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Optimizing the Dyeing Process of Wool/Nylon Blend Fabric Pretreated with Protease Enzyme Using Cutch Natural Dye

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ABSTRACT: Surface modification of wool/nylon blended fabric was carried out with protease enzyme to improve their dyeabilities to natural dyes. Cutch (*Acacia Catechu)* was selected and used in this study. The effect of enzyme concentration on the dye uptake (K/S) was studied at fixed treatment conditions: pH, temperature and treatment time.

The obtained results of K/S were compared to the corresponding values obtained for the control samples which were dyed without enzymatic pretreatment. Treatment with protease was found to increase the absorption capacity of both wool and nylon fibers to the natural dye leading to higher K/S compared to untreated samples.

The dyeing parameters were also studied including, dyeing pH, temperature, time and mordant concentration along with concentration of dispersing agent. The colour strength was observed to increase by increasing the pH of dye bath, temperature and concentration of dispersing agent, which may be attributed to increasing dye solubility and as a result the rate of diffusion and penetration of the dye inside the fibers of both nylon and wool.

Fastness properties to washing, perspiration and light were also assessed and were observed to range between good and excellent.

KEYWORDS: Wool/ nylon, blend, protease, natural dye, cutch, dyeing.

1 INTRODUCTION

The use of enzymes in textile industry is one of the most rapidly growing fields in industrial enzymology **[1]**. Because of the new environmental directives, the development of clean technologies such as enzymatic finishing processes is a priority **[2]**. The use of enzymes in the textile chemical processing is rapidly gaining globally recognition because of their non-toxic and eco-friendly characteristics with the increasingly important requirements for textile manufactures to reduce pollution in textile production. **[1]** The use of enzymes in the textile industry is an example of white/industrial biotechnology, which allows the development of environmentally friendly technologies in fibre processing and strategies to improve the final product quality. **[3]** Enzymes not only work efficiently and rapidly, but they are also biodegradable. **[2]**

Wool textile industry is one of the most promising areas for many countries, but there is no real improvement in the Middle East. Regarding that most of the chemicals used in wool treatment are patently protected and environmentally unfriendly; enzymatic treatment will be the best solution. Proteases are being used to decrease the felting tendency of wool and to improve the feel of the fabrics by imparting soft and smooth handle. **[4]**

Enzyme treatment of woven woolen fabric causes the scales to be flattened thereby made the fabric smooth and soft. It also improved other physical properties including hand, drapability, absorbency, dyeability and colour fastness properties. **[2]** Enzyme pretreatment of wool fabric decreases the resistance of the fiber to dye diffusion and so it increases the adsorption rate constant and decreases the apparent activation energy for the dyestuff when compared to untreated fabric. **[5]**

On the other hand, enzymatic hydrolysis of synthetic fibers to improve some of their undesired properties, such as hydrophobicity, low dyeability, and insufficient washability, is of interest to industrial chemists. Studies showed that nylon oligomers can be hydrolyzed by proteolytic enzymes. **[6]**

Importance of mixing and blending of fibers that is to reduces costs by mixing a cheap fibre with a more expensive one, combines properties of fibres in order to cover up less desirable characteristics in one fibre and give improved fabric performance, gives different texture and colour effects and improves wearing qualities.

As for nylon/wool blended fabrics, the blending of nylon with wool makes the fabric more absorbent and softer. It becomes more strong and durable. **[7]**

Wool/polyamide is a very popular blend for woven apparel and carpets. It can show the complementary properties compared to pure polyamide or wool fibers in terms of crease recovery, durability, abrasion resistance, fast drying, and dimensional stability. **[8]**

