(REFEREED RESEARCH)

THE EFFECT OF PLASMA TREATMENT ON THE DYEABILITY OF SILK FABRIC BY USING *PHYTOLACCA DECANDRA* L. NATURAL DYE EXTRACT

İPEKLİ KUMAŞIN *PHYTOLACCA DECANDRA* L. BİTKİSİNDEN ELDE EDİLEN DOĞAL BOYA İLE BOYANABİLİRLİĞİNE PLAZMA UYGULAMASININ ETKİSİ

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ABSTRACT

The aim of this study is that plasma treatment effect on dyeability properties of silk fabric with natural dye is investigated. For this purpose, in this study, silk fabric was dyed by the conventional method with natural dye extracted from Phytolacca Decandra L. Before the dyeing process, the sericin on silk fabric was removed. After then, plasma treatment was applied the samples with using oxygen and nitrogen gas for 1, 5 and 10 minutes at low frequency. Furthermore, plasma treated samples were mordanted with potassium aluminum sulfate before the dyeing process. After the dyeing process, colour strength, colour fastness, surface properties, moisture absorption, chemical groups and tensile strength of the dyed samples were investigated. According to the results, the plasma treatment and mordanting process caused to improve the colour yields. The scanning electron microscope images showed that the plasma treatment causes microcracks on the surface of the silk fiber. After the plasma treatment, the hydrophility of samples increased. Moreover, plasma treatment creates microcracks on the silk fiber surface, resulting tensile strength decreases.

Keywords: Natural Dyeing, Phytolacca Decandra L., Plasma Treatment, Colour Strength, Fastness Properties

ÖZET

Bu çalışmanın amacı ipek kumaşa plazma uygulamasının, ipek kumaşın doğal boya ile boyanabilirlik özelliklerine etkisinin incelenmesidir. Bu amaçla, bu çalışmada, ipek kumaş Phytolacca Decandra bitkisinden elde edilen doğal boya ile konvansiyonel yönteme göre boyanmıştır. Boyama işleminden önce, ipek kumaşın serisini giderilmiş ve ardından numuneler oksijen ve azot gazı ile düşük frekansta 1, 5 ve 10 dakika plazma işlemine tabi tutulmuştur. Plazma işlemine maruz kalan numuneler potasyum alüminyum sülfat ile mordanlanmıştır. Boyama işleminden sonra, renk kuvveti, renk haslıkları ve yüzey özellikleri incelenmiştir. Sonuçlara göre plazma uygulaması ve mordanlama işlemi renk verimini artırmıştır. Taramalı elektron mikroskobu görüntüleri plazma uygulamasının ipek liflerinin yüzeyinde mikro boyutta çatlakların oluşmasına neden olduğunu göstermektedir. Plazma uygulamasından sonra, numunelerin hidrofilitesinin artığını görülmektedir. Ayrıca plazma uygulaması ipek liflerinin yüzeyinde mikro çatlakların oluşturmuş ve numunelerin mukavemetleri azalmıştır.

Anahtar Kelimeler: Doğal Boyama, Phytolacca Decandra L., Plazma Uygulaması, Renk Kuvveti, Haslık Özellikleri

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1. INTRODUCTION

From the first era to nowadays, people have used to dye their costumes with different dyes to show themselves aesthetic and attractive. The dyes used in the textile industry mainly are synthetic and natural dyes. Until 19th century, the natural dyes were used in most of countries including Turkey. When Alizarin chemical produced in 1868, the production and usage of the synthetic dyes started to use in textile industry (1). On the other hand, the natural dye consumption started lately to increase as they have nontoxic, anti-bacterial, environmental and relatively less allergic properties (2-4). Natural dyes are produced from plants, molluscs and minerals to be used on textiles as well as on food and drug industry (5).

Phytolacca Decandra L. natural dye regionally called as pokeweed, poke, inkberry, common pokeberry, redink plant, and poke root. The original root of the *Phytolacca Decandra* L. grows in the south and west part of North America and Mexico as well as Europe, Africa and Asia. The chemical combination of *Phytolacca Decandra* L. *is* mainly derived from phytoloccatoxine, glycoprotein, phytolacceine and tannin.

