Eco-dyeing of Nylon Fabric Using Natural Dyes Extracted from Onion Outer Shells: Assessment of the Effect of Different Mordant on Color and Fastness Properties.

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Abstract: Onion (allium cepa) extract has been used in textile and leather industry as a colorant. Natural colors have attracted the attention of the entire world because of their non-hazardous nature. In the present study, nylon fabric was dyed with onion (allium cepa) natural dye using various mordants such as alum, copper sulphate and potassium dichromate by HTHP dyeing methods. The dyeing behavior of dyes was assessed by colorimetric evaluations of fabrics were carried out by spectrophotometer. Good wash-fastness, rubbing-fastness, light-fastness, water-fastness and perspiration-fastnesswere obtained.

Keywords: Onion (Allium cepa) natural dye, HTHP, Mordant, Nylon fabric.

1 Introduction

Recently environmental concerns have created an increasing demand for natural dyes which are friendlier to the environment than synthetic dyes. Synthetic dyes have a wide range of hazardous effect. They are toxic or poisonous, corrosive (destructive to living tissues), irritants (induce local inflammatory reaction in living tissues), infection (represent a potential source of the transmission of diseases to human, domestic animal or wild life), radioactive etc. Natural dyes are non-carcinogenic, produce soothing and exclusive color to the textiles, and have better biodegradability and higher compatibility with the environment. Among the natural dyes, plant dyes are potential sources because of their easy availability and abundant nature. Natural dyes have many advantages, such as low toxicity and allergic reactions in addition to bio-degradability because they are taken from animal or plant matter without chemical processing. However, the use of natural dyes declined to a great extent with the advent of synthetic dyes, which have moderate-to-excellent color fastness properties in 1865. During the decade of the 1990s, the textile and apparel industries, particularly the coloration industry, have been widely criticized for their role in polluting the environment. For these reasons, the use of carcinogenic dyes has been restricted and the use of natural dyes has increased [1,2,3,4,5,6,7,8,9,10].The use of synthetic dyestuffs during their application in the dyeing and printing industries has been criticized due to introduction of contaminants into the environment. This has led to the desire to turn to the traditional/more natural way of life (i.e. biological (organic) farming, natural food etc.) with a belief that “All natural things are good for life on the Earth”. In line with this trend, there is now an ever increasing lobby for using natural coloring matters for textile substrates both natural and synthetic [11,12]. The contemporary textile processing industry is getting more and more inquiries regarding “Dyeing with Natural Dyes” and therefore the subject of natural colors has assumed a great significance. Recently, an exhaustive review on the subject of natural dyes in textile applications has been published by Taylor [13].Acid dyes in general, are more resistant to ozone fading than disperse dyes and hence the latter almost entirely have been replaced by acid dyes in the nylon carpet dying industry [14].The poor resistance to ozone fading of disperse dyes has been attributed to their relatively small molecular size and lack of ionic character [15].Ozone is a strong oxidizing agent that destroys the chromophores of certain type of dyes. For example: ozone can attack the anthraquinone ring of a dye molecule and convert it into colorless phthalic acid derivatives [16].The outermost dry papery skins of Onion are the best source of the color, which contain flavonoid quercetol, kaempferol, quercetin-3-glucoside and some tannin. Lac is the resinous protective secretion of the tiny Lac insect, which is a pest on a number of plants. The insects secrete a thick resinous fluid, which envelops their bodies, forming a hard continuous encrustation over the twigs. The twigs are harvested and the encrustation scraped off dried and processed to yield shellac or the dye [17]. Nylon is a polyamide that is mostly manufactured through condensation polymerization of di-amine and di-acid. Generally, nylon is dyed with acid dyes as well as reactive and disperse dyes [18, 19].Some researchers have studied dyeing nylon with natural dyes such as indigo, onion, lac, turmeric, kamala and henna [20, 18, and 8]. But the total share of natural dyes in the textile sector is approximately only 1 % due to certain technical and sustainability issues involved in the production and application of these dyes such as non-availability in ready-to-use standard form, unsuitability for machine use, and limited and non-reproducible shades. Natural dyes per se are sustainable as they are renewable and biodegradable but they cannot fulfill the huge demand from the textile sector in view of the preferential use of land for food and feed purposes.

