of cationization , dyeing and mordanting were applied in one bath using various concentrations of cationic agent ranging from 0to10% o.w.f at constant conditions of dyeing and mordanting processes ,the results were cited in **Figure (3)**. It was found from the results that the colour strength increased as the concentration of cationic agent increased till reach 8% after which the K/S was slightly decreased . The decrease in K/S as a result of increasing the concn. of cationic agent over 8% may be attributed to the electrical repulsion between the excess concn. of cationic agent in the bath and the positively charged fabric surface. The presence of excess cationic agent in the bath enhances the attraction between some natural dye and the cationic agent leading to minimizing the rate and degree of dye exhaustion.

Cationization of cotton made the fabric receptive to the natural dye which usually has low or no affinity for cellulosic materials. The color strength was found to increase from (4.53) for the uncationized fabric to (8.09) for cationized cotton when dyeing with brazilwood natural dye. This great change in the dyeability is attributed to the introduction of amine groups in the structure of cotton which play an essential role in determining the rate and magnitude of dye exhaustion. Therefore, the sorption of the ionized natural dyes by the cationized cotton fabric will be dependent on the number of bound amine nitrogen available for ionic attraction between positively charged nitrogen atoms and the negatively charged dye anions. [20,21]

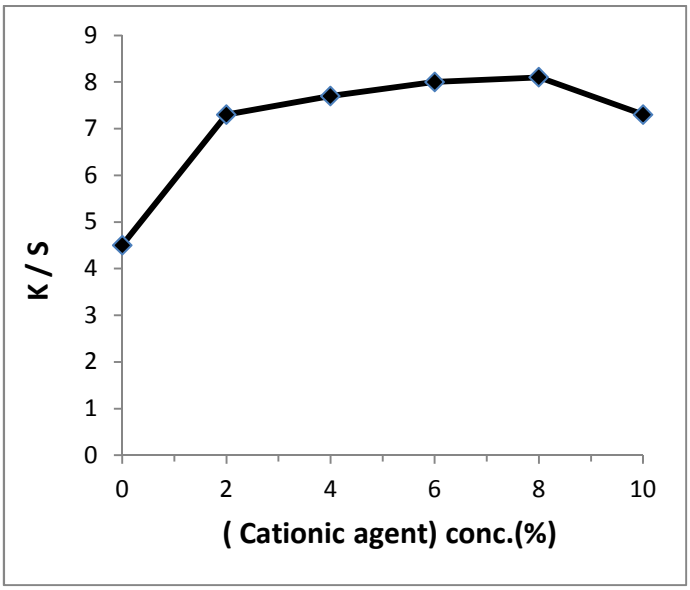


Fig. 3. Effect of cationic agent conc. on the color strength of cotton fabric dyed with Brazilwood natural dye.

Dye bath contents:4% dye concn.– x% cationic agent –5g/l mordant – temp.60^{o} C- time 30/60/30min. (which represent the time of each one of the three stages) – pH 6 – L.R 1:70.

The rate and degree of ionic attraction between dye and fibre will depend to great extent on the following factors:

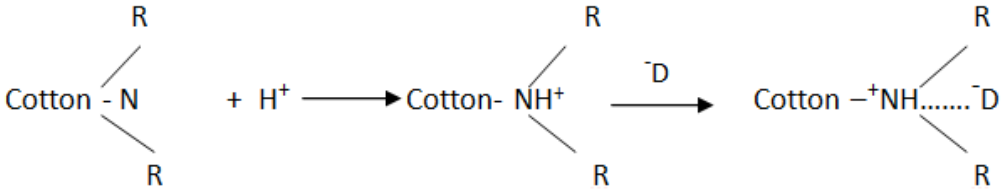
1- The hydrophilicity and magnitude of negative charges on dye molecules (No. of ionized –OH groups)

2- The molecular weight of dye molecule.

3- The number of cationic sites on the fibre available for ionic attraction with the natural dye.

4- The degree of protonation of nitrogen atoms on cationized cotton fabric.

The great enhancement in the dyeability of cationized cotton towards the natural dye under the dyeing condition is essentially attributed to ionic attraction along with the physical forces of attraction.



