

Improving Dyeing Properties of Cotton Fabrics to Natural Dyes via Cationization and Nano Chitosan Treatments

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Abstract: Cotton Fabric was treated with Cationic agent after which another treatment with nano chitosan PAA was carried out to impart cationic character to the fabric capable of attracting dye anions . Cochineal (*Dactylopuscoccus costa*) natural dye was used throughout this study . Nano chitosanpolyacrylic acid (CS – PAA) was prepared for treatment of cotton fabric before dyeing with cochineal natural dye . The particle size was analyzed on the particle size analyzer since it was found to be 50 nm . Many factors for the dyeing process that may affect the dye uptake and K/S such as dye concn, dyeing pH , temp and time were also studied . The effect of mordant concn. on the final colour yield was also studied . The dye uptake expressed as K/S was measured by spectrophotometer and the colour fastness to washing , perspiration , crocking and light were assessed according to standard methods . The wettability of the treated and dyed fabric was also tested . The colour strength of the dyed fabric was greatly increased as a result of cationization and chitosan PAA treatment due to the higher ionic attraction between dye anions and fabric cations . Maximum K/S was achieved at pH 4 since most of amine groups on fabric surface are existed in protonated form .

Keywords: cotton , natural dyes , cochineal , dyeing , chitosan , cationization .

I. Introduction

Various wet processing operations of textiles from initial preparatory process to final finished clothes are now focused for green technology. Several conventional non-ecofriendly chemicals are being replaced by natural based products that are safe to environment and health during manufacturing and usage. Applications of enzymes in preparatory and in bio-polishing, natural dyes for colouration, biopolymers and their derivatives in fiber production and finishing processes, etc. are some of them. One such biopolymer of great interest in recent years is chitosan. (1-2)

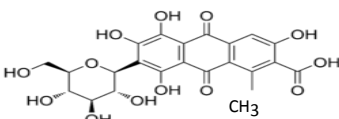
Natural dyes are soft in colour shades compared to synthetic dyes. Besides, with the increase of the worldwide concern for the environment , the possibility of using natural dyes is being studied because natural dyes may overcome the defects of synthetic dyes such as harmfulness to human body, pollution and waste water. Accordingly there have been active researches for the natural dyeing. (3-8)

Chitosan, the cationic (1-4)-2-amino-2-deoxy- β -D-glucan partly acetylated to the typical extent close to 0.20, is industrially produced from marine chitin, the linear (1-4)-2-acetamido-2-deoxy- β -D-glucan. Both of them have attracted attention owing to their superior characteristic properties, among which biocompatibility and absence of toxicity. (9,10) Chitosan and chitosan derivatives are a polymers of interest in cotton colouration due to its favorable properties such as affinity, fiber compatibility and water solubility. (11-14) Many researchers have investigated their applicability in improving aspects of colourations such as, affinity improvement, coverage improvement and in special finishes like antimicrobial activity. (15-19) This work is aimed to improve the dyeability and the fastness properties of cotton fabrics dyed with Cochineal by using cationic agent (Zestal F) followed by treatment with nano Chitosan – poly acrylic acid (CS-PAA).

II. Materials and Methods

2.1. Materials

100% prewashed Cotton fabric was received from EL Shorbagy- Egypt (plain weave 1/1, 142g/cm², 40/1). The natural dye in powder form was used throughout this work called Cochineal (*Dactylopuscoccus costa*, Toblomas Co. U.S.A.).

English Name	Latin Name	Structure	The Source
Extracted Cochineal Natural Dye	<i>Dactylopuscoccus costa</i>		Toblomas Co. U.S.A.

Chitosan, with initial 85% degree of deacetylation from Sigma (U.S.A).Tissocyl RC9 (Detergent and wetting agent from Z&S Company, Germany).TanacidUNA (Acid Buffer &Neutralizing agent from (Tanatex) Ewaika Association for Chemicals, Egypt).Acrylic Acid, Ammonium Persulphate, Sodium Bisulphate, Sodium Carbonate. Ferric chloride and Alum (ELgomhorya Company, Egypt) were of laboratory grade chemicals.Zetesal F Conc. (Cationic agent from Z&S Company, Germany).ArkofixNZF(Crosslinking agent formaldehyde free, from Clariant Co.).Ebcasperse RJL (Anionic Dispersing agent from Egyptian British Company, Egypt).

