A Novel Eco-Friendly Pre-Mordnating Technique For Dyeing Cellulose/Wool Fabrics Using Allium Cena Natural Dye

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Abstract: Coloration of fabrics is a major process in the production of textile material. In the current study, natural dye was extracted from onion skin (Allium Cena) using microwave irradiation technique and used to dye wool/cotton blended fabrics, via eco-friendly natural mordants, i.e., aloe vera and chitosan. Factors that may affect pre-mordnating process were studied like mordant conc., curing time/ temperature. Various parameters that affect on the dyeing process were investigated such as dye concentration, dyeing time/temperature as well as pH value of the dyeing bath. The fastness properties gave results ranged from good to excellent.
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Key words: natural mordant; chitosan; aloe vera; Allium Cena; wool/cotton.

1. Introduction

Cotton/wool blended fabrics are growing in popularity, due to increased consumer demand for styling, comfort and for natural fibers. There is a resurgence of interest in blending these two natural fibers throughout the developed world, because they are perfect complements of each other. When blending of cotton and wool takes place, the strengths of one fiber tempers the weaknesses of the other. The popularity of these blends is due to their light weight, good strength, drapability, easy wash ability together with low cost. Blended worsted yarns containing approximately equal proportions of wool and cotton have been long established in knit wear, dress wear, under wear, children's clothing, light weight shirting's, pajamas clothes and blankets.(1)

Dyeing a cotton/wool blend is difficult because the two fibers have different chemical makeups. Wool, which is sheep hair, is made of animal proteins, while cotton is made of plant cellulose-the main part of a plant's cell wall. Normally, when wool and cotton are blended together, two separate dye baths are required.

In the conventional procedure cotton is dyed first and wool second. Wool is dyed in an acidic environment at high temperatures, and cotton is dyed in a nonacidic "alkaline" environment. This difference requires that the wool and cotton be dyed either separately or sequentially in one bath in which the pH and temperature levels are changed. (2)

Today, dyeing is a complex, specialized science. Nearly all dyestuffs are now produced from synthetic compounds. This means that costs have been greatly reduced and certain application and wear characteristics have been greatly enhanced. But many practitioners of the craft of natural dying (i.e. using naturally occurring sources of dye) maintain that natural dyes have a far superior aesthetic quality which is much more pleasing to the eye. On the other hand, many commercial practitioners feel that natural dyes are non-viable on grounds of both quality and economics. In the west, natural dyeing is now practiced only as a handcraft, synthetic dyes being used in all commercial applications. Some craft spinners, weavers, and knitters use natural dyes as a particular feature of their work.(3)

In many of the world`s developing countries, however, natural dyes can offer not only a rich and varied source of dyestuff, but also the possibility of an income through sustainable harvest and sale of these dye plants. Many dyes are available from tree waste or can be easily grown in market gardens. Detailed comparisons of the advantages and disadvantages of natural dyes relative to synthetic dyes were presented in previous literature.

Few natural dyes are colour-fast with fibres, therefore the use of mordants which increases the dye fastness to the fabric is often necessary. Mordants are essentially substances which are used to fix a dye to the fibres, they also improve the take-up quality of the fabric and help improve colour and light-fastness. Mordants are usually metallic salt of aluminium, chromium, iron, copper and tin, as well as other substance such as tanning agents.

Mordants found in nature include wood ash, stale urine and acidic fruits extracts such as lime. The use of mordant in dyeing not only increase the dye take up and colour fastness but the use of different mordants can yield different colours and shades. (4-8)

In the present work, chitosan and aloevera were used as natual mordants. Chitosan is a modified carbohydrate polymer derived from the chitin component of the shells of crustaceans. When chitin is deacetylated to about 50% of the free amino form, it is called chitosan (poly(1,4)-2-amino-2 deoxy-*b*-D-glucan). Chitin and chitosan have different physical properties. Chitin is insoluble in most common solvents, whereas chitosan dissolves in many common aqueous acidic solutions. In aqueous media at pHs lower than 6.5, the amine group of chitosan acquires a proton and ionizes positively, and this gives the biopolymer a special capacity to fix anions and to fix itself to negatively ionized fibers. Chitosan has several useful properties, such as nontoxicity, biocompatibility, biodegradability, antimicrobial activity, and chemical reactivity. In the field of textiles, chitosan has been used as a shrink-resisting agent and as an agent for improving the dyeability of wool.m Moreover, it has been used to improve dyeability, soil release properties, and the handle of cotton. Chitosan, because of its polycationic character, has an affinity for interaction with oppositely charged molecules of cellulose surfaces, such as enzymes. Because of its biocompatibility, biodegradability, water-binding capacity, and nontoxic properties, it can be considered an environmentally acceptable substitute for synthetic polymers in textile finishing.[9-10]