Recently there has been revival of the growing interest on the application of natural dyes on natural fibres **[9]** and synthetic ones as well, although little information is available on dyeing of synthetic filament **[10-11]**, due to worldwide environmental consciousness. **[9]** Dye compounds from natural resources especially from plants are increasingly becoming important alternatives to synthetic dyes for use in the textile industry. Unlike synthetic dyes which have been found to be toxic and harmful to the environment, natural dyes are biodegradable, non- toxic and generally have higher compatibility with the environment when compared with their synthetic counterparts. Natural dyes can provide a wide range of beautiful shades with acceptable levels of colour fastness. Hence there is considerable research work being undertaken across the world on the application of natural dyes in the textile industry. **[12]**

In the present study an attempt has been made to develop a complete eco-friendly system of bio-treating and dyeing of wool/ nylon blended fabrics with cutch natural dye and analyzing all factors that may affect the dyeing process in order to achieve maximum colour strength by applying the optimum conditions.

2 EXPERIMENTAL

2.1 MATERIALS

2.1.1 FABRIC

Three different types of knitted fabrics were used throughout this study, namely: 100% wool fabric with weight 180 gm/m^2, 100% nylon (poly-amide) fabric with weight 140 gm/m^2 and 50/50% blend fabric (wool/nylon) with weight 165 gm/m^2. These fabrics were received from Delta Textile Egypt Company, Cairo, Egypt.

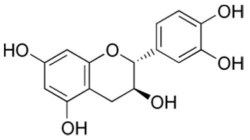
2.1.2 DYES

Cutch natural dye (extracted powder) was produced by “Table rock Llamas Fiber Arts Studio, Inc.”, Colorado, USA.

Cutch/Catechu/Katha is a brown natural dye obtained chiefly from the heartwood of Acacia catechu, found in most of the Indian sub-Himalayas. The chief colouring component present in cutch is catechin having molecular formula $C_{15}H_{14}O_6$. **[13]**

The structure of Cutch dye is shown in table (1).

Table 1. Structure of Cutch dye

Common name	Botanical name	Part used	Chemical structure	C.I No.
Catechin	*Acacia catechu*	Heartwood of Acacia catechu		**Natural Brown 3**

2.1.3 ENZYMES

Protease enzyme was kindly supplied from TRANS CHEM. Company, Egypt.

2.1.4 CHEMICALS AND AUXILIARIES

Acetic acid, hydrochloric acid and sodium carbonate of laboratory grade were used.

Non-ionic detergent (Chromatech 3.Q.J) supplied by Chromatech Co., England, and a dispersing agent (Ebcasperse RJL) supplied by Egyptian British Co., Egypt, were also used.

Ferrous sulphate ($FeSO_4.7H_2O$) and Alum (Aluminum Sulfate) were used as mordants throughout this work.

2.2 METHODS

2.2.1 TWO- BATH (ENZYMATIC TREATMENT THEN DYEING)

Wool, nylon and wool/nylon blended fabrics were bio-treated first in a bath containing 2gm/L enzyme at L.R. 1:50, the process was performed at pH= 8 and at 50°C for 40 minutes , as determined in our previous published work **[14]**

Then the pretreated samples were rinsed with cold water and then with hot water at 85°C for 15 minutes to denature the enzyme. Finally the samples were rinsed with cold water and air- dried.

After which the treated samples were dyed with cutch natural dye in a separate bath at L.R 1:50 with 4% dye with usage of different concentrations of dispersing agent, i.e. (0, 1, 1.5, 2, and 3 gm/L).

The dyeing process was carried out at various pH values ranging from 4 to 9 to study the impact of pH value of the dyeing bath on the received colour strength. Also the dyeing temperature factor was studied, so the dyeing process was performed at different temperatures namely; 60, 70, 80, 90, 94°C.

The dyeing process was carried out for different durations ranging from 30-90 min, after which the mordant was added to the same bath using different concentrations (0-10 gm/L) at 90°C, and the dyeing process was continued for another 30 minutes. Then the washing process was performed with 2 gm/L non-ionic detergent at 50°C for 15 minutes.

The following diagram explains the used two- bath method (enzymatic treatment then dyeing).