3.3 FACTORS AFFECT THE DYEING STAGE

3.3.1 EFFECT OF DYE CONCENTRATION

Cotton fabrics were dyed with different concentration of Brazilwood dye, i.e 2-10% (owf) to determine the effect of dye concentration on the color strength(K/S)of dyed cationized cotton fabric. The dyeing were carried out under fixed condition of cationic agent conc., pH, temperature, time, ferric chloride conc. , liquor ratio and the results are cited in **Figure(4)**.

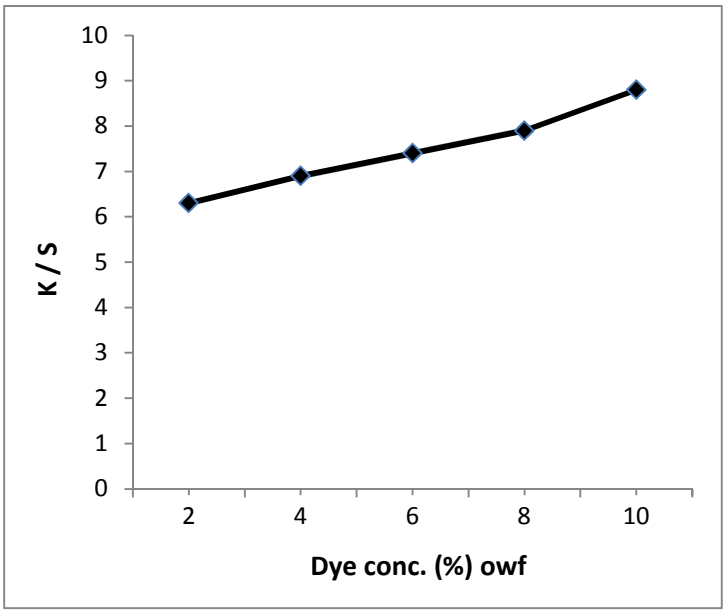


Fig. 4. Effect of Brazilwood natural dye conc. on the color strength (K/S) of dyed cotton fabrics

Dye bath contents: x % dye conc. -6% cationic agent 5g/l mordant – temp.60^{o} C- time 30/60/30min. – pH 6 – L.R 1:50.

It can be observed from **Figure(4)** that the color strength (K/S) increases as the concentration of dye increases which may be attributed to greater attraction between the positive charge on cationized cotton fabric and the anionic Brazilwood dye which depends on the hydroxyl groups found in its structure .Increasing of dye conc. In the dye bath means the existence of greater number of dye molecules available of adsorption on fibre surface to occupy the positively charged dye - sites with formation of ionic bonding .This increased number of dye on cotton fabric results in realizing higher color yield (K/S). It is clear that presence of cationic groups on cationized cotton fabrics lead to more attractive sites of sorption for anionic dye by electrostatic attraction.[20, 21]

The degree of saturation of these positive sites on fibre surface will depend on the dye conc. in the dye bath and the exhaustion percentage.

3.3.2 EFFECT OF PH VALUES

The dyeing properties of any substrate depend on its physical and chemical properties. The physico- chemical properties of the dyeing process such as, dyeing equilibrium ,degree of exhaustion and rate of dyeing are pH- dependent

The cationized cotton fabrics have a number of functional groups such as hydroxyl and amine groups which are very sensitive, during their dyeing, to variation of pH of the dye bath.

In order to investigate the influence of pH on the adsorption capacity of cationized cotton fabric using 8% Brazilwood dye, experiments were conducted under different pH values from 6 to 9 to evaluate the effect of pH on the dyeing stage during continuous operation of cationizing, dyeing and mordanting. The results are presented in **Figure (5)**.