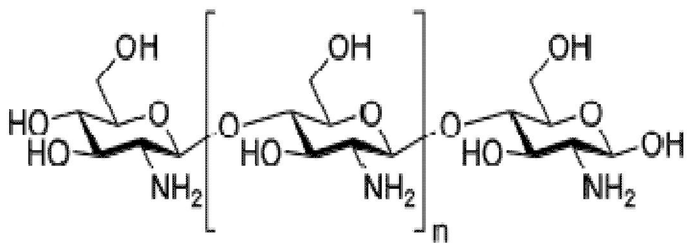
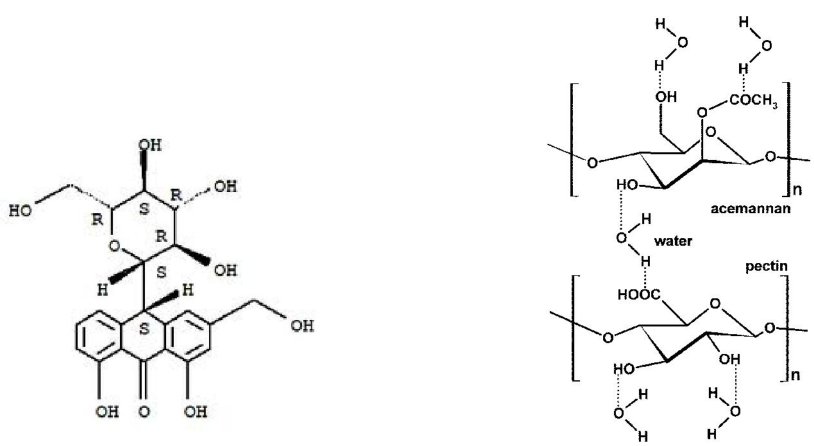


Fig.1 chitosan chemical structure

Aloe vera: Aloes is the dried juice of the leaves of Aloe vera belonging to the family Liliaceae. Anthraquinones (aloin, aloe-emodin), resins, tannins and polysaccharides are the major chemical constituents; Aloe vera gel consists primarily of water and polysaccharides (pectins, hemicelluloses, and glucomannan, acemannan, and mannose derivatives). It also contains amino acids, lipids, sterols (lupeol, campesterol), minerals (magnesium, calsium, zinc,…ect.) and enzymes. Clear gel has a dramatic ability to heal wounds, ulcers and burns, application of a protective coat on the affected area speed up the rate of healing. The chemical structures of both mannose and uronic acid are shown in Fig. 2. It can be noticed that mannose contains a few important functional groups, including hydroxy (–OH) and acety (–COCH3) at the terminals; whereas in uronic acid, the functional groups connected to its terminals are hydroxy and carboxy (–COOH). The main role of these functional groups is to provide an interface for the interaction of the respective polysaccharide chain with other molecules via hydrogen bond-ing due to dipole–dipole attraction forces. [11-15]



Mannos Component Uronic acid

Fig.2 Aloe vera chemical structure

Onions (Allium cepa) also known as bulb onions are vegetable. The skin of onions is inedible however it contains a dyestuff called "Pelargonidin" (3, 5, 7, 4 tetrahydroxy antocyanidol) which has a structural formula represented in Figure 3.

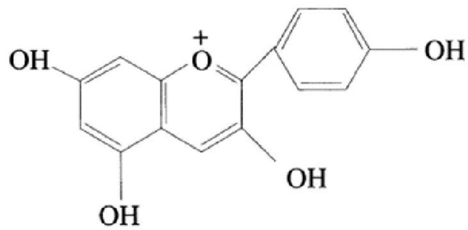


Figure 3. Structure of "Pelargonidin" (3, 5, 7, 4 tetrahydroxyl antocyanidol - a dye stuff in onion skin.

2. Materials and Method

2.1 Materials

2.1.1 Natural Dye Source

The collected onion skin were cleaned, dried and used to extract the natural dyestuff.