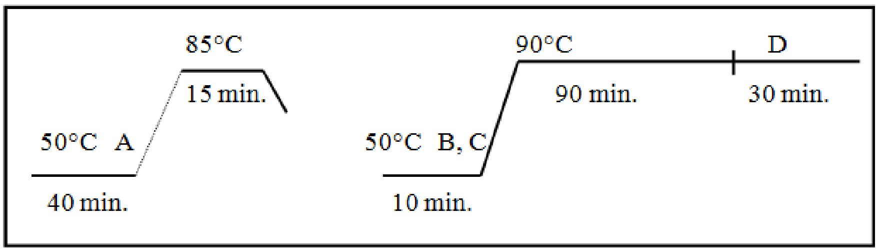


Fig. 1. (A) protease enzyme, (B) Ebcasperse a dispersing agent, (C) cutch dye, (D) mordant

2.3 MEASUREMENTS AND TESTING

2.3.1 COLOUR MEASUREMENTS

The dyed samples were subjected to colour measurement by using reflection spectrophotometer model Optimatch 3100, SDL Company, England. The K/S values were obtained directly according to 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.

2.3.2 COLOUR FASTNESS

Fastness properties of the dyed fabrics and mordanted with alum and ferrous sulphate were evaluated according to ISO standard methods. The specific tests were: colour fastness to domestic and commercial laundering: ISO 105-C02 and colour fastness to perspiration: ISO 105-E04. The samples were also subjected to light fastness standard test (Xenon Lamp), according to ISO test method: ISO 105-B02.

3 RESULTS AND DISCUSSION

3.1 PROTEOLYTIC SURFACE MODIFICATION OF FIBRE BLEND BY PROTEASE ENZYME

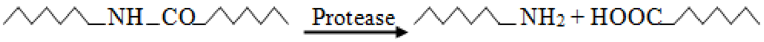
Wool/ nylon blend as well as wool and nylon fabrics were treated with protease to modify their fibre surface for improving their accessibility to dyeing with cutch natural dye. The dyeing results were compared to that of untreated samples and dyed at similar conditions. The results are shown in table (2):

Table 2. The colour strength (K/S) of protease treated samples and dyed with cutch dye compared to the untreated fabrics

Fabrics	K/S of dyeings		% increase in K/S
	untreated	treated	
wool	16.45	20.20	22.80
nylon	3.46	3.65	5.49
blend	9.81	11.23	14.48

As can be seen from table (2), compared to unmodified samples, modification with enzyme led to obvious increase in the dye uptake (K/S) of fabrics dyed with cutch. The surface modification of both wool and nylon fibres facilitate the penetration of dye molecules inside the fibres. Protease catalyses proteolytic reaction to scales of wool fibres attacking the peptide links and at the same time hydrolysis some of the amide groups of nylon polymer chains. **[15]** As a result, the fine structures of both fibres were open up which facilitate the diffusion of dyes and result in more dye to penetrate inside the fibres. **[16]**

The biohydrolysis reaction of amide groups by protease is shown below:



The change in the chemical structure of both wool and nylon fibres in the blend was accompanied with obvious increase in dye uptake. Surface modification of fibres was carried out by proteolytic hydrolysis of amide links under the action of protease.

3.2 OPTIMIZING THE DYEING CONDITIONS WITH CUTCH

The different dyeing parameters were studied to optimize the dyeing conditions for realizing highest colour yield on the different fibres with maximum colour uniformity.

3.2.1 DYE BATH PH

The effect of pH of dyeing process on the dye uptake and colour strength was studied and the results are shown in figure (2).

