A Studyon Colour, Antimicrobial Activites and Fastness Values of Green WalnutHuskDyed Wool

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Abstract— The aim of this work is to investigate the dyeability of wool yarns without using metal salt with waste green walnut husk.Color measurement method with spectrophotometer was used to control the color standard in the study.First of all, dyeing extract was prepared by means of using walnut green husks.The extracts obtained were used in dyeing wool yarns.The dyeing process was repeated five times. Then,color coordinates, antimicrobial activity and fastness values were determined. Measurements of the colours obtained in consequence of mordant and non-mordant dyeing were made by means of X-Rite portable spectrophotometer. Color stability was investigated by making individual color measurements of each color.Extract obtained from the green walnut husks is effective against reducing the microorganisms of gram (+)Candida albicansATCC 10231. The colour fastness to washing and rubbing after dyeing the wool yarns was investigatedthe results of which showedgood fastness.

Keywords: Textile material, natural dyeingmaterial, organic coating, spectrophotometer, textile science, fastness, wool yarn

1 INTRODUCTION

There is an increasing demand for textile products dyed with natural dyestuffs together with the increasing environmental consciousness in recent years. With the thought that chemical agents have negative effects on environment and people, there is a buyer part who accept to buy the clothes having high prices and partly less colour fastness, however dyed by natural dyestuffs.

Ecological dyeing by means of natural dyestuffs can be developed for textile materials including wool, cotton, silk and nylon. The researches about this topic stopped at the beginning of the century. In terms of being either economical or applicable, natural dyeing having a very significant place at textile sector has many advantages due to its properties such as health, ecological cycle, cost, refining and providing biological benefit. The purpose is both to make dyeing by the extracts obtained from 100% natural resources.

Generally, natural dyestuffs do not contain metal; however, many plants do not dye the fiber directly, therefore, mordants are used. Metal salts called as mordants are used to increase in efficiency of dyeing. Metal salts pull natural colourants to fiber surface and increase dyeing efficiency by constituting complex. It is possible to state most known and used chemical mordants as copper sulphate, iron sulphate, aluminium sulphate, potassium sulphate. Besides, some natural mordants such as nutgall, vinegar of grapes are also available [1-3].

Increase at consciousness of environment, ecology and pollution control gains popularity for dyeing applications in which textile products are dyed by natural dyestuffs all over the world for the last ten years. By means of using natural dyestuffs commonly, natural resources of our world will be polluted less, people will be able to consume healthier products, and chemicals will decrease from expenditures and export of natural products having higher value added tax will increase the earnings (profits) of the manufacturers [4-5].Hereafter, by means of using natural dyestuffs, new textile products must be designed and new markets must be created. Still the use of natural dyes involves some disadvantages such as requirement of large amounts of plant material, limited success in dyeing synthetic materials, need for the use of mordents, poor light stability.

Tannin, essential oil and a matter called juglone are present in the green shell and leaves of the walnut fruit. Either leaves or fruit coat is a much-used dyestuff [6]. It has been known in a wide geography around the world for many centuries that brown hues are obtained by the dyestuff in which walnut leaves include. Besides, it is used as an auxiliary dye to obtain the colour of black on fabrics [7].It had been used for obtaining the colour of black by means of being used together with iron sulphate until chemical dyes were invented [8].The husks of the black walnut Juglones nigra were once used to make an ink for writing and drawing, having been used by artists including Leonardo da Vinci and Rembrandt. Walnut husk pigments are used as a brown dye for fabric as once applied in classical Rome and medieval Europe for dyeing hair. The average worldwide walnut yield was about 3.5 tons per hectare in 2013. Eastern European countries had the highest yield, with Slovenia and Romania each harvesting about 22 tons per hectare [9].Redevoping dyeing with walnut green husks extract in the countries which are quite rich in terms of walnut trees also provides great superiority in terms of consumers who are looking for ecology.

According to the literature, walnut green husks may become important in the obtainment of a noticeable source of compounds with health protective potential and antimicrobial activity. All the extracts inhibited the growth of Gram positive bacteria, being