In textile industry, in order to meet the consumer requirements and reducing the costs, the innovation methods have been used. In this context, the plasma, ultrasonic and microwave applications can be defined as innovative methods in the textile industry. In textile industry, the plasma treatment is used as a pre-treatment before the dyeing process. Plasma is known as the materials 4^{th} state and described as an ionized gas consists of electrons, neutrons, ions and radicals (6). In textile industry, the plasma application is classified as thermal and cold plasma. Since the thermal plasma energy cause faster ignition on the textile materials, the cold plasma application become in use. The cold plasma application can be classified as low and atmospheric pressure plasma treatments depending the used pressure. The plasma application on the textile materials recently found more use since it causes various modifications on the fiber surface. After plasma treatment as there become more modifications on the fiber surface, there seen recovery on wettability (7-10), water repellence (11-13) and dyeability (14,15) behavior on the fiber. After different gas plasma application on the textile materials, the dyeability behaviors of the textile materials improve as a results of surface modifications and forming new functional groups (16,17).

Silk fiber called as the queen of the fibers, since it is used in textile industry for more than 5000 years, as well as its great mechanical and chemical properties. In order to improve the plasma effect, the sericin should be removed from the silk fiber. This treatment also increases the water absorption, dyeability and water repellency (18-20).

In this study, silk fabric without sericin was applied on plasma treatment with oxygen and nitrogen at 1.0, 5.0 and 10 mins., and then some of these plasma treated samples were mordanted with potassium aluminium sulphate. Samples with and without plasma treatment, was dyed with *Phytolacca Decandra* L. extract with and without mordant by conventional method. The effect of plasma treatment on colour intensity, colour strength and surface morphology of the fabric samples was analysed. The purpose of this study is to investigate the dyeability behaviour of *Phytolacca Decandra* L. natural dye on plasma and mordant treated silk fabric.

2. MATERIALS AND METHODS

2.1.Materials

In this study, plain weave silk fabric with the weight of 80 $g.m^{-2}$ was dyed with the *Phytolacca Decandra* L. natural dyes. The chemical structure of such extracted dye is given below (Figure 1). The silk fabric was supplied from Odemis Ipek Company.

Phytolacca Decandra L. fruit was harvested from the Black Sea region. The fruits were cleaned and 1000 grams fruit and 20 litres of distilled water were added and this mixture was boiled for one hour and was filtered.

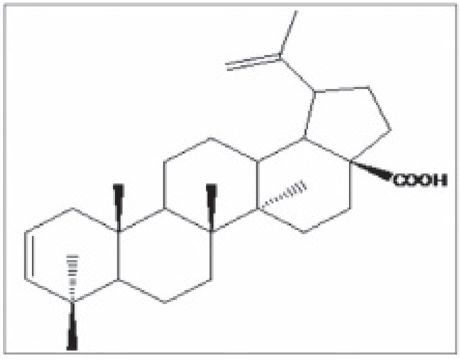


Figure 1. The chemical structure of *Phytolacca Decandra* L. (1-Isopropenyl-5a,5b,8,8,11a-pentamethyl-1,2,3,4,5,5a,6,7,7a,8,11,11a,11b,12,13,13a,13b-octadecahydro cyclopenta [a]chrysene-3a-carboxylic acid) (21).

2.2. Methods

The method used on this study is given in Figure 2.

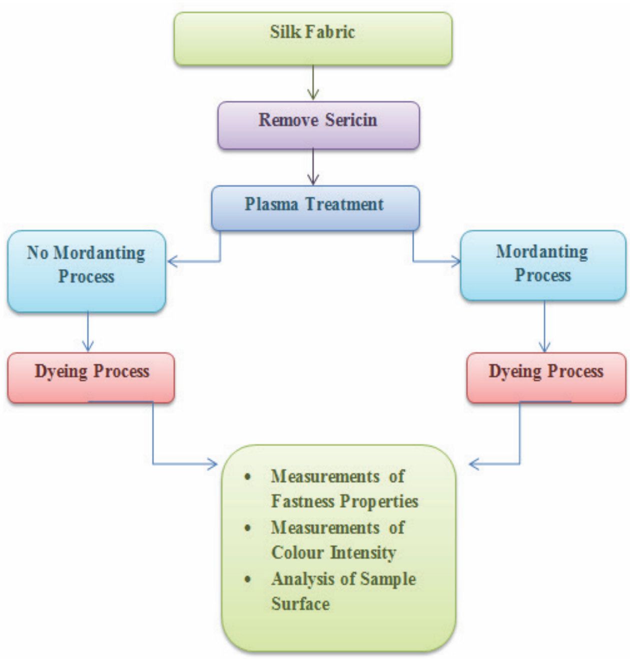


Figure 2. The method used on this study.