2.2.Methods :

2.2.1. Preparation OfChitosan Acrylic Acid Nano Solution By Polymerization:

Chitosan –poly acrylic acid (CS-PAA) was obtained by polymerizing (AA) in chitosan by dissolving (CS) in an aqueous (AA) solution 0.5% for 12 hr. at low speed stirring. Next 0.3gm ammonium persulphate (APS) per 100gm (AA) was added to the CS-AA solution under continuous stirring at 55°C for 1hr. followed by a drop wise add of 0.15gm sodium bisulphate (SbS) in 10 ml H₂O with continuous stirring (50 rpm) to obtain an opalescent solution. The mixture was allowed to stand overnight, filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The synthesized nano-PAA was applied to the cotton fabrics within 24 hrs. Since the stability of nano CS-PAA gets adversely affected with time. The particle size was analyzed on the particle size analyzer.⁽²⁰⁾

2.2.2. Prewash Bath:

Firstly the cotton fabrics samples were washed in the following bath:1 g/L Tissocyl RC9,1.2 g/L Soda Ash,at 80 °C,for 30 min,L: R : 1:20 .Secondly the fabrics samples were neutralized in a bath contains: 0.5 g/L Tanacid UNA , at 80 °C, for 20 min, L: R : 1:20. Then they were rinsed with hot then cold water.

2.2.3. Treatment With Cationic Agent Followed By Chitosan Acrylic Acid Nano Solution Treatment Then Dyeing With Natural Dyes:

The cotton fabric samples were treated with Cationic agent (Zetesal F Conc.) as follows: 10%ZetesalF.Conc.at70 °C for 30 min, L.R. 1:20 at pH:5 , then they were squeezed and dried.The cationizedcotton fabrics were then treated with 1% nano chitosan acrylic acid solution with 4% crosslink (o.w.chitosan) as follows:

Pad once- with pick up 70-80% -dry then cured at 130°C for 3min.The treated fabrics were dyed in a bath containing 2% Natural dyein presence of 2 g/l wetting agent and 2 g/l dispersing agent at pH :4 ,At 90 °C for 60 min,L.R. 1:20. The samples were then mordanted with two different types of metal salts: 10 g/l alum or 5g/l Ferric Chlorideat 80°C for 60 min ,then soaped and rinsed with hot then cold water.

Washing the samples:

The dyed samples were washed in a bath contains:1 g/L Nonionic detergent at temp. 80°C for 20 min. after which they were rinsed with hot and cold water and air – dried.

III. Measurements and Analysis

The colour strengths of dyed samples expressed as K/S,were measured by using reflectance spectrophotometer model DatacolourSpectrophotometer SF600+, Datacolour Company, U.S.A.The K/S values were obtained from the equation:

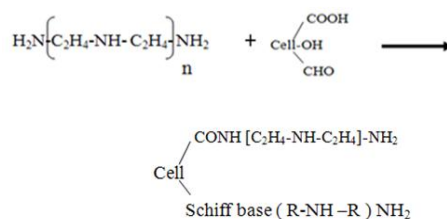
$$K/S = (1-R)^2 / 2R$$

where K is constant associated with the light absorption of the fabric, S is a constant associated with the light scattering of the fabric, and R is the reflectance of dyed fabric measured at the wavelength of maximum light absorption, expressed in fractional form. Wettability Test was done for both samples(untreated and treated) were carried out by putting 5 drops of water on the surface of each sample and calculating the time that will pass until the fabric absorb the water drops. And this according to AATCC test method 79-1986.Colour fastness to wash and Colour fastness to light were done for the dyed samples according to ISO 105 washing test method (B.S. CO2 1989) for Colour fastness to light and British Standard (B.S.1006 1995).