2 Application of natural dyes on textiles

Natural dyes are mostly employed for dyeing of natural fiber textiles to enhance their eco-friendly characteristics. They are usually applied to textiles by dyeing. Apart from indigo, other natural dyes are usually not used for printing directly. For producing printed fabrics, the printing is usually done with mordant and the whole material is dyed whereby only the area printed with mordant picks up the color. Natural dyes, like synthetic dyes, can also be used to dye textiles at all stages such as fiber, yarn, or fabric. Fiber dyeing has the advantage that any shade variation can be easily adjusted by blending and

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therefore has been practiced at industrial scale also but is costly due to problems in spinning and loss of dyed fibers. Wool is generally dyed in yarn form and traditional dyers prefer yarn dyeing for all materials as it offers versatility in designing during weaving. Dyeing is normally carried out by hand in large vessels. Iron, stainless steel, copper, and aluminum vessels are used. Dyeing in copper vessels is considered to produce bright shades. Aluminum vessels are normally stained with a particular dye hence should be used if only one type of dye is used. Stainless steel vessels are most preferred for the natural dyeing process. On a larger scale, hank-dyeing machines have been successfully used.

3 History of Nylon Fibers

Nylon is a manufactured fiber in which the fiber forming substance is a long-chain synthetic polyamide in which less than 85% of the amide-linkages are attached directly (-CO-NH-) to two aliphatic groups. Nylon is a synthetic polymer, a plastic, invented on February 28, 1935 by Wallace Carothers at the E.I. du Pont de Nemours and Company of Wilmington, Delaware, USA. The material was announced in 1938 and the first nylon products; a nylon bristle toothbrush made with nylon yarn (went on sale on February 24, 1938) and more famously, women's stockings (went on sale on May 15, 1940). Nylon fibers are now used to make many synthetic fabrics, and solid nylon is used as an engineering material.

3.1 Characteristics of Nylon Fibers

- Exceptionally strong
- Elastic
- Abrasion resistant
- Lustrous
- Easy to wash
- Resistant to damage from oil and many chemicals
- Can be pre-colored or dyed in wide range of colors
- Resilient
- Low in moisture absorbency
- Filament yarns provide smooth, soft, long-lasting fabrics
- Spun yarns lend fabrics light weight and warmth

3.2 Chemical structure of Nylon 6, 6 Fibers

Shows nylon 6,6 fibers structure draws using by the chemical software JChem.

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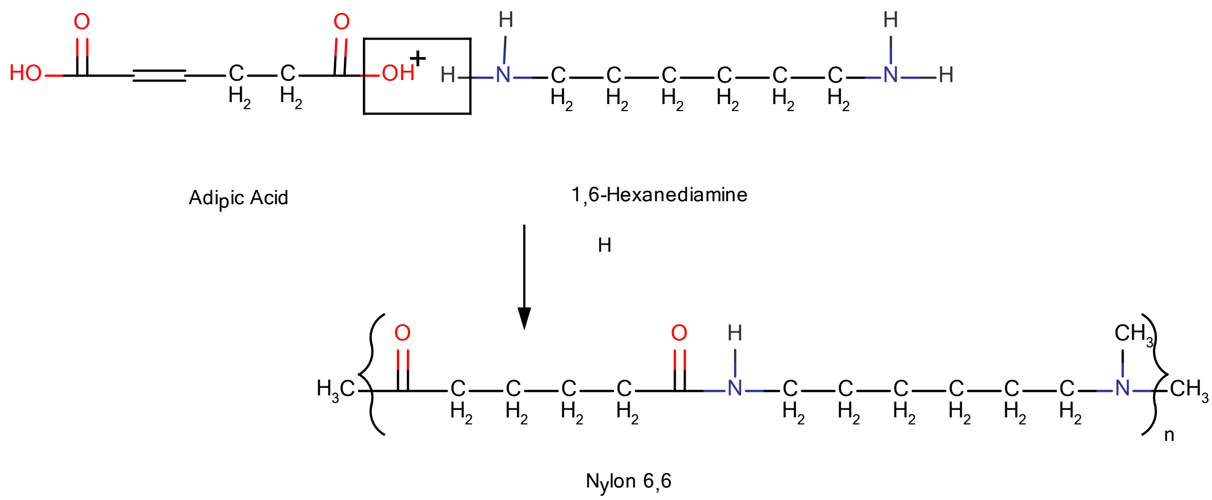