2.1.2 Natural Mordants

Chitosan and Aloe vera were used as natural mordants. Chitosan (medium molecular weight, deacetylation 82.9% Dalton, Vanson Inc. Co. USA).

The collected fresh leaves of Aloe Vera washed thoroughly, hence the outer green surface was peeled off and the linear white mass was collected and crushed to semi solid consistency 200ml of the aloe vera semi liquid was mixed with 500ml of water and then filtered.

2.1.3 Synthetic Mordants

Copper sulphate, Alum.

2.1.4 Substrates

Mill- scoured and bleached cotton /wool blended fabrics 70/30 (235 g/m^2) were used in this study.

2.2 Methods

2.2.1 Extraction of the Natural Dye

Traditionally, extraction of natural dyes with aqueous extraction method involve several hours. A rapid extraction technique which applied in textile dyeing was microwave irradiation. [13] A 100g of the processed onions skin was subjected to aqueous extraction with 1 liter of distilled water and heated using microwave oven at 560W for 10 min. and the extract was filtered and allowed to cool. The microwave oven which used was as a sharp modle R-210B, with an 800-W output operating at frequency of 2550 MHz.

2.2.2. Pre-mordnating using Natural mordants

The cotton/wool blended samples were mordanted with Chitosan and Aloe Vera respectively using pad-dry-cure technique. The samples were padded twice with pick up 70-80% in an aqueous solution contains the natural mordant at pH (4-7) then dryed at 85 °C for 3 min then cured at (110-160°C) for (1-4) min.. At L:R 1:20. A separate fabric was also dyed with no mordant.

2.2.3 Pre-mordanting using synthetic mordants

For each of the selected synthetic mordants cupper sulphate and Alum were carried out using the traditional exhaustion technique. The samples were mordnated in a solution contains 5 g/l mordant at 70 ^{o}C for 60 min., at L.R 1:50. Then the fabrics were dried without washing.

2.2.4 Dyeing

The pre-mordnated cotton/wool blended fabrics were dyed in a solution contains the extract dye with different concentrations (5-75%) without salt or any more additives, at (30-100) ^{o}C, for (30-60) min., at L.R 1:50.

3. Tests and Analyses

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

The colour strength expressed as K/S values was assessed by applying the Kubelka Munk equation.

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.

Fastness properties of dyed samples were tested according to ISO standard methods. The specific tests were: ISOX12 (1987), colour fastness to washing; and ISO 105-E04, colour fastness to perspiration: Furthermore the dyed samples were subjected to tests, for fastness to light by AATCC test method 16-1993.

4. Results and Discussion

4.1 Effect of type and concentration of the natural mordant

The effect of the type and concentration of the natural mordant, chitosan and aloe vera was evaluated by measuring K/S of the pre-mordnated fabrics at different concentrations (0 -10 g/l) of mordant using pad-dry-cure technique. First the samples were impressed in a solution contains one of the natural mordant at pH 5 then padded twice with pick up 70-80%, then dryed at 85 ^{o} C for 3 min., finally cured at 150 ^{o} C in case of chitosan and 120 ^{o} C in case of using aloe vera for 3 min. hence dyeing of the blended fabrics were applied. The results in Table 1 show that the color strength, K/S values, of all chitosan-pre-mordnated fabrics had higher values than the unmordnated. The K/S values increased gradually by raising the chitosan concentration. The results indicated that chitosan treatment on fabric provided more dye sites than unmordnated fabric. These can be explained that natural dyes contain unsaturated moiety bearing ionizable groups such as 2. hydroxyl and carboxylic groups. In water with right pH value, they become water soluble due to their presence in anionic forms. Cellulose by its nature is negatively charged in water, thus exhibiting poor absorption for natural dyes due to repulsion effect. The application of chitosan could help improve the absorption of natural dyes thanks to its cationic characteristic. The sorption of chitosan on the substrate is due to: i) ionic interaction between negative charges (hydroxyl anions in cellulose polymer (OH^{-}) and carboxylate anions (COO^{-}) in wool polymer), ii) protonated amino groups of chitosan ($^{+}NH3$), iii) hydrogen bonding and van der waals' forces. It is clear that, chitosan at 8 g/l concentration was selected to be the most suitable concentration for attaining the desired color yield K/S value.