IV. Results and Discussion

4.1. CationizationAndChitosan-PAA Treatments:

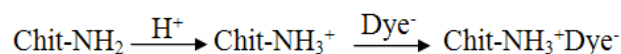
It was observed from table 1 that cationization improved significantly the dyeability of cotton to cochineal dye compared to the untreated fabric. The increased colour strength on cationized cotton may be attributed to the creation of a positive dye sites on cellulose macromolecules resulting in higher accessibility to attract negatively charged dye anions via ionic attractive forces. The mechanism of cationization may be suggested to carryout as follows.



Thus the colour yield will be affected with the magnitude of ionic attraction between fibers and dyes. Thus, the number of positive charges on the fabric surface as well as the degree of dye ionization will be a decisive factor in determining the magnitude of ionic attraction between dye anions and fiber cations and subsequently the obtained colour strength.

On the other hand, treatment of cationized cotton fabric with nano chitosan polyacrylic acid was found to increase the dye uptake to great extent giving higher colour strength as observed from table 1 . It was stated that chitosan form a surface film on cotton fabric to impart cationic character capable of attracting negatively charged dye anions increasing the intensity and strength of colour.

Chitosan can easily absorb anionic dyes such as direct, acid and reactive dyes by electrostatic attraction due to its cationic nature in an acidic condition as shown:



The affinity of chitosan to cotton would be by Van der waals forces between them because of the similar structure of chitosan and cellulose. Another possibility mentioned for binding the chitosan to cellulose was cross linking by formation of Schiff base between both.

The samples were then rinsed thoroughly before mordanting under the optimum conditions of mordant bath which contains 10g/l Alumor with 5g/l Ferricchloride at 80°C for 60 min, then soaped and rinsed with hot and cold water. The results of colour strength (K/S) of the dyed samples are postulated in tables(1).

Table 1: Effect of Cationization and Chitosan treatments on K/S of cotton fabric

Treatment	K/S of dyed cotton fabric	
	Alum	Ferric chloride
Without treatment (dyed only)	0.33	0.33
Chitosan Treatment	3.03	10.36
Cationization and Chitosan	7.36	11.73

4.2. Dyeing Of Treated Cotton Fabrics With Cochineal Natural Dye.

The cotton fabrics were treated with Cationic agent at optimum condition :10% ZetesalF. Conc. at 80 °C ,for 15 min ,L:R : 1:20 at pH : 5. Then they were squeezed and dried.

The cationized fabrics were treated with nano chitosan acrylic acid solution with Conc. of chitosan 1% and 4% Cross linking Arkofix NZF (o.w.chitosan), Pad once- dry with pick up 70-80% then cured at 140C for 3min. The cationized and CS-PAA treated fabrics were dyed with Cochineal natural dye. The dyeing parameters that may affect the dyeing process were subjected to study in order to determine the optimum dyeing condition.

4.2.1. Effects of Dye Concentration:

Different concentrations of cochineal natural dye were used for dyeing the fabrics that cationized and followed by treatment with CS-PAA under fixed conditions. The dye bath was formulated as follows: X% Cochineal natural dye, 2 g/l wetting agent ,2 g/l dispersing agent at pH : 5 at 90°C for 60 min. and L:R : 1:20. The dyeing process was started at 50° C , then the temperature was gradually raised to 90° C since the dyeing continued for 60 min. after which the dyed samples were rinsed with warm water .

The samples were then mordanted with 10g/l Alum or with 5g/l Ferric chloride at 80°C for 60 min then soaped and rinsed with hot and cold water. The colour strength of the dyed fabrics was measured and the results are formulated in table (2).

It is obvious, from table (2) that with increasing the conc. of the natural dye in dye bath, a gradual increase in colour yield expressed as (K/S) was attained on the cotton fabrics with the two mordants.

Cationized and chitosan treated cotton fabrics were found to have high adsorption capacity with the applied natural dye. This observation may be attributed to the fact that the hydrophilic character of cotton along with presence of functional hydroxyl group in its chemical structure enhances and facilitates the rapid approach of cationic agent as well as the adsorption and formation of chitosan film on the fiber surfaces.

The relatively greater amount of both cationic agent and chitosan on cotton fiber impart a cationic surface which attracts negatively charged dye anions along with the formation of some physical forces of attraction between dye molecules and fibers i.e. hydrogen bonding and Van der Waal's forces.