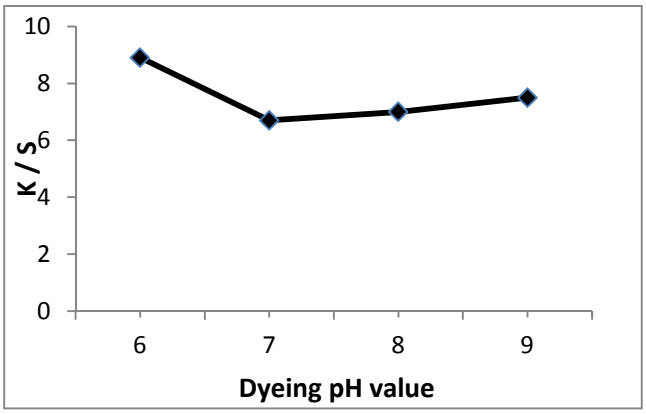


Fig. 5. Effect of pH of dyeing on the color strength (K/S) of cotton fabrics dyed with Brazilwood dye

Dye bath contents: 8% dye conc. – 6% cationic agent – 6 g/l mordant– temp.60^{o} C- time 30/60/30min. – pH x – L.R 1:50

It was found that the highest adsorption capacity of cationized cotton fabrics was achieved at pH 6 .Basically, the mechanism of dyeing with Brazilwood natural dye is associated with ionic interactions between dye anions and positively charged basic groups present in the cationized cotton fiber .The highest dyeability of cationized cotton in acidic medium arises from an increase in the protonation sits on the fabric surface, to be capable of attraction with ionized Brazilwood dye.Therefore under slight acidic condition there was high electrostatic interaction resulting in achieving maximum color strength [22].

It was found that the adsorption capacity decreased clearly by increasing the pH of dyeing. This observation indicates that at pH > 6, there is reduction in electrostatic interaction between dye molecules and cationized cotton fabrics due to the presence of few protonated binding sites on cotton surface.

3.3.3 EFFECT OF DYEING TEMPERATURE:

Temperature plays an important role in dyeing because at high temperatures dyes may undergo chemical degradation and at low temperatures, incomplete dyeing may occur. Moreover the dyeing equilibrium may also be altered under the action of variation of temperature. The effect of temperature on the dyeability of the cotton fabrics dyed with Brazilwood natural dye was conducted at different temperatures 60-90°C and the results of K/S measurements are illustrated in (**Figure 6)**.

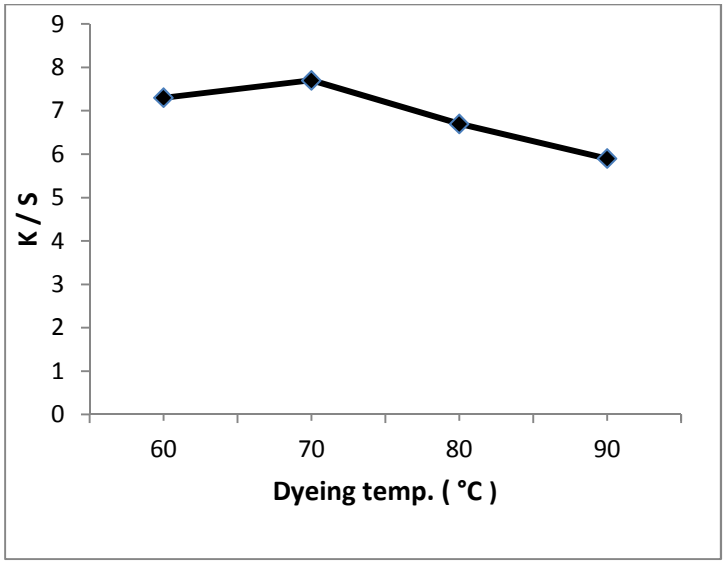


Fig. 6. Effect of dyeing temperature on the colour strength (K/S) of cotton fabrics dyed with Brazilwood dye

Dye bath contents: 8% dye conc. – 6% cationic agent – 6 g/l mordant-temp. x ° C-time 30/60/30min. – pH 6 – L.R 1:50 .

It was noticed, from Fig. 6, that the dye uptake and subsequently the K/S increases with raising the temp. and reaching its maximum value at 70°C beyond which a such decrease in K/S is carried out.