Figure 1Nylon 6,6

3.3 Chemical structure of Nylon 6 Fibers

Shows nylon 6 fibers structure draws using by the chemical software JChem.

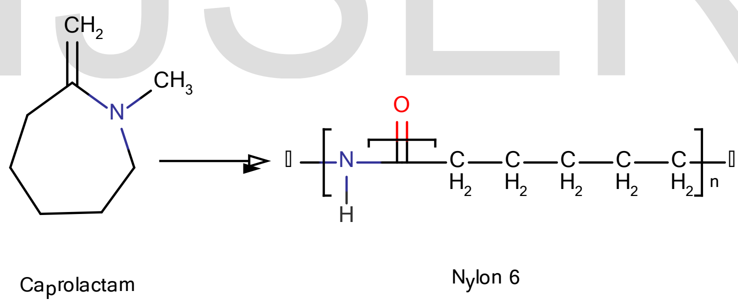


Figure 2Nylon 6

4 Experimental

4.1 Materials

Copper (II) sulphate pent hydrate ($CuSO_4$ .5 H_2O), Potassium di-chromate ($K_2Cr_2O_7$), Alum (KAl $(SO_4)_2$. $12H_2O$ used as mordants, provided from commercial sources. All mordants, except alum, were of analytic grade. All chemicals were used without purification.

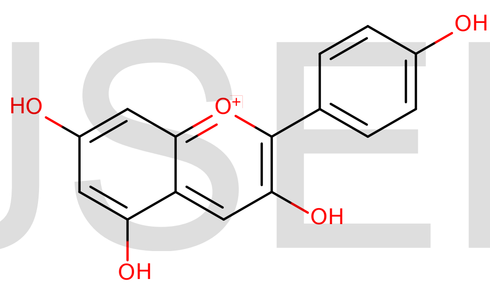
4.2 Instrument

Onion shells, 100% (Nylon fabric), Different types of chemicals, Milling machine, Automatic Heater (ZNHW HEATER Co.), Automatic Stirrer, Laboratory dyeing machine, Hot air dryer, Crockmeter, Color-fastness tester, ISO grey scale.

Onion (Allium cepa) belongs to the Lilliaceaefamily and is grown all over the world. Yellow onion outer shells create a golden range of earthy colors. With a concentrated dye bath and enough time for the fibers to soak, the colors achieved are a combination of red and yellow, usually resting in the middle as an orange. The results radiate warmth and happiness, combining the physical energy and stimulation of red with the cheerfulness of yellow. Protein fibers such as wool and silk dye deep to medium shades of ochre, creating pigments in the cadmium-orange families.

Onion outer shells are the most commonly discarded household and commercial food waste which can be used as dyes for coloring natural textile materials. These dyes, which are known as pelargonidin (3,5,7,4'-tetrahydroxyanthocyanidin), work like acid dyes that can dye the protein fibers at high efficiency. The amount of pelargonidin was found to be 2.25% in certain solvent extraction process using soxhlet apparatus. Due to presence of four hydroxy groups (Auxochrome groups) pelargonidin exhibits good dyeing properties for dyeing of natural fibers.