In case of using aloe vera as a mordant, increasing its concentration results in an improvement in the K/S values after dyeing. The aloe vera-pre-mordnated fabrics had higher values than the unmordnated. It is obvious that, aloe vera at 6 g/l concentration was selected to be the more suitable concentration that attains the highest color yield (K/S) value. It is known that, aloe vera has phenolic groups and many minerals in its ingredients. Which form hydrogen bonding with hydroxyl groups of the cellulose polymer and amino/hydroxyl groups of protein polymer. Aloe vera also react with the substrate and the natural dye as the metallic mordant because it is already has many minerals like magnesium, calcium, zinc,…ect.[15]

Table 1. Effect of natural mordant concentration on the k/s values of the cotton/wool dyed fabrics.

Mordant conc. g/l	**K/S**	
	Aloe vera	**Chitosan**
0	2.78	2.78
2	3.04	3.16
4	4.53	4.67
6	5.11	5.61
8	5.43	5.68
10	5.49	5.80

Pre-mordnating conditions: pH 5,(0-10g/) lmordant, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: 25% natural dye, at 70 ^{o} C for 45 min., L.R 1:50.

4.2 Effect of pH of the pre-mordnating bath

As it can be seen in table 2, the appropriate pH for both mordants is 5. The present table is shown that increasing the pH for both mordants led to minimize the color values of the dyed fabrics. This may be attributed to reduce the extent of the cotton/wool blend modification, as well as the extent of the subsequent natural dyeing.

Table 2. Effect of the pH values on K/S values of the cotton/wool dyed fabrics.

Pre-mordnating pH	**K/S**	
	Aloe vera	**Chitosan**
3	3.16	3.27
4	4.35	4.51
5	5.45	5.61
6	3.76	3.97
7	1.94	2.54

Pre-mordnating conditions: pH (3-7), (8gl/) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: 25% natural dye, at 70 o C for 45 min., L.R 1:50.

4.3 Curing temperature of Pre-mordnating

It was found from table 3, that with raising temperature there was gradually increasing of K/S of dyed fabrics for both mordants. Curing at 150°C was the optimum degree in case of chitosan as a pre-mordant. It was 120°C in case of using aloe vera[16], noticed that with increasing temperature the fabrics become yellower.

Table 3. Effect of curing temperature on the K/S values of the coton/wool blended fabrics.

Curing temp. °C	**K/S**	
	Aloe vera	**Chitosan**
110	2.94	4.43
120	3.42	5.43
130	4.11	5.63
140	4.86	6.08
150	5.44	6.24
160	5.69	6.71

Pre-mordnating conditions: pH 5, (8gl/) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at (110-160°C) for 3 min. in case of chitosan and (110-160)°C for 2 min. in case of Aloe vera. Post dyeing condition: 25% natural dye, at 70 o C for 45 min., L.R 1:50.

4.4 Curing time of pre-mordnating

Figure 4 reveals the effect of treatment time on the reaction of mordants with cotton/wool blended fabrics. As is evident, table 4, increasing the treatment time from 1 to 4 min leads to an increase in the K / S values with both mordants. The optimum curing time for the dyed fabrics is 3 min in case of chitosan using and 2 min with aloe vera. But further increase in the pre-mordnating time leads to a change in the color hue in case of each chitosan and aloe vera as a pre-mordant.

Table 4. Effect of curing time on the K/S values of the cotton/wool blended fabrics.

Curing time min.	**K/S**	
	Aloe vera	**Chitosan**
1	3.97	4.83
2	4.79	5.45
3	5.42	6.09
4	5.97	6.90

Pre-mordnating conditions: pH 5, (8gl/) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C. in case of chitosan and 120°C in case of Aloe vera, for (1-4) min. Post dyeing condition: 25% natural dye, at 70 o C for 45 min., L.R 1:50.

5. Dyeing of pre-mordnated cotton/wool blended fabrics

5.1 Effect of dye concentration

The pre-mordnated cotton/wool blended fabrics were dyed using extract of onion skin natural dye with different concentrations (5, 15, 25, 35, 45%) (o.w.f) under fixed dyeing conditions.

It is clear from table 5 that generally, within the range examined, an increase in dye concentration is accompanied by an improvement in K/S values. After 35% of the natural dye concentration, almost stable K/S values were observed with both mordants; because there is no further increase in the K/S after saturation was observed even although more dye was available at a higher dyebath concentration.