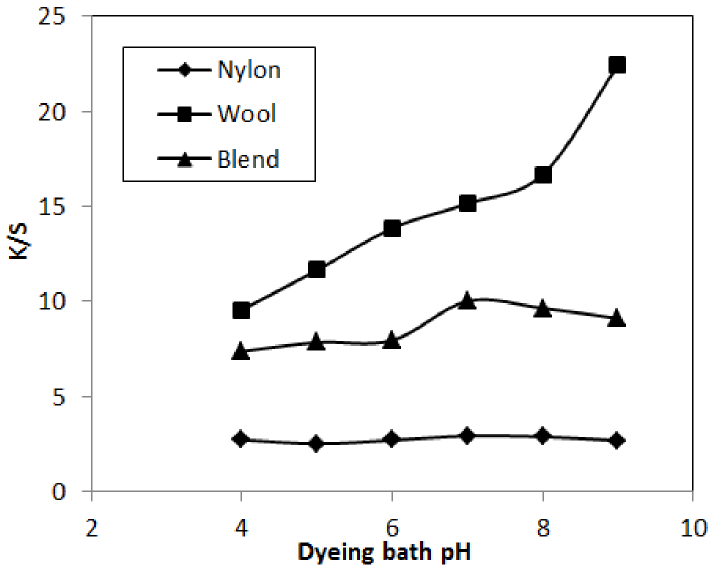


Fig. 2. Effect of pH value of the dyeing bath on the K/S of the fabrics dyed with cutch natural dye

It was observed, from fig. (2), that the K/S was gradually increased on the different fabrics as the pH increased from 4 up to 7. The maximum % increase in K/S reached about 58.31%, 35.54% and 7.27% for wool, blend and nylon fabrics respectively. It is well known that most natural dyes aggregate in aqueous solution like disperse dyes **[17].** These aggregates attributed essentially to intermolecular attraction which is mainly due to hydrogen bonding and van der waals forces **[18].** These aggregates are broken down under the action of either high pH values or by addition of surfactants as well as temperature. The overall result is to increase dye uptake **[17].**

Natural dyes contain aromatic hydroxyl groups in their chemical structure capable of ionizing under alkaline medium, leading to greater solubility. The degree of dye solubility depends on the number of hydroxyl groups contained in dye molecule and the pH of aqueous solution. Increasing dye solubility will accelerate the disaggregation of micelles and the dye will present in solution in lowest molecular size. As a result, the rate of diffusion and penetration of dye molecules inside the fibres was accelerated and the dye uptake increased.

The colour strength of wool fibre was observed to be greater compared to nylon fibre which may be attributed to the difference in morphological structure of the two fibres. The great hydrophilicity and lower crystallinity of wool, compared to nylon fibre, facilitates the diffusion of dye molecules inside the fibres. The polar groups contained in nylon are predominately amide –CO-NH- and the number of strongly hydrophilic groups is very limited. Consequently the swelling of nylon in water is small compared to wool fibre. Therefore, the absence of swelling greatly hinders the penetration of dye molecules into nylon fibre.

It may be concluded, from the previous results, that maximum colour yield (K/S) was attained on wool/nylon blend at pH=7 due to the disaggregation of dye micelles which accelerates the rate of diffusion and penetration of dyes inside the fibres.

3.2.2 ACTION OF DISPERSING AGENT

The effect of dispersing agent on efficiency of dyeing wool/nylon, as well as wool and nylon fabrics with cutch dye was studied and the results are plotted in figure (3).