Table (2): Effect of Dye Conc. on K/S of The Dyed Fabrics With Cochineal Natural Dye Using Alum Mordant.

Dye Conc. (%)	K/S of dyed cotton fabrics	
	Alum	Ferric Chloride
1	5.59	9.63
2	7.70	7.70
3	10.24	8.01
4	11.06	8.74
5	11.69	8.58

4.2.2. Effect Of Dyeing Ph:

The physico-chemical properties of the dyeing process such as the dyeing equilibrium, degree of exhaustion and rate of dyeing are pH dependent especially in case of ionic dyeing system. In order to optimize the pH of the dyebath, dyeing were performed with the suitable dye concentration, i.e. 2% owf.

Therefore the relation between the uptake of natural dye on treated fabrics and the pH of dyeing was studied in details. The Cochineal natural dye was applied for dyeing the treated fabrics using constant dyeing condition except the pH level which was changed. The colour strength of the dyed fabrics were measured and obtained data are plotted in table(3). It was noticed that the maximum dye uptake was observed at pH value (4) for the Cochineal natural dye.

The dye behavior during dyeing process of cochineal, exhaustion and fixation of natural dye on the cationized fabrics depend on the ionic attraction between dye anions and fiber cations, therefore the colour yield will be affected with magnitude of ionic attraction which may be influenced with the pH of the medium.

Table (3): Effect of pH level of the dyeing bath on K/S of the dyed fabrics using Cochineal Natural dye.

pH level	K/S of dyed Cotton fabrics	
	Alum	Ferric Chloride
4	6.24	7.98
5	6.01	7.23
6	5.49	7.17
7	5.41	7.14
8	5.50	5.74
9	5.00	5.88

The Fabrics treated with CS-PAA may be representing as follows:

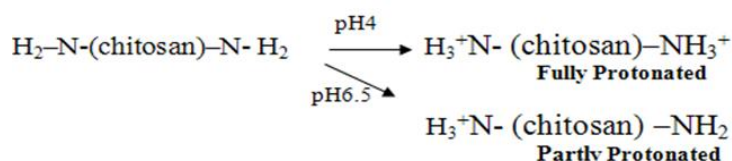
(a) cotton – chitosan –NH2

It may be concluded from the obtained data that maximum dye exhaustion and subsequently higher K/S were realized at acidic medium (pH 4) for most of natural dyes.

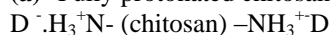
This result may be explained on the fact that chitosan behaves, in acid solutions, as a cationic polyelectrolyte due to protonation of the amino groups, since the pK value of the amino groups of the chitosan is 6.3, the amino groups would be only partly (about 20% at pH 6.9) protonated into-NH3+ above pH value 6.5. (21)

Therefore, under acidic condition (pH4) most of the amino groups of chitosan will be existed in protonated form (- NH3+), which enhance the ionic attraction between the anionic dyes and cationic groups of the chitosan and fibers (as a result of cationization and CS-PAA).

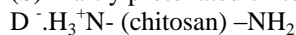
Interaction of chitosan and dyes:



(a) Fully protonated chitosan (pH4)



(b) Partly protonated chitosan (pH6.5)



The cotton samples which were previously cationized and treated with nano-chitosan acrylic acid, were dyed in dyebaths containing a fixed conc. of natural dye and the dyeing processes were performed under constant conditions except for temp. which was ranging from 70°C to 130°C. The colour strengths of the dyed and mordanted samples were measured and the obtained results of K/S are plotted in table (5).

The influence of the dyeing temperature on the colour strength of dyed fabrics will be observed from table(5) the temp. which gave higher K/S was found to be 70°C with Alum. mordant and with increasing the temp. the shade become lighter and the hue of dyeings changed, while with Ferric in table (5) an opposite results were noticed since highest colour strength were achieved at 130°C.

Table (5): Effect of dyeing temperature on K/S of the dyed fabrics Cochineal Natural Dye.

Dyeing Temperature °C	K/S of dyed cotton fabrics	
	Alum	Ferric Chloride
70	6.73	6.97
80	6.58	8.65
90	6.28	9.20
100	6.13	9.74
110	4.97	11.31
130	5.40	13.10

The influence of dyeing temp. on the dye uptake expressed as (%) increase / decrease in K/S is illustrated in table(6).