2.1.1. Sericin Removal from Silk Fabric

The silk fabric boiled for one hour in 10 g/l sodium stearate solution at 1:50 liquor ratio and then first rinsed with hot water (90°C) and finally cold water (25°C) for 3 mins., respectively with same liquor ratio. It was observed that about 25% of the present sericin was removed by this procedure.

2.2.2. Plasma Treatment

The plasma treatment was applied on silk fabrics by use of Diener vacuum plasma device. Commercially available oxygen and nitrogen plasma was discharged into the chamber and the silk fabrics were placed in the discharge chamber. In this study, the effect of different gas, frequency intensity and duration of plasma treatment on dyeing properties of silk fabrics were investigated. The silk fabrics were treated with oxygen and nitrogen plasma for 1, 5 and 10 mins. at 40 kHz frequency with 100 W at 4 mbar.

2.2.3. Analysis of Surface (SEM Analysis)

The surface morphology of the samples was analysed by using scanning electron microscope (SEM) by using ZEISS/EVO 40 electron microscope.

2.2.4. Moisture Absorption Measurement

The moisture absorption measurement test was carried out according to AATCC195 test method (25) by using SDL Atlas M290 MMT instrument.

2.2.5. Surface Analysis with X-Ray Photoelectron Spectroscopy

The functional groups analysis was carried out by using Thermo Scientific K-alpha XPS X-Ray Photoelectron Spectroscopy. In order to evaluate the functional groups on the treated samples, the bonding energies were determined by getting reference from the literature (26,27).

2.2.6. Measurement of Tensile Strength

The tensile strength of samples was analyzed with use Instron 4410 instrument, according to the EN ISO 13934-1/ASTM D 5034-09 standard (29).

2.2.7. Mordanting Process

The mordant solution was prepared by use of 10 grams of potassium aluminium sulfate in 1000 ml of distilled water. Then the fabrics were treated in a liquor ratio of 1:50 for one hour at the boiling temperature of about 98°C.

2.2.8. Dyeing Process

In this study, the samples were dyed with *Phytolacca Decandra* L.extracts via conventional dyeing method at a liquor ratio of 1: 50 at boiling temperature for one hour. Before dyeing process, the samples were exposed to plasma treatment. After the plasma treatment the samples were exposed to mordanting process.

2.2.9. Colour Measurements

The reflectance values of the dyed fabrics were measured by using Gretaq Macbeth – Colour Eye 2180 UV spectrophotometer and the CIELab values were calculated using illuminant D65 at 10° standard observer values. The colour strength (K/S) values of samples were calculated with the Kubelka-Munk equation as follows,

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where K, S and R is absorption of dye, scattering of dye and reflectance value respectively. The calculation of K/S values was achieved in accordance with the maximum absorption in 540 nm.

2.2.10. Fastness Properties

Colour fastness to washing was tested by using Gyrowash/ James H.Heal Co.Ltd test instrument according to ISO105:C06 (22). Colour fastness to light of samples was tested using Atlas Alfa 150 S test instrument according to EN ISO 105 – B02 and the rubbing fastness by use of James H. Heal 255 crockmeter according to ISO 105 X12 (23,24).

3. RESULTS AND DISCUSSION

3.1. Surface Analysis (SEM Analysis)

The scanning electron microscope micrographs of samples were given in Figure 3.