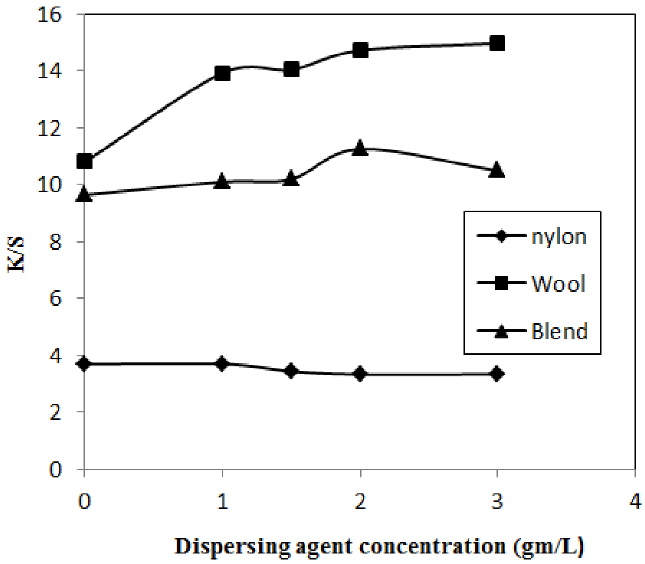


Fig. 3. Effect of dispersing agent concentration on the colour strength of the fabrics dyed with cutch natural dye

Increasing the concentration of dispersing agent in the dye bath was found to improve the dye uptake (K/S) especially on wool and wool/nylon blend until reached about 2 gm/L conc. An improved levelling of dyeing was also attained. The colour strengths of wool and blend fabrics were increased by about 36.26% and 16.68% respectively compared to samples dyed without dispersing agent.

There is a correlation between the function of dispersing agent on the rate of dyeing and the dye bath pH. Disaggregation of dye molecules (micelle) under the action of dispersing agent was found to increase dye solubility, as in case of pH, hence lowering dye size and increasing the rate of dye diffusion inside the fibre phase **[17].**

3.2.3 DYEING TEMPERATURE

Different samples of fabrics were dyed with 4% cutch dye (owf), under fixed dyeing parameters except for temperature which ranged from 60°C to 100°C. When increasing the dyeing temperature from 60°C up to 90°C (fig.4), the colour strength (K/S) was gradually increased for the different fabrics; wool/nylon, wool and nylon, over 90°C there was a decrease in the (K/S).

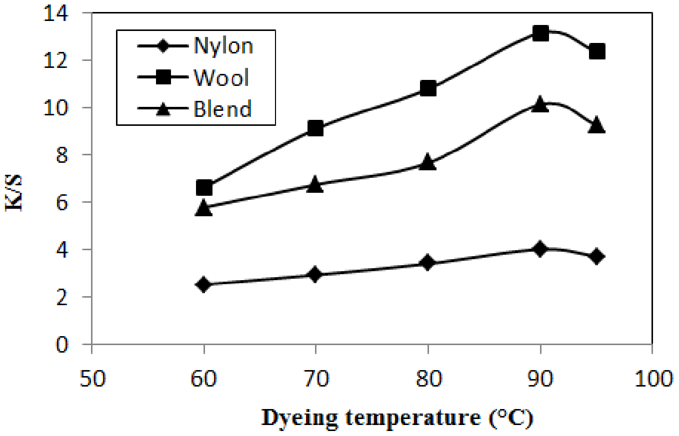


Fig. 4. Effect of dyeing temperature on the colour strength of the fabrics dyed with cutch natural dye

The difference in the rate of dyeing and the gradient increase in K/S differ from one substrate to another owing to difference in their chemical and morphological structures. By raising the dyeing temperature from 60°C to 90°C the K/S were increased by about 98.04%; 75.13% and 58.27% for wool; wool/nylon blend and nylon fabrics respectively. The great increase in colour strengths at higher temperatures can be attributed to the higher kinetic energy of the dye and to easier diffusion of dye molecules in the more open fibre structure due to swelling. High temperature accelerates and facilitates the rate of dye adsorption and penetration inside the fibre and enhances the migration to attain higher levelling of dyeing.

By raising the temperature of dyeing over 90°C to reach 100°C, the K/S was observed to decrease owing to the possibility of desorption of dye and the breaking of some dye-metal-fibre complexes on the fibres. Hence, it may be concluded, from the previous results, that the optimum dyeing temperature which attaining maximum dye absorption and fixation of cutch natural dye on wool/nylon blended fabrics is at 90°C.