The molecular structure of onion skin dye (pelargonidin) is shown in below figure.



Structure no-6: Pelargonidin.

4.3 Extraction of dyes

As natural dye-bearing materials contain only a small percentage of coloring matter or dye along with a number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, among others, extraction is an essential step not only for preparing purified natural dyes but is also required to be carried out by users of crude dye-bearing materials. As natural coloring materials are not a single chemical entity and the plant matrix also contains a variety of non- dye plant constituents, extraction of natural dyes is a complex process. The nature and solubility characteristics of the coloring materials need to be ascertained before employing an extraction process. The different methods for extraction of coloring materials are:

- ✓ Aqueous extraction
- ✓ Alkali or acid extraction
- ✓ Microwave and ultrasonic assisted extraction
- ✓ Fermentation

- ✓ Enzymatic extraction
- ✓ Solvent extraction
- ✓ Super critical fluid extraction.

4.3.1 Types of Mordant

➢ Alum Mordant

Alum commonly called Aluminum sulphate is the most common mordant. It is classified as the brightening mordant, because it usually produces a pale and bright color. It does not affect the color being produced. Moreover, it can easily obtain from most chemists and is safe as well as cheap to use.

Potash alum, which is the double sulphate of potassium and aluminum, is the most widely used aluminum mordant for natural dyeing. The amount of mordant required depends on the shade to be dyed. If deeper shades are being dyed, more mordant is needed.

Alum is produced as white crystals which are non-combustible and soluble in water. It has been used by human since 2000 BC when the Egyptians used the mineral alum as a mordant in dyeing .Alum or other metallic mordants fix dyes on fiber by chemically combining with the functional groups of the natural dyes to form covalent bonds, hydrogen bonds and other interactional forces as shown in Figure.

Alum occurs in nature but also found in many plants. Alum reacts chemically with water first, whereby the aluminum forms a mildly basic hydroxide which is no longer soluble in water. Alum attaches itself to the mildly acidic groups of the protein molecules of the wool or silk fibers and heat can accelerate the process. During dyeing, the aluminum then binds the molecules of the mildly acidic dyestuff, thereby creating the so-called lac which is insoluble. Hence, the dyes material is colorfast when washed.

➢ Copper Mordant

Copper mordant is copper sulphate, sometimes it is called blue vitriol because it is available as a bright blue crystal. It is a one kind of dull mordants. Copper mordant also reacts with water to form a mildly basic hydroxide .Dyed textiles sometimes having a dull-khaki gold color obtained from a plant will become a yellow-gold color when treated with the alum, chrome and tin mordant respectively. However, the copper mordant produces a dull chestnut color. It is mostly used for fixing the wool colors to produce brown shades . However, Copper mordant is less frequently used than the other mordants. In addition, it is more toxic. The disposal of small amounts of copper mordant and well diluted can reduce the environmental hazard.

➢ Chrome Mordant

Chrome is known as potassium dichromate and is a kind of brightening mordant. It produces a deep version of the prevailing dye color, and leaves wool with beautiful soft, while other mordants will harden the wool.

Chrome is toxic and can cause irritation to skin. Care should be taken to avoid inhaling either the fumes of the mordant bath or the chemical dust. It is better to purchase chrome that looks slightly damp as opposed to a fine, as risk generated from the dust is greatly reduced.

4.3.2 Mordanting

Mordanting can be achieved by pre-mordanting (before dyeing), simultaneously mordanting and dyeing or post mordanting system (after dyeing). For mordanting the fabric at first we weigh the dry materials. Then rinse fabric with cold water. Then we took mordant, water and fabric in a vessel. For this project we used 5% Alum, 5% copper sulphate and 5% potassium dichromate.