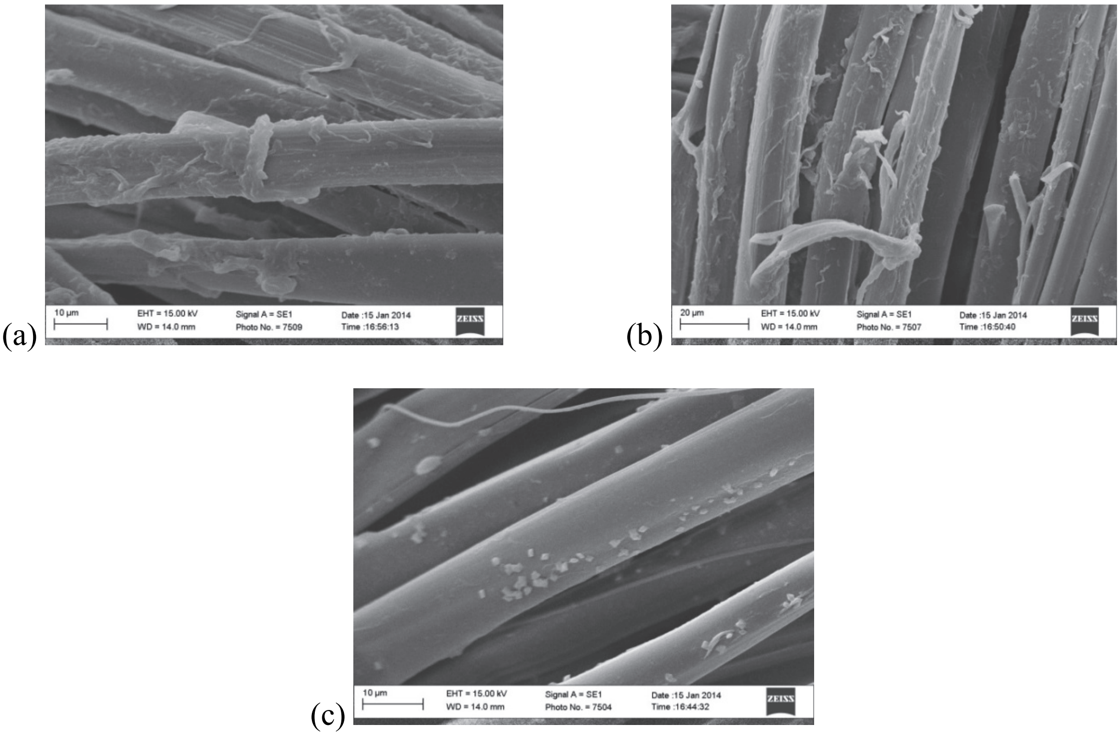


Figure 3. SEM micrographs of samples ((a). The sample applied nitrogen plasma for 10 mins., (b). The sample applied oxygen plasma for 10 mins., (c). The sample untreated plasma application).

According to the SEM micrographs, one can conclude that nitrogen and oxygen plasma treatment caused deformation on the surface of silk fabric. It was considered that the deformation of the plasma treatment increased in the capillarity of plasma treated sample.

3.2. Moisture Measurement Tests

The results of moisture measurement test were given in Table 1.

Table 1. Moisture measurement test results.

	Wetting Time Top (sec)	Wetting Time Bottom (sec)
Raw Silk Fabric	7.688	8.719
Oxygen Plasma Treated Fabric (10 mins)	3.094	2.906
Nitrogen Plasma Treated Fabric (10 mins)	2.906	3.188

In accordance to SDL ATLAS M290 MMT scale, the results below 3 seconds means the fabric wetted very fast. Moisture measurement test results show that oxygen and nitrogen plasma treatment cause to increase welting. Plasma treatment causes microcracks and new functional groups in silk fibers (16).

3.3. X-Ray Photoelectron Spectroscopy Analysis

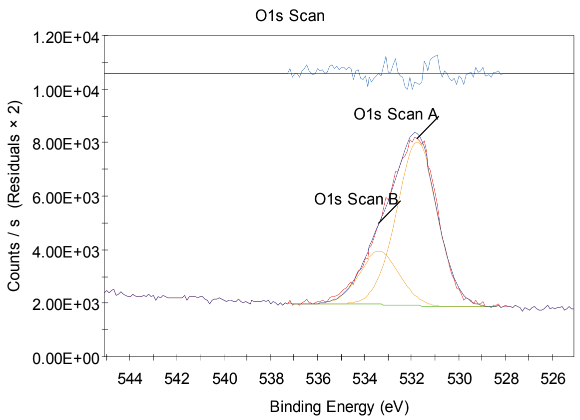
The results of X-ray photoelectron spectroscopy analysis were given in Table 2.

Table 2. Atomic concentration of samples.

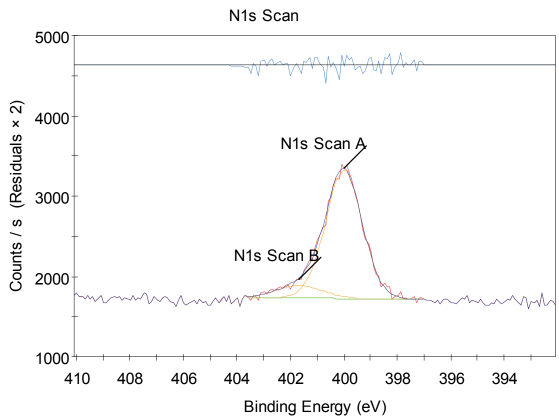
XPS	% Atomic Concentration		
	Raw Fabric	After Oxygen Plasma	After Nitrogen Plasma
C1s Scan A (C-C /C-H)	51.06	28.87	47.27
C1s Scan B (C-O/C=O)	12.19	9.81	8.42
C1s Scan C (COOH)	15.78	19.5	12.61
O1s Scan A (C=O/-OH)	12.39	23.06	16.71
O1s Scan B (C-O/-C=O/C-O-C)	3.97	2.66	2.41
N1s Scan A (R-NH$_2$)	4.12	14.1	12.15