Table (6): (%) Increase / Decrease of K/S as function of raising dyeing temp. from 70°C up to 130°C

Natural Dye	Mordant	(%) Increase / Decrease of K/S
Cochineal	Alum	-19.76
	Ferric	87.95

The action of temp. of dyeing process may be summarized as follows:

1. Increasing the swelling of cotton fibers to permit easier penetration or diffusion of dye molecules inside the fiber.
2. Disaggregate the dye molecules which exist in aqueous medium as micelles since dissolution of the dyes in water is an endothermic process, the aqueous solubility increases with increasing temperature.(26)
3. Accelerating the diffusion coefficient of the natural dyes in the solution and thus increasing the rate of adsorption on fiber surface.
4. Increasing the rate of reaction of dye molecules with the cationic sites in the fiber.
5. Determine the partition coefficient of the natural dyes between the aqueous phase and the fiber phase which will depend to great extent on the type and structure of the dye itself as well as its hydrophilic character taken into consideration the hydrophilic nature of cotton (cellulose) fiber.

4.2.5. Effect Of Dyeing Time:

The dyeing time and its impact on the obtained colour strength was studied in order to determine the suitable dyeing time for achieving maximum colour strength.

The treated fabrics were dyed with Cochineal natural dyes for different durations under constant dyeing parameters except the time of dyeing. It is observed that maximum colour yield are attained after dyeing for 45min. beyond which there are slight decrease in dye uptake with lasting dyeing time. The dyeing time gives the opportunity of the natural dye to penetrate and diffuse inside the fabrics attaining maximum dye absorption capacity when reaching the dyeing equilibrium state.

In fact, the rate of dyeing is generally, affected by some factors such as:

- The molecular size of the coloured species of natural dye.
- The rate of diffusion either in aqueous solution or within the fiber itself.
- The degree of dye aggregation in aqueous solution.
- The substantivity of the natural dye to the fiber.
- The dyeing temperature.
- The pH of the dyebath which determine the degree of ionization of amino groups of Chitosan/Acrylic acid and thus the rate and magnitude of electrostatic attraction between fiber and dye.

Table (7): Effect of dyeing time on K/S of the dyed fabrics with Cochineal Natural Dye.

Dyeing Time (min)	K/S of dyed cotton fabrics	
	Alum	Ferric Chloride
30	6.76	7.69
45	8.17	8.33
60	7.90	7.45
90	7.26	7.60

4.2.6. Effect of Mordant Concentration:

In the dyeing of textiles with natural dyes mordants play an important role because they have substantivity for both the dye and the fiber and form insoluble complex with the dye on the fabric.

The element composition and nature of the mordants had a significant effect upon colour change leading to noticeable change in values of the hue angle, resulting into varied colour locations in the a*, b* colour coordinates.

The effect of mordant on colour change depended to certain extent upon the composition of the dye, the range of colours produced by the same dye using different mordants was remarkable and this is one of the advantages of natural dyeing, each mordant had an individual limited range of colour change.

Two mordants were used in this study Alum. (potassium Aluminum sulphate) and Ferric Chloride to notice their effect on the natural dye used in this study by post- mordanting method, dyeing was carried out in the absence of mordant, followed by mordanting in a separate bath containing a mordant at 80°C for 60 min. The influence of mordant concentration on the colour strength was studied and the K/S values were measured and plotted in table (8). The colour coordinates, L*, a*, b*, of the dyed samples under the action of mordanting with various conc. of mordant were measured and illustrated in tables (9)

Table (8): Effect of Mordant conc. on K/S of the dyed fabrics Cochineal Natural Dye with Alum Mordant .

Mordant conc.(g/l)	K/S of Cotton	K/S of Cotton
0	8.84	8.84
2	8.84	10.53
4	7.78	9.62
6	8.39	8.57
8	7.59	7.58
10	7.14	8.16

The dye has significant change in lightness and it has clear change in the hue of the shade which become more bluer/redder and this appear in the colour coordinates results. The concentration of 6 g/L of Alum gives more or less the same lightness of each shade without mordant. Effect of Ferric Chloride shown in table (33), the dye has gradual increase in K/S with increasing the mordant concentration also the shade become more yellow and brown in hue, Cochineal has remarkable change in hue with Ferric as mordant, as the shade change from redder bluer to yellow.