1. Pre-mordanting method

The textile material is first immersed into the mordant solution for 30 to 60 minutes at the room temperature to 100 °C with a liquor ratio of 1:10 to 1:20. The textile material treated with mordant is then dyed. After dyeing, the dyed material is washed with a non-ionic detergent. It is the most frequently used procedure by natural dyers because large quantities of textile can be treated and stored until dyeing.

2. Simultaneous mordanting method

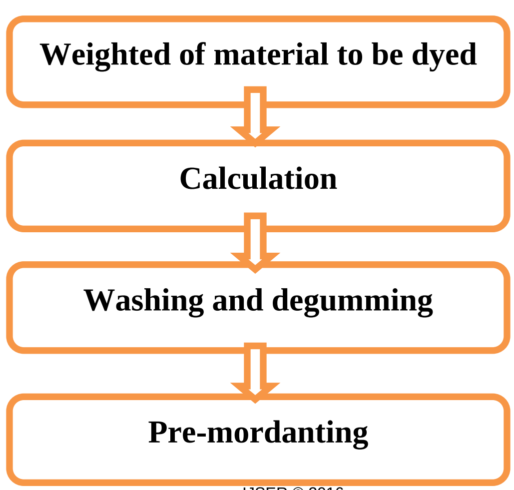
As for the simultaneous mordanting and dyeing, the textile material is immersed in a dye bath solution containing both mordant and dye. Dyeing auxiliaries can be added during the dyeing process. For the optimization of dyeing condition, dyeing process variables can be studied for the specific fibre-mordant-natural dye system in order to improve the color yield of textiles. After dyeing, the textile material is washed with the non-ionic detergent.

3. Post-mordanting method

The dyeing process is carried out on the bleached textiles in the dye bath without mordant. The dyed fabric then is treated with another bath called saturator containing the mordanting solution. Treatment condition may vary depending on the type of fibre, dye and mordant system being used. After dyeing, the textile material is washed properly with non-ionic detergent. When using this mordanting method, the colors are usually different and often less strong if the mordant and plant are boiled together. In all these three applications, mordants act as dye setters that will prevent the color from running or streaking after dyeing

4.3.3 Dyeing

It is necessary to follow each stage of the onion dyeing process with care. The stages are:



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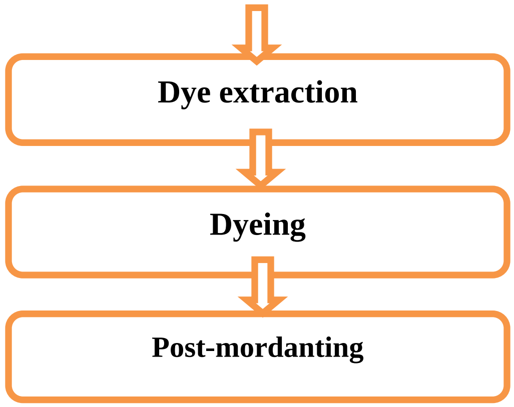

4.3.4 Evaluation of color fastness

For evaluation of wool dyed fabrics, the following tests were performed:

- Colorfastness to washing, according to ISO 105-C01
- Colorfastness to rubbing, according to ISO 105-X12
- Colorfastness to light, according to ISO 105-B02
- Colorfastness to water, according to ISO 105-E04
- Colorfastness to Perspiration, according to ISO 105-E04

4.3.1 Color Measurement

The various color changes such as depth, tone, λmax etc. Were measured with a spectra flash SF300 (Data color International, USA) in terms of K/S values and CIE L*a*b* data with illuminant D65 at 10^0 observer.