It is seen from Table 2 that, the amount of carbon reduced while the amount of oxygen and nitrogen increased on the surface of the oxygen and nitrogen plasma treated silk fabric. The increased oxygen and nitrogen ratio arisen from the oxygen and nitrogen plasma treatment. It is concluded that, the reduced carbon ratio could be originated from the functional groups increase around the oxygen and nitrogen atoms.

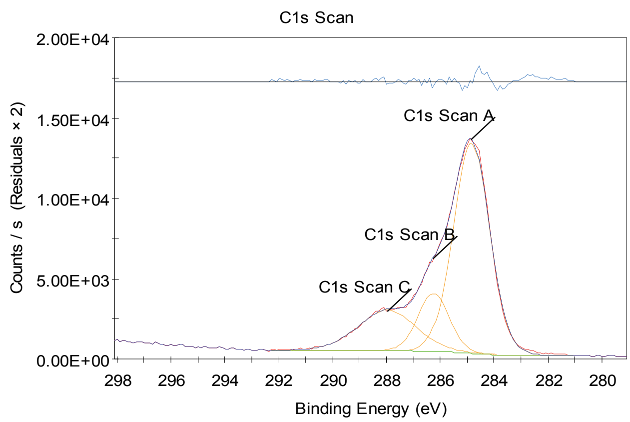
In order to observe the changes on the surface of the fibers, the peaks on the graphs have to be analysed explaining which functional groups belong to which chemical structure given on binding energy on C1$_s$ Scan A, C1$_s$ Scan B, C1$_s$ Scan C, O1$_s$ Scan A, O1$_s$ Scan B, N1$_s$ Scan A, N1$_s$ Scan B, S2$_{sp}$3 Scan A and S2$_p$3 Scan B peaks.



A



B



C

Figure 4. Photoemission spectrums for raw silk fibers (A. O1$_s$, B. N1$_s$, C. C1$_s$).