Table 5. Effect of dye conc. on the K/S values of the pre-mordnating blended fabrics.

Dye conc. % (o.w.f)	**K/S**	
	Aloe vera	**Chitosan**
5%	3.66	3.72
15%	4.14	4.40
25%	5.40	5.49
35%	7.25	7.51
45%	7.56	7.78

Pre-modnating conditions: pH 5, (8g/l) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: (5-45%) natural dye, at 70 ^{o} C for 45 min., L.R 1:50.

5.2 Effect of the dyeing temperature

From the recorded data in table 6, it was found that the maximum K / S of the dyed samples was obtained at 70^{o}C for both used mordants but above that temperature the K/S tends to decreased. Because of the fibre swell ability is enhanced and, in turn, there is an increase in the rate of dye penetration into the vicinity of the substrate. But with a further increase in temperature, the affinity of the dye for the fibre minimized and, at the same time, the rate of hydrolysis of the dye increased.

Table 6. Effect of dyeing temperature on the K/S values of the pre-mordnating blended fabrics.

Dyeing temp. °C	**K/S**	
	Aloe vera	**Chitosan**
30	3.26	4.11
50	6.15	6.42
70	7.56	7.67
90	7.02	7.16

Pre-mordnating conditions: pH 5, (8g/l) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: 35% natural dye, at (30-90 ^{o} C) for 45 min., L.R 1:50.

5.3 Effect of the dyeing time

Results of table 7 signify the effect of the dyeing time on the K/S of the pre-mordanted fabrics.

It was seemed that the color strength gradually increased as the time increase. This can be attributed to the slight diffusion with short dyeing time. Because coloring component attained equilibrium from dye bath to fabric, which increases with time.45 min. was chosen to be the optimal dyeing time because after this period no remarkable increasing found.

Table 7. Effect of dyeing time on the K/S values of the pre-mordnating blended fabrics.

Dyeing time min.	**K/S**	
	Aloe vera	**Chitosan**
15	5.97	6.09
30	7.06	7.13
45	7.30	7.50
60	7.41	7.65

Pre-mordnating conditions: pH 5, (8g/) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: 25% natural dye, at 70 ^{o} C for (15-60 min.), L.R 1:50.

6. Fastness properties

The color fastness is usually rated by loss of depth of color in original sample. The results of fastness properties of dyed cotton/wool blended fabrics by using extract of onion skin natural dye via pre-mordnating technique with traditional synthetic mordants (Copper sulphate, Alum) and eco-friendly natural mordants (chitosan, aloe vera) are illustrated in table 8. It can be concluded that fastness properties were good to excellent by using the synthetic or natural mordants. The chemistry of binding of natural dyes to fibers is complex. It involves direct bonding, Hydrogen- bond and hydrophobic interactions. Mordants help binding of dyes to fabric by forming a chemical bridge from dye to fiber that is clear in case of using the synthetic or natural mordants, thus decreasing the staining ability of a dye along with increasing its fastness properties.

Table 8. Colour fastness properties of pre-mordnating cotton/wool blended fabrics dyed with onion skin (Allium Cena) natural dyes

Cationising Agent	**K/S**	**Washing Fastness 60 °C**	**Prespiration Acidic alkaline Cotton wool**		**Light**
Aloe vera	7.14	3-4	4	4	7
Chitosan	7.67	5	4-5	5	6-7
$CuSO_4$	6.29	5	4	5	6-7
Alum	7.19	4-5	4	5	6

Pre-morrdnating conditions: pH 5, (8g/) in case of using chitosan (6g/l) in case of using Aloe vera, drying at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. Post dyeing condition: 25% natural dye, at 70 ^{o} C for 45 min., L.R 1:50.

Conclusion:

Cotton/wool blended fabrics were dyed using Allium Cena natural dye (extracted from onion skin using microwave irradiation technique). The fabrics were pre-mordnated using chitosan and aloe vera. The fabrics were padded in a solution contains (8g/) in case of using chitosan (6g/l) in case of using Aloe vera, then dried at 85°C for 3 min., curing at 150°C for 3 min. in case of chitosan and 120°C for 2 min. in case of Aloe vera. The fabrics post dyeid in solution contains 25% natural dye (Allium Cena), at 70 ^{o} C for 45 min., L.R 1:50.

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