Effect of mordants on λmax for dyeing of nylon with Onion dyes:

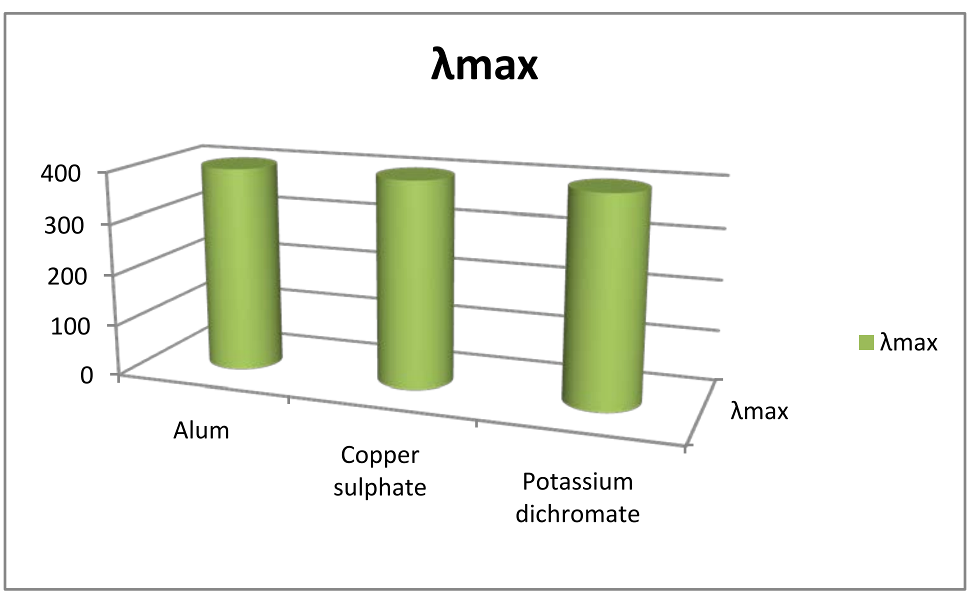

Figure 3 Effect of mordants on λmax

5 Result & Discussion

5.1 Optimization of extraction condition

Table 1: Color Fastness to Wash of nylon fabric

Fabric Type	Mordants	Method of Mordanting	Mordant Concentration (%)	Washing (Dyed with methanol extracted onion dye)		Washing (Dyed with water extracted onion dye)	
				Color Changing	Color Staining	Color Changing	Color Staining
Nylon	Alum	Pre-Mordanting	1	5	3-4	4	3-4
		Simultaneous Mordanting	2	5	5	4	4
		Post-Mordanting	3	4-5	5	4-5	4
	Copper sulphate	Pre-Mordanting	1	4	4	4	4
		Simultaneous Mordanting	2	5	5	4-5	4
		Post-Mordanting	3	5	4-5	5	4-5
	Potassium dichromate	Pre-Mordanting	1	4	3-4	3-4	3-4
		Simultaneous Mordanting	2	4-5	5	4-5	4-5
		Post-Mordanting	3	5	4-5	5	3-4

Table-2: Color Fastness to Rubbing of nylon fabric

Fabric Type	Mordants	Method of Mordanting	Mordant Concentration (%)	Rubbing fastness (Dyed with ethanol extracted onion dye)				Rubbing fastness (Dyed with water extracted onion dye)			
				Dry Rub		Wet Rub		Dry Rub		Wet Rub	
				CC	CS	CC	CS	CC	CS	CC	CS
Nylon	Alum	Pre-Mordanting	1	5	5	4-5	4-5	5	4	4	4-5
		Simultaneous	2	5	5	4-5	4-5	5	4-5	5	4-5

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	Mordanting									
	Post-Mordanting	3	5	5	5	5	5	5	4	5
Copper sulphate	Pre-Mordanting	1	5	4-5	5	4-5	4-5	4	5	4
	Simultaneous Mordanting	2	5	5	5	4-5	4-5	4-5	5	4-5
	Post-Mordanting	3	5	5	5	5	4-5	5	5	4-5
Potassium dichromate	Pre-Mordanting	1	5	4	4-5	4-5	4-5	4-5	5	4
	Simultaneous Mordanting	2	5	5	5	4-5	4-5	5	4	4-5
	Post-Mordanting	3	5	5	5	5	5	5	5	5