Table (9): Effect of mordant concentration on the colour coordinates of dyed fabrics

Mordant concn. (g/l)	Colour coordinates of dyed fabric					
	Alum			Ferric Chloride		
	L*	a*	B*	L*	a*	B*
0	35.02	27.42	-7.65	35.02	27.42	-7.65
2	35.60	30.43	-7.93	44.76	12.10	6.42
4	37.85	32.22	-8.02	52.84	10.08	13.32
6	36.89	32.22	-7.92	60.98	9.48	19.94
8	38.65	33.35	-7.62	63.10	8.83	19.96
10	38.85	31.97	-8.27	65.91	10.01	24.46

The magnitude of alteration in the final colour strength was observed to vary from metal salt to another. The great increase in K/S under the action of mordant reflect the great change in the dye structure inside the fiber as a result of metal complexation reaction.

It may be concluded, from the previous data that the optimum concs. of the used mordant for realizing highest K/S are illustrated in table (10).

Table (10): Optimum Mordant conc. for attaining highest K/S

Natural Dyes	Mordant	Optimum Conc. (g/l)
Cochineal	Al	2
	Fe	2

The mechanism of mordanting may be suggested to carry out via one of the following reaction mechanism:

1- Formation of dye-metal complexes of 2:1 or 1:1 types which interact with the positively charged functional groups in the fiber through electrostatic attraction

Fiber-NH₃⁺...-[Me-D] (electrostatic attraction)

2- Formation of fiber-metal-dye complexes through coordination reaction

Fiber-NH₂ → Me-D (Coordinate link)

The preferential reaction mechanism will depend on some factor which may be summarized as follows:

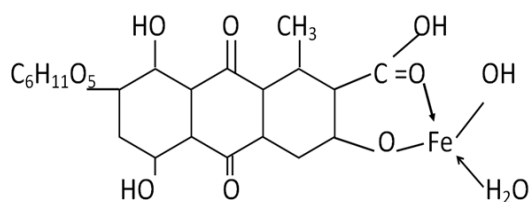
- 1- The presence of available functional group containing strong electronegative character inside the fiber capable of interact with the metal ions i.e. amino (NH₂) groups of chitosan along with (OH) groups of both cellulose and chitosan polymer.
- 2- The number and position of (OH) groups in the dye molecule.
- 3- The amount and type (valency) of the metal ions.
- 4- The pH of the reaction medium which determine the electrical properties of both fiber and metal ions.

It is well known that amines form stable complex with metal ions. Some previous studies indicated that the participation of the primary amine of the polymer in the formation of complex with divalent metal ions since one metal ion is chelated with one nitrogen atom of the polymer. (27)

Another amines rather than the primary amine may be also participated in the complexation reaction in presence of high conc. of metal ions. In addition , the carbonyl groups in acetylated polymer may also contribute the metal binding. Carboxyl groups in either the fiber or in dye molecule (Cochineal dye) were also suggested to play a role in the binding with metal cations. (28)

On the other hand, it was stated that the stability of chelate formation between the amine- containing fiber and metal ions is correlated to the electronegativity of the metal (the electronegative values of Fe and Al are 1.6 and 1.5 respectively), increasing the electronegative character of the metal result in higher stability of the formed chelate between fiber and metal.(27)Hence, the stability of (Fe) chelates will be more stable than (Al) chelates.

The mode of binding of dye seems different with iron (Ferric) and Aluminum (Alum) ions as shown in following:



1:1Metal Complex of Cochineal dyes

Alum doesn't affect the colour , but the Ferric darkened the colour, and make it more yellow.

V. Fastness Properties

The fabrics treated and dyed with Cochineal natural dye and mordanted with Alum and Ferric chloride were tested to wash, perspiration, rubbing and light. The obtained results are shown in table (36). It is clear from tables that there are improvements in fastness properties of natural dye used in this study.