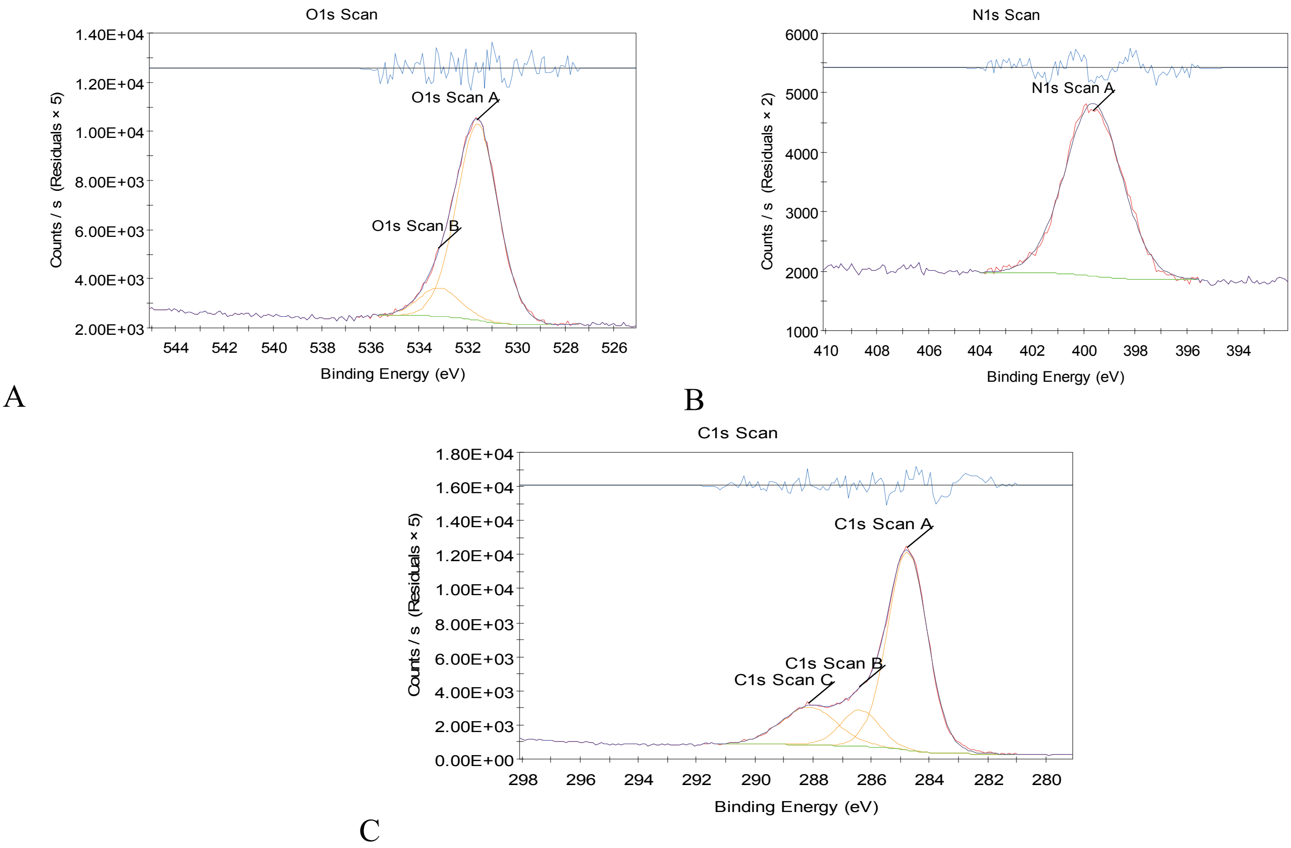


Figure 5. Photoemission spectrums for oxygen plasma applied silk fibers (A.O1_s, B.N1_s, C. C1_s).