At 70°C the affinity of dye molecules to the cellulosic fabric was maximum and even dyeing was observed .However, the decline in shade depth after 70^0C of dyeing temperature could be due to the loss of affinity for substrate with the increase in temperature as a result of desorption of some cationizing agent to the dyebath specially with the presence of dispersing agent.Raising the dyeing temp.may function also as a disaggregating factor for natural dyes, enhancing their solubilities in the aqueous solution and accelerate their rates of diffusion and adsorption on the fibre surface .The chosen temperature for dyeing stage was 60^0C .

3.3.4 EFFECT OF DYEING TIME

Time of dyeing process is very important parameter because long- and short-time dyeing gives the same effect as the variation of temperature.During constant heat for a long-time, decomposition of the dye material might occur while short-time causes incomplete dyeing. [23] The influence of dyeing time on the color strength values of dyed cotton fabric with Brazilwood displayed in **Figure (7)** . The higher color strength was observed at 75min. that because a longer time provides better opportunity for better contact among the reactants and, therefore, a higher extent of reaction, but 60 min. was chosen to save time.The decline in the dyeability after 75 min. may be attributed to the desorption of the dye molecules as a consequence of long dyeing time .

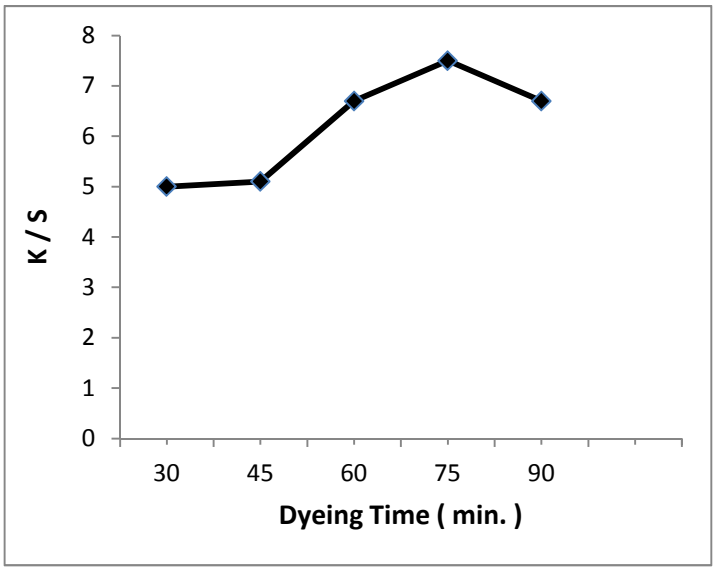


Fig. 7. Effect of dyeing time on the color strength (K/S) of cotton fabric dyed with Brazilwood dye.

Dye bath contents: 8% dye conc. – 6% cationic agent – 6g/l mordant – temp. 60 °C- time 30/ x / 30min. – pH 6 – L.R 1:50.

3.3.5 EFFECT OF MORDANT CONCENTRATION

Mordants play an important role in natural dyeing because they usually have substantivity for both the fiber and the colorants. They form coordination bonds with fiber and at the same time, form insoluble chelate with the dye.

Chemically, mordants are defined as polyvalent metallic compounds that can form coordinate and covalent complexes with certain dyes and fibers. Thus, the metal atom typically forms both a covalent bond with oxygen of hydroxyl or carboxyl groups on the dye (or fiber) and a coordinate bond with an adjacent lone pair of electrons on a double-bonded oxygen. Mordants can chelate several dye molecules together to create a larger complex and provide a link between the dye and fiber. [24]

For studying the influence of mordant conc.on the obtained colour strength which will be altered as a result of metal complexation reaction inside the fibre, different mordant concns. were added to the dyebath (after dyeing for 60 min.).The mordanting was carried out for 30 min. at constant conditions of pH and temperature.

From the results in Fig. 8, it is observed that mordanting or fixing agents, resulting in greater depth of shade and colorfastness specially at 4% of ferric chloride, after this concentration the value of K/S almost constant. In the case of simultaneous dyeing and mordanting method, some of the dye is lost because of the formation of an insoluble complex in the dyebath itself. On the other hand, during post-mordanting some of dye is stripped out in the bath and subsequently forms an insoluble complex with metal ions in the solution. These phenomena lead to a decrease in the effective dye concentration in the dyebath [25].