5.1. Wash Fastness:

Treated Fabrics dyed with Cochineal natural dye without post mordanting have very good (4) fastness, on the dyed fabrics which post mordanted with (Alum and Ferric Chloride) were given very good to excellent (4- 4/5) fastness.

5.2. Perspiration Fastness:

The fastness to both acid and alkaline perspiration were increased after mordanting with either alum or ferric chloride as observed from table (11). The fastness to acid perspiration was changed from moderate (2) for unmordanted samples to very good (4) after mordanting with alum or ferric chloride. For the alkaline perspiration a similar result was observed since the fastness increased from good (2-3) to very good (4) after mordanting.

5.3. Crocking Fastness:

Dry crocking test on the dyed fabrics were not so far than the washing fastness which gave grade (4) very good. The fastness to wet crocking was improved after the mordanting process , since the fastness rating changed from good (3) to very good (4) with the two mordants.

5.4. Light Fastness:

Fastness to light is one of the important properties for dyed fabrics. Anthraquinones and indigoids are noted for their excellent light fastness. However, the light fastness of Anthraquinones is decreased as the number of hydroxyl substituent groups is increased.

The used natural dye Cochineal isanthraquinone the light fastness of it was improved from good (5) to very good (6) using different mordants to exhibit very good fastness, the fastness of a mordant dye depends on the mordant and mordanting method, because different metal dye complexes are formed, which may differ in their stability to light and also because the metal may have a positive or negative catalytic effect on the photochemical degradation of the dye.

Table (11): Colour Fastness of Dyed Fabrics with cochineal Natural Dyes

Type of treatment	Washing			Perspiration						Crocking		Light
				Acid			Alkali					
	SL.PES	SL.CO	SL.WO.	SL.PES	SL.CO	SL.WO.	SL.PES	SL.CO	SL.WO.	Dry	Wet	
Chationized with cationic agent followed by CS-PAA treatment (cochineal dye without mordant)	4	4	4	2	2	2	2-3	2-3	2-3	4	3	5
Chationized with cationic agent followed by CS-PAA treatment (cochineal dye alum mordant)	4-5	4-5	4	4	4	4	4	4	4	4	4	6
Chationized with cationic agent followed by CS-PAA treatment (cochineal dye ferric mordant)	4-5	4-5	4	4	4	4	4	4	4	4	4	6

VI. Wettability Test:

Increasing in the surface Wettability of fiber is due to formation of several hydrophilic groups such as amine group(-NH₂) and(-OH) on the fiber surface. The increased surface polarity enables polar interaction or hydrogen bonding with water molecules, thus increasing the water wettability of the fibers.

The wettability of the treated and untreated fabrics were measured and the results are formulated in table (12).

Table (12): Wettability Test of Untreated and Treated Fabrics

Treatment of Fabrics	Wetting time of Fabrics (Sec.)
Untreated	56
Cat. / CS-PAA	98

These results may be explained as follows:

- 1- Cationic agent block the negatively sites on cotton fibers during the pretreatment process resulting in diminishing their capability to absorb water molecules. As result the Wettability of cotton fabrics were observed to be less than the untreated fabrics.
- 2- The fixation of CS-PAA on the fabrics via crosslinking agent (dihydroxy ethylene urea) will reduce the number of hydroxyl groups of cellulose fibers beside the possible crosslinking reaction between the cellulose polymer chains on the expense of the OH groups. This suggestion is in good agreement with increasing in tensile strength of the treated fabrics.

VII. Conclusion

Cotton fabrics were dyed in deep shades with cochineal natural dye with high level of fastness properties. Cotton fabrics were treated with cationic agent at 10% conc (owf) under fixed and suitable conditions, then followed with a second treatment with chitosan polyacrylic acid which was prepared in nano particles. The dye uptake was greatly increased with both cationization and chitosan treatments, due to the creation of positive centres on fabric surface capable of attracting the negatively charged dye anions. A better dyeing properties for cotton fabrics with cochineal dye was obtained with treatment in a bath containing 10% cationic agent at 50° C and pH 8 for 40 min and dyeing process at 90°C and pH 4 for 60 min. The color fastness properties of dyed cotton with cochineal were also found to be good.

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