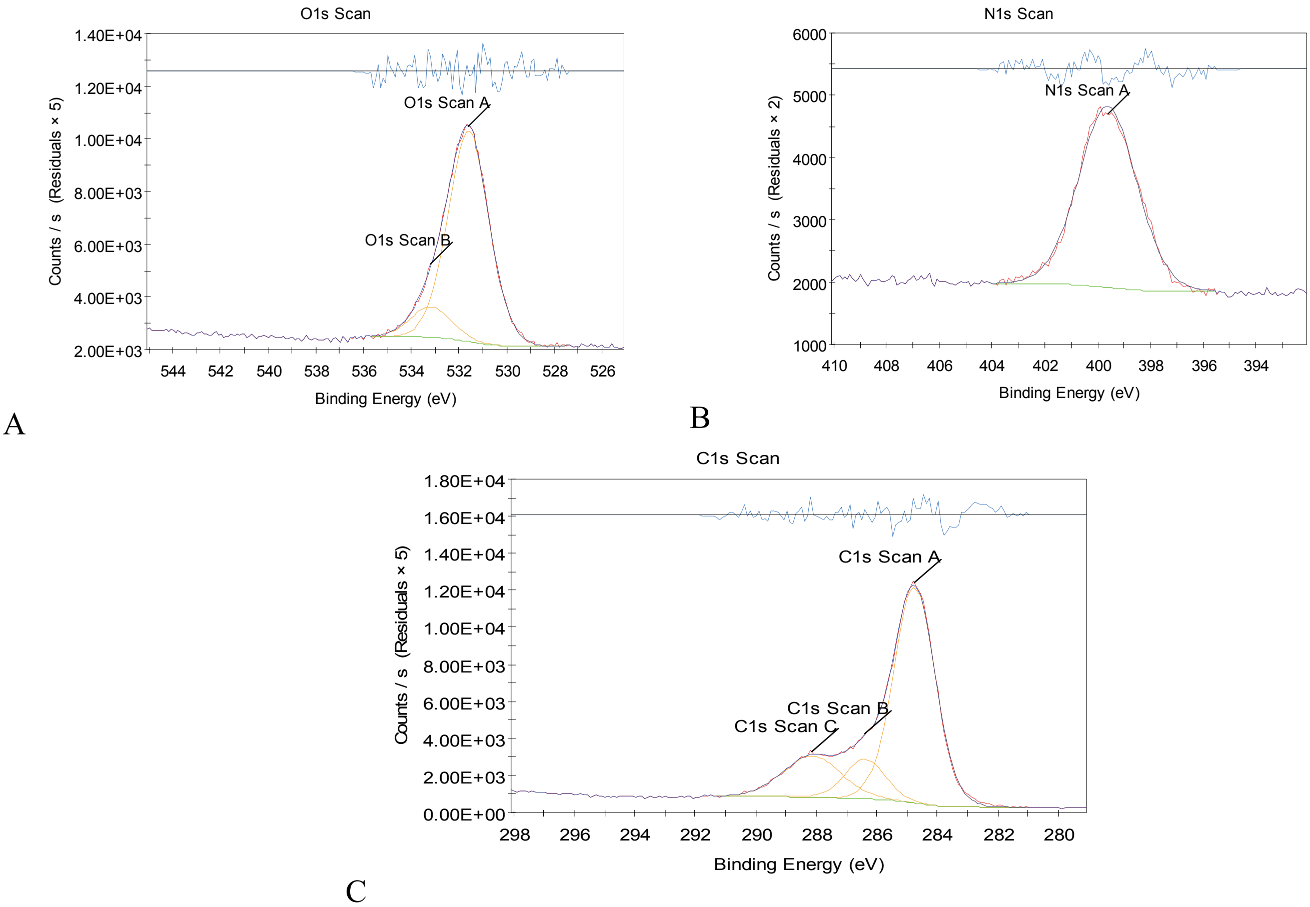


Figure 6. Photoemission spectrums for nitrogen plasma applied to silk fibers (A.O1_s, B.N1_s, C. C1_s).

The XPS analysis of oxygen and nitrogen plasma applied silk fabric, the results shows that the amount of carboxyl, hydroxyl and amine groups increased. Besides, by the analysis of the results, it can be said that the nitrogen plasma occurred amid groups to some extend by making chemical reaction on with carboxyl groups.

3.4. Results of Tensile Strength

The results of tensile strength analysis of samples were given in Figure 7.

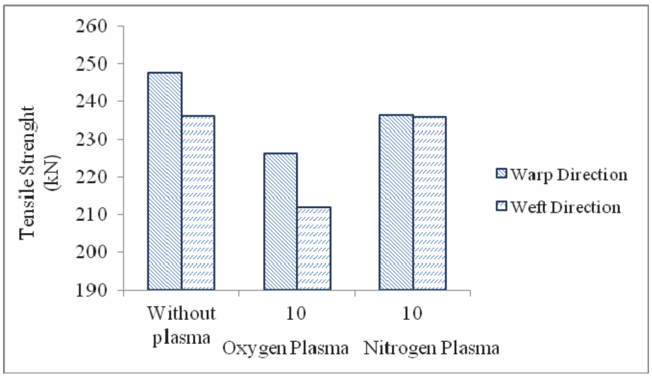


Figure 7. Tensile strength results of samples.

It is seen from the results that, the plasma application reduced the fabric strength. According to the SEM micrograph images, after the plasma treatment microcracks occur on the silk fibers surfaces and showing severe damage on the surface (15). Furthermore, oxygen plasma treatment causes to etch on silk fiber surfaces more than nitrogen plasma treatment (15).

The oxygen plasma treatment reduced the fabric strength more than the nitrogen plasma treated samples. The SEM micrograph images also supported to these results. The strength reduction on silk fabric for the oxygen plasma can be attributed its less inert properties than nitrogen (29).

3.5. Colour Measurements

The results of colour strength (K/S) values of the dyed at 540 nm samples were given in Figure 8.

According to the colour strength results, the plasma application increased the colour strength of samples. It is known that the oxygen and nitrogen plasma increased the amounts of functional groups within the silk, leading dyestuff increase (23). This suggestion also correlated by the SEM micrographs as seen the microcracks on the silk fiber surface.

It was observed that the colour strength of dyed samples increased while the duration of plasma treatment was increased. This can be explained by increased functional groups of fiber samples with the increase of plasma treatment time. Besides, it was assumed that, the increased plasma treatment time leads to increase the cracks of fiber surface causing high dye uptake.

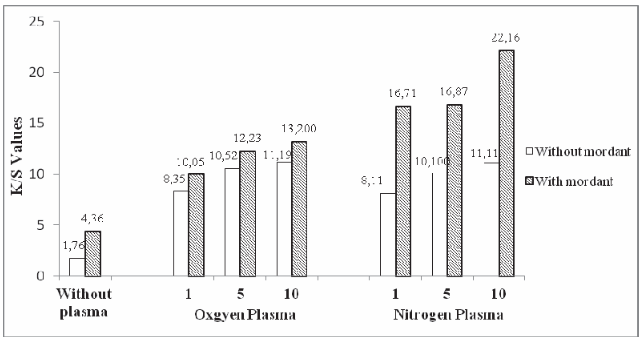


Figure 8. Colour strength values of dyed samples.