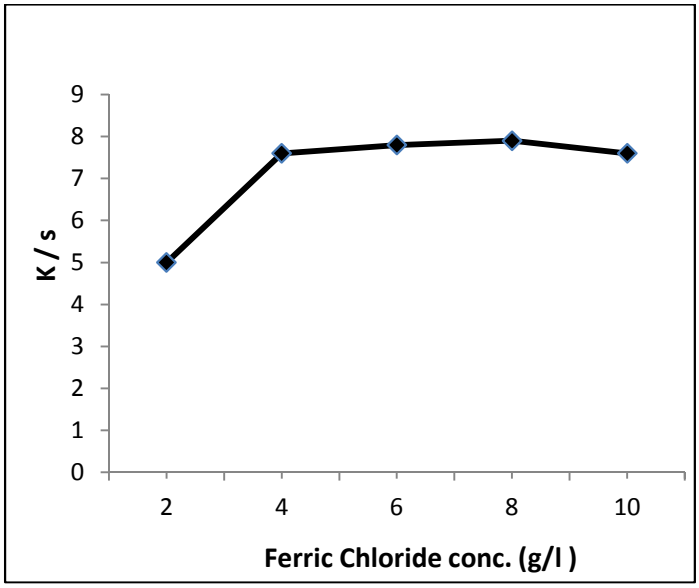


Fig. 8. Effect of mordant conc. on the colour strength (K/S) of cotton fabrics dyed with Brazilwood dye.

Dye bath contents: 8% dye conc. –6% cationic agent – x g/l mordant –temp.60^{0}C- time 30/60/30min. – pH 6 – L.R 1:50

3.4 COLOR HUE VARIATION

One of the problems encountered during the dyeing with natural dyes is their high sensitivity to some parameters, which may affect the obtained colour hue.

During this study a serious trial is made to shed light on the relationship between some parameters and variation of the received color hue. Hue is defined as the quality of color described such as green or red. The colour component of the dyed cotton samples were measured since the values of a*, b* were determined since a* indicates the degree of redness-greenness while b* is the indicative of the degree of yellowness- blueness. The increased values of a*, and b* define more reddish, and more yellowish, respectively, the a*, b* values can explain the difference in each shade. [26]

Some factors can affect the color hue of cotton fabrics such as using mordant, pH of dyeing and cationic agent concentration. The results of measurement of a* and b* are illustrated in **Figures (9-11).**

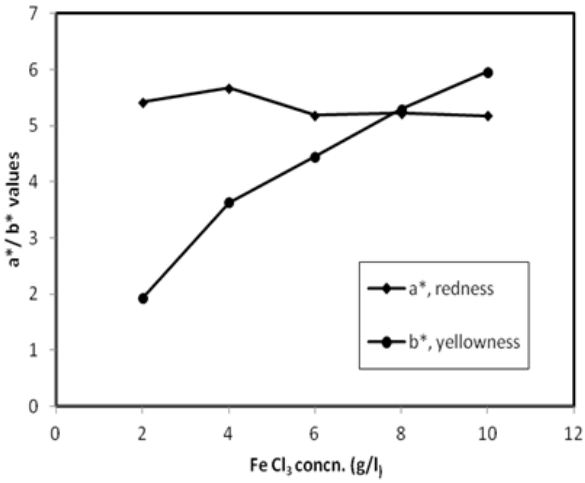


Fig.(9): Effect of Fe Cl_3 concn. on the colour hue of cotton fabric dyed with Brazilwood dye

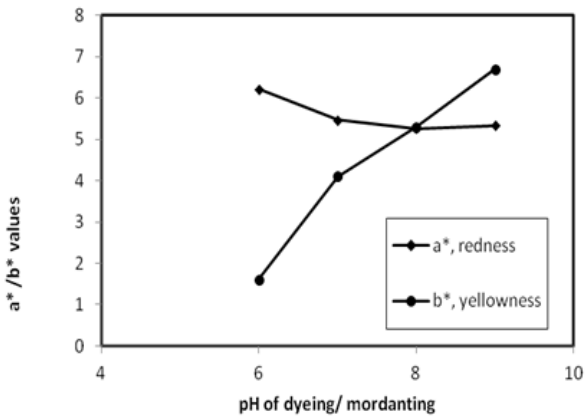


Fig. (10): Effect of pH value of dyeing on the colour hue of cotton fabric dyed with Brazilwood dye