3.2.4 DYEING TIME

The dyeing process was carried out on the three kinds of fabrics, i.e. nylon, wool and nylon /wool blend by using 4% cutch dye, at pH= 7 and at 90°C for different durations e.g. (30, 45, 60, 75 and 90) and the results are shown in **Fig. (5).**

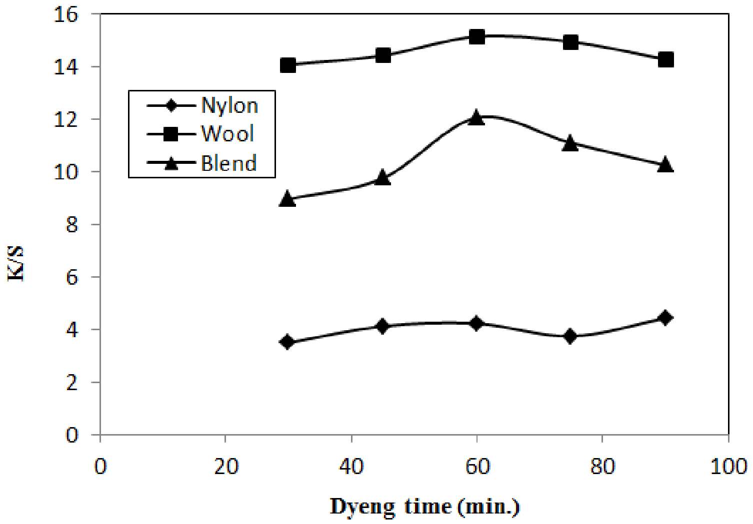


Fig. 5. Effect of dyeing time on the colour strength of the fabrics dyed with cutch natural dye

It is observed from figure (5) that by lasting time of dyeing the colour strength for the different fabrics was gradually increased. Maximum dye absorption giving the highest colour strengths were attained after dyeing for 60 minutes, beyond which the K/S was decreased.

This result may be explained by the possibility of attaining dyeing equilibrium at 60 min., depending on the rate of dye diffusion inside the fibre. **[19]**

3.2.5 MORDANTING

Mordant dyeing is known to carry out for fixing the fugitive natural dyes on the fibre to increase their fastness to washing. Mordant dyeing may be carried out in one stage, i.e. simultaneous dyeing and mordanting as in the present study, or in two separate stages, i.e. pre- mordanting or post- mordanting.

Two metal salts were used at different concentrations to determine the most suitable concentration for mordanting dyeing with cutch natural dye on wool/nylon blended fabrics. The variations in K/S of dyed samples as a function of increasing mordant concentration from zero to 10 gm/L are shown in figure (6).