It is seen from the Table 2, the oxygen plasma application oxidized some of the chemical groups to –COOH, -OH and -NH_2 more than the nitrogen plasma on the silk fabric. The increased dye uptake on nitrogen plasma applied silk fabric can be attributed to the increased coordinative and other chemical bonds between the silk macromolecules and dye.

Plasma application after mordanting process increased the colour yield. This can be attributed to the dye molecule to make coordinative bond with metal. By accepting nitrogen becomes in the form of amine, within the fiber, this may make covalent bond with dyes leading increased dye uptake.

After mordanting process the nitrogen plasma treatment gave better dye uptake results than oxygen plasma treatment. It is seen from the SEM micrographs that, the lower molecule size atoms as nitrogen to oxygen are more effective on the fiber surface. Because the lower molecule size atoms for nitrogen as oxygen are more effective on the fiber surface.

3.6. Fastness Properties

The fastness properties of dyed samples are given in Table 3 and Table 4.

Table 3. The Fastness properties of dyed fabrics (without mordant).

		Light fastness	Washing fastness							Rubbing fastness	
			Colour change	Staining						Dry	Wet
				CA	CO	PA	PE	PAN	WO		
Dyeing method											
Without plasma		1	1	3	4/5	4	4/5	4/5	4/5	4/5	4
Oxygen plasma	1 min.	1/2	2	3	4/5	4	4/5	5	5	4/5	4
	5 mins.	1	3	3/4	4/5	4	4/5	5	5	4/5	4/5
	10 mins.	1	3/4	4	4/5	4	4/5	5	5	4/5	4/5
Nitrogen plasma	1 min.	1	3	5	5	5	5	5	5	5	5
	5 mins.	2	3	5	5	5	5	5	5	5	5
	10 mins.	2	3/4	5	5	5	5	5	5	5	5

Table 4. The Fastness properties of dyed fabrics (with mordant).

		Light fastness	Washing fastness							Rubbing fastness	
			Colour change	Staining						Dry	Wet
				CA	CO	PA	PE	PAN	WO		
Dyeing method											
Without plasma		1	2	3/4	4/5	4	4/5	5	5	4/5	4/5
Oxygen plasma	1 min.	1	2/3	3/4	4/5	4	4/5	5	5	4/5	4/5
	5 mins.	1	3	3/4	4/5	4	4/5	5	5	4/5	4/5
	10 mins.	2	4	4	5	4/5	4/5	5	5	4/5	4/5
Nitrogen plasma	1 min.	1	4	5	5	5	5	5	5	5	5
	5 mins.	2	4	5	5	5	5	5	5	5	5
	10 mins.	2	4/5	5	5	5	5	5	5	5	5

According to the colour fastness to light results, the plasma application and mordanting process do not effect on colour fastness to light properties of samples. It is seen from the results the colour fastness to light of samples is low. The reason of this result is considered that the chemical structure of natural dyes damaged very quickly with light.

Furthermore, it is seen from the results that the colour fastness to washing and rubbing of samples applied nitrogen plasma gave slightly better results than other samples.

4. CONCLUSION

In this study, silk fabrics were dyed with natural dye extracted from *Phytolacca Decandra* L. Before dyeing process, the sericin was removed from the silk fabric and then the samples were applied to plasma treatment by using oxygen and nitrogen gas for 1, 5 and 10 minutes at low frequency. After the plasma treatment, the samples were mordanted with potassium aluminum sulfate. According to colour strength results, the oxygen and nitrogen plasma treatment increased the dye uptake tremendously. Mordanting process increased the dye uptake much more than nitrogen plasma treated silk fabric than oxygen plasma treatment.

The better colour yield on nitrogen plasma treatment can be attributed to the lower molecular weight of nitrogen atom diffusing move easily inside the fiber and also leading to nitrogen bounding to silk fabric causing move dye-fiber saturation value. There was slight increase on colour fastness results on plasma treated silk fabric. After the plasma treatment, the hydrophility of samples increased. The results of XPS show that functional groups which provide the increase of hydrophility occurred. In addition, the results of XPS clarify the increase of colour strength and hdrophility. Moreover, plasma treatment creates microcracks on the silk fiber surface, as a result tensile strength of samples decreases.

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