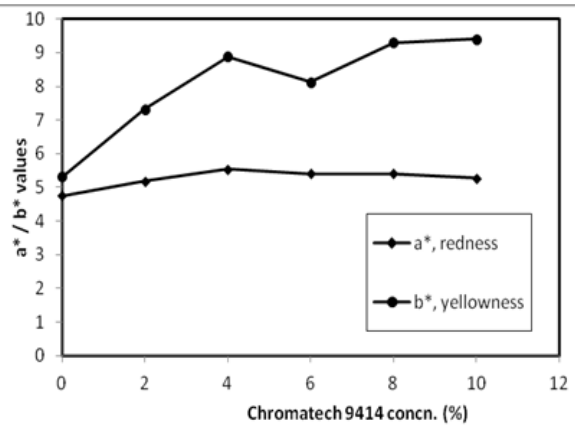


Fig. (11): Effect of Chromatech 9414 concn. on the colour hue of cotton fabric dyed with Brazilwood dye

It can be noticed from the figures that the b* value was increased as increasing of the three factors which means more yellowness, while a* value was increased by increasing of cationic agent concentration with more redness , but it was decreased with the other two factors .

3.5 DETERMINATION OF THE WETTABILITY OF COTTON FABRIC

To evaluate the effect of cationic agent conc. on absorbability of cotton fabric, the wettability of the treated fabrics with cationic agent were carried out at different concentration (0-10% owf) comparing the result with the blank (scoured and bleached sample). The data are illustrated in **Table 2**, the wettability of blank cotton fabrics was high compared with the treated samples which showed decreasing in the wettability as the concentration of cationic agent increase and that may be because of the cationic agent coat the surface of the fabric which affect its wettability. On cationically modified cotton fabrics, water retention value is minimally reduced because cationization occurs mainly on primary hydroxyl groups of C-6 atom of cotton cellulose, so certain number of functional groups is blocked for water molecules. The formation of a layer of cationic polymer on the outer fiber surface will also suggested to prevent the ease penetration of water molecules inside the polymer chains of cotton fiber resulting in slight decrease in wettability.

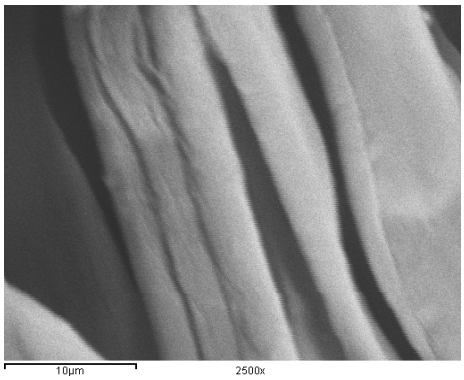
Probably, the fabric pore structure is slightly changed, resulting also in slightly reduced water retention values. Very small change of hydrophilicity of cationized samples cannot negatively affect cotton fiber swelling during dyeing. [20]

Table 2: Effect of the cationic agent conc. on the wettability of treated cotton fabric

Cationic agent conc.%	Wettability (absorption time of water drop)
0	1 sec.
2	5 sec.
4	8 sec.
6	19 sec.
8	27 sec.
10	28 sec.