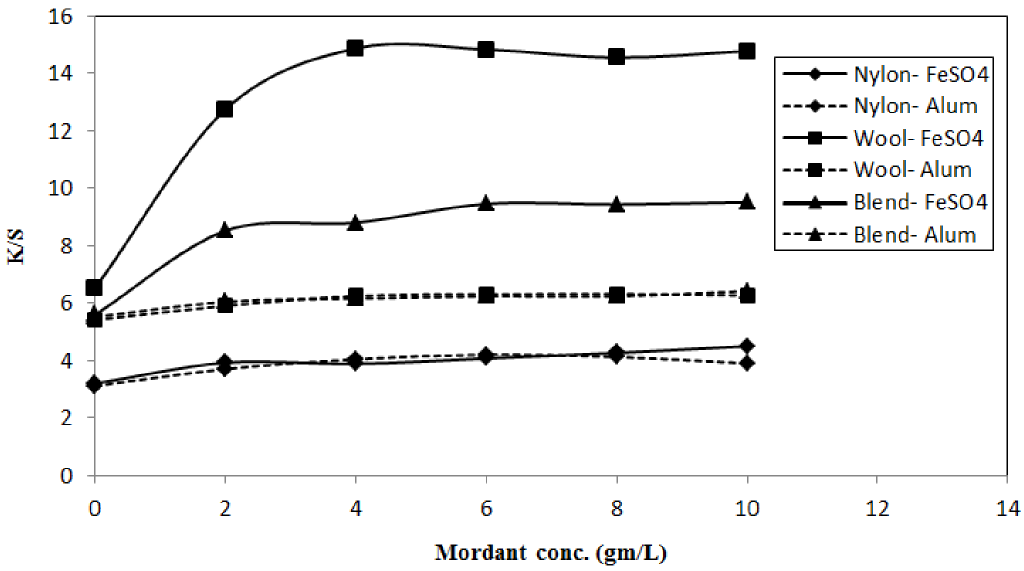


Fig. 6. Effect of mordant concentration on the colour strength of the dyed fabrics with cutch natural dye

A gradual increase in K/S is clearly observed by increasing the mordant concentration in the dye bath. The similar trend may be observed for the different fabrics; wool/nylon, wool and nylon. Maximum K/S were attained by using 10 gm/L $FeSO_4$ for both nylon and wool/nylon blend, whereas the suitable concentration was 4 gm/L for wool fabric. For alum mordant, 6 gm/L concentration was observed to be the most suitable for achieving highest K/S on both nylon and wool fabrics and 10 gm/L for the blend. Thus, considering the dyeing cost and colour strength especially on the blended fabric, the optimum mordant concentration was chosen to be 6 gm/L for both mordants.

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

a) Formation of dye- metal complexes of 2:1 or 1:1 types which interact with the positively charged dye sites in wool fibre through electrostatic attraction. **b)** Formation of dye- metal- fibre complexes through coordination reactions. It is well known that amines form stable complexes with metal ions, some previous studies indicate the participation of the primary amine of the polymer in the formation of the complex with divalent metal ions.**[20]**

Carboxyl groups in the polypeptide molecules were also suggested to play a role in the binding with metal cations. **[21]** If the coordination linkages between the fibre, the metal and the dye were the major form of intermolecular interaction, then the dyes would by virtue of these quite strong bonds, be expected to exhibit very high wash fastness. **[22]**

The reaction mechanism of mordanting may be represented in the following figure (7).

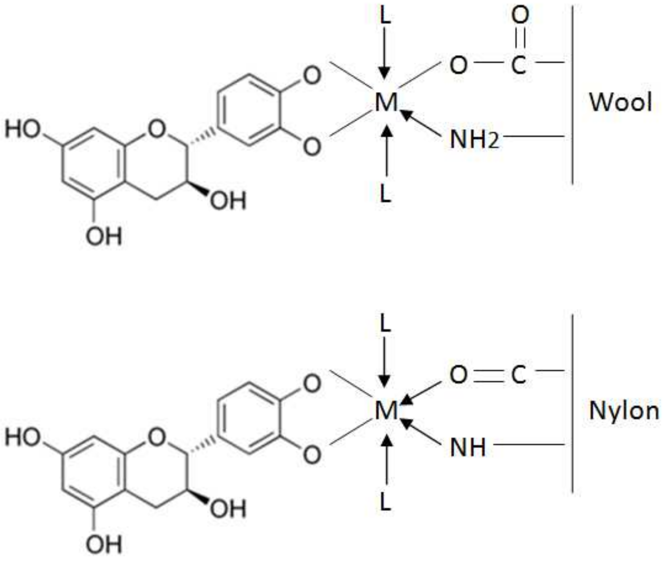


Fig. 7. The proposed reaction mechanism of mordanting of dyed wool and nylon fabrics with cutch dye

It was stated that the stability of chelate formation between the amine- containing fibre such as proteins and the metal ions is correlated to the electronegativity of the metal, increasing the electronegative character of the metal result in higher stability of the formed chelate between fibre and metal. **[20]**

The efficiency of mordanting, i.e. the rate and degree of metal complexing reaction, was found to be depend on the pH of the reaction medium. **[21]** Metal hydroxides react faster than other forms of metal with –OH groups of natural dyes. Thus, by elevating the pH value the metal tend to exist in the hydroxide form which accelerates the complexation reaction. In the present work the mordanting was carried out in the dye bath since the pH was adjusted at 8.