Table-3: Color Fastness to Light and color fastness to water of nylon fabric

Fabric Type	Mordants	Method of Mordanting	Mordant Concentration (%)	Light (Dyed with methanol extracted onion dye)	Light (Dyed with water extracted onion dye)	water (Dyed with methanol extracted onion dye)	Water (Dyed with water extracted onion dye)
				CC	CS	CC	CS
Nylon	Alum	Pre-Mordanting	1	3-4	2-3	3-4	2-3
		Simultaneous Mordanting	2	4	3	4	3-4
		Post-Mordanting	3	5	3-4	5	4
	Copper sulphate	Pre-Mordanting	1	3-4	2-3	4-5	3
		Simultaneous Mordanting	2	4	3	5	3-4
		Post-Mordanting	3	5	3-4	5	4
	Potassium dichromate	Pre-Mordanting	1	3-4	2-3	3	3-4
		Simultaneous Mordanting	2	4	3	4	4-5
		Post-Mordanting	3	5	3-4	4-5	5

Table-4: Color Fastness to Perspiration of nylon fabric

Fabric Type	Mordants	Method of Mordanting	Mordant Concentration (%)	Perspiration fastness (Dyed with ethanol extracted onion dye)		Perspiration fastness (Dyed with water extracted onion dye)	
				Acidic		Alkalin	
				CC	CS	CC	CS
Nylon	Alum	Pre-Mordanting	1	4	3-4	4-5	2-3
		Simultaneous Mordanting	2	4	3-4	4	2-3
		Post-Mordanting	3	4	3-4	4-5	2-3
	Copper sulphate	Pre-Mordanting	1	4	3-4	4	2-3
		Simultaneous Mordanting	2	4	3-4	4-5	2-3
		Post-Mordanting	3	4	34	4	2-3
	Potassium dichromate	Pre-Mordanting	1	4	3-4	4-5	2-3
		Simultaneous Mordanting	2	4	3-4	4	2-3
		Post-Mordanting	3	4	3-4	4-5	2-3

Dyed samples:

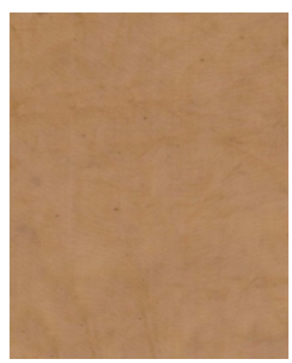
Fabric Type	Alum mordanted	Mordant type Copper sulphatemordanted	Potassium dichromate mordanted
Nylon			

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Figure 4 Dyed samples (dyed with ethanol extracted onion dye)

Dyed samples:

Fabric Type	Alum mordanted	Mordant type Copper sulphatemordanted	Potassium dichromate mordanted
Nylon			

Figure 5Dyed samples (dyed with water extracted onion dye)

6 Conclusion

In this research, I was tried to explore the difference between two types of solvents used for onion dye extracted from onion's outer shells. The result was very positive for methanol extracted dyed nylon fabric than water extracted wool fabric. Dye can be successfully used for dyeing of nylon to obtain a wide range of soft, pastel and light colors by using metallic mordants. With regards to colorfastness test samples exhibited excellent fastness to washing (except pre and post mordanting), excellent fastness to rubbing (except pre, simultaneous and post mordanting- Potassium dichromate).Among the different fiber-mordanting systems studied, the use of 3% of Copper sulphate applied by simultaneous mordanting for subsequent dyeing on nylon with extract of onion dye 3% of Alum applied by simultaneous mordanting for sub-sequent dyeing on nylon with 3% of Potassium dichromate applied by simultaneous mordanting for subsequent dyeing on nylon with onion dye by extracts has a good prospect in the field of textiles dyeing sector.

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