3.6 SURFACE MORPHOLOGY OF COTTON FIBRES:

The microscopic examination by scanning electron microscopy was carried out seen to confirm the cationization action on the surface of cotton fabrics. The observed morphological changes can be seen in **Figure 12 (a-b).**



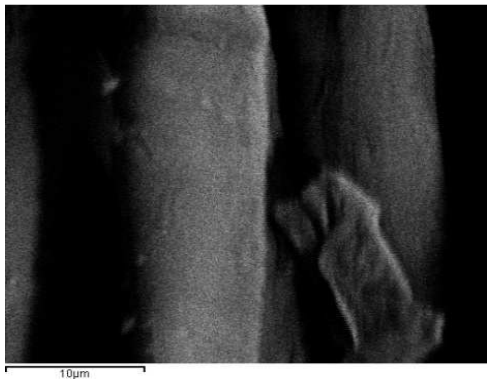


Figure (12a): untreated cotton sample ***Figure (12b): treated cotton sample***

Figure 12(a) shows a micrograph of untreated cotton fiber surface where Figure 12(b) depict micrograph of cationized fiber surface. It can be noticed, based on these micrographs, that there are some changes in surface morphology, though the cationized fiber surfaces are slightly rougher than that of untreated cotton fiber,due to the formation of polymer film on fibre surface as shwon in figures (a-b).

3.7 EVALUATION OF THE NEW ONE- BATH METHOD

To evaluate the efficiency of the new process, the concns. of materials and application conditions that were used in the one – bath process were applied by the conventional two – baths process in which cationization was performed in a separate bath and dyeing in a second fresh bath.

The obtained results of K/S were (7.85) for one – bath and (7.9) for the conventional two – baths. These results confirm the high efficiency and applicability of the new one – bath method compared to that of the conventional two – baths method.

3.8 FASTNESS PROPERTIES

The color fastness properties of cationized cotton fabrics dyed with Brazilwood in one bath and in two separate baths are evaluated **.**The results of wash-fastness (WF), perspiration (PF) andlight fastness (LF) of dyed fabric with and without cationic agent are shown in **Table 3.** The fabrics were compared with grey scale to obtain the color change compared with fabric before testing. The specimens of dyed fabrics were attached with multifiber fabric consisting of wool, polyester, polyamide, acrylic, cotton, and cellulose acetate. The color changes of the dyed samples as well as the staining of the multifiber fabrics were assessed using the grey scale and the results are shown in **Table 3**.Prespiration and light fastness for dyed cationized and uncationized samples show results ranges from very good to excellent. Washing fastness for dyed cationized and uncationized samples show very good fastness. The explanation of these results is the metal ions can chelate several dye molecules together, thus creating a larger complexes and providing a link between the dye and fiber [27]. The formation of these insoluble complexes within the fiber resulting in increasing depth of shade and fastness of color. [28]

Table 3: Color fastness properties of cationized cotton fabrics dyed with Brazilwood

Perspiration								
Samples		Color Change	Staining					
			Wool	Polyester	Polyamide	Acrylic	Cotton	Cellulose acetate
Alkaline	Cationized dyed cotton (Two baths)	4-5	5	5	5	5	4-5	5
	Cationized dyed cotton (one bath)	4-5	5	5	5	5	4-5	5
Acidic	Cationized dyed cotton (Two baths	4-5	5	5	5	5	4-5	5
	Cationized dyed cotton (one bath)	4-5	5	5	5	5	4-5	5
Light								
Samples		Color Change						
Cationized dyed cotton (Two baths)		4						
Cationized dyed cotton (one bath)		3-4						
Washing								
Samples		Color Change	Staining					
			Wool	Polyester	Polyamide	Acrylic	Cotton	Cellulose acetate
Cationized dyed cotton (Two baths)		2	5	5	5	5	4	5
Cationized dyed cotton (one bath)		2-3	5	5	5	5	4	5

4 CONCLUSION

The purpose of this study is to carry out cationization, dyeing and mordanting cotton fabric in one bath at three stages to save energy and water using Brazilwood natural dye.Cationization can improve colour intensity of cotton because it provides a cationic dye sites rather than untreated fabrics .The optimum conditions of dyeing stage were investigated which showed best results at8% Brazilwood natural dye, pH6 , 60 min., 60^{o}C and the best colour strength was observed at 6%(Chromatech9414) , 8g/l ferric chloride. The obtained results offer an option of one – bath, cationization and dyeing process, replacing the water and energy consuming two – baths method and conventional dyeing process.Fastness properties were ranged from very good to excellent for perspiration and from fair to good for washing.

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