3.3 FASTNESS PROPERTIES

Wool/ nylon blend fabric dyed with cutch natural dye as well as wool and nylon fabrics and mordanted with alum and $FeSO_4$ were subjected to fastness tests to washing, perspiration and light. The obtained results are formulated in table (3).

Table 3. Fastness properties of enzymatic pre-treated, dyed and mordanted fabrics

Fastness Test		**Fastness to washing**			**Fastness to perspiration**						**Light Fastness**
					Acidic			Alkaline			
		Alt.	SC	SW	Alt.	SC	SW	Alt.	SC	SW	
$FeSO_4$ **mordant**	W	4	3-4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	N	4	3-4	4	4-5	4	4-5	4-5	4-5	4-5	4
	B	4	3-4	4	4-5	4	4-5	4-5	4-5	4-5	3
Alum mordant	W	4	3-4	4	4-5	4	4-5	4-5	4-5	4-5	3
	N	4	3-4	4	4	4	4-5	4-5	4	4-5	3
	B	4	3	4	4	4	4-5	4-5	4-5	4-5	2-3

N.B.:*- Alt. = Alteration or change in colour. , SC= Staining on Cotton. and SW= Staining on wool.*
- (W) for wool samples, (N) for nylon samples and (B) for blend samples.

It is showed from table (3), that there are general improved fastness properties especially with $FeSO_4$ mordant. Fastness to washing of dyed samples and mordanted with both alum and ferrous sulphate gave a similar results ranges between very good (4) for colour change and from good to very good (3-4) for staining. The wash fastness depends on the strength of the binding forces between the mordant and both fibres and dye molecules **[23]**.

The high fastness to washing of metal complex dyes is due to the ability of the dye molecules to aggregate into large particles in the fibre, and not because of the additional forces of attraction between fibre and metal ions. **[24]** Thus, the metal complexation reaction between the various phenolic hydroxyl groups present in the cutch molecule and metal cation lead to formation of big precipitates on fibre surface or/ and inside the fibre with higher resistance to wet treatments.

Fastness to perspiration was found to be ranged from very good (4) to very good- excellent (4/ 4-5) with the two used mordants. As for light fastness, it was observed to be good (3) on wool/nylon blend to very good on nylon and excellent on wool fabrics with ferrous sulphate. Light fastness of the dyed fabrics depends on constitution of dyes , textile structure and fibre type

4 CONCLUSION

This study illustrates the importance of enzymatic treatment with protease enzyme and how it would affect the efficiency of dyeing wool/ nylon blended fabric with cutch natural dye. Treating the different fabrics, namely: wool, nylon and wool/nylon blended fabrics with 2gm/L enzyme at pH= 8 and at 50°C for 40 minutes led to valuable increase in the colour strength for the different fabrics. This is due to the surface modification of fibres done by the bio- treatment using the protease enzyme.

All dyeing parameters were studied in details in order to figure out the optimum conditions for applying cutch natural dye on pre-treated wool/ nylon blended fabrics. It was found that maximum colour yield (K/S) was attained on wool/nylon blend when adjusting the dyeing pH at 7 due to the disaggregation of dye micelles. It was also concluded that attaining maximum dye absorption and fixation was established, when performing the dyeing process at 90°C for 60 minutes. It was found that using 2 gm/L dispersing agent in the dye bath, increase dye solubility, leading to better uniformity and increase the dye uptake as well, in case of wool and wool/ nylon blended fabric. The fastness properties of dyed fabrics to washing, perspiration and light were found to range between good to very good- excellent for the two mordants used, i.e. ferrous sulphate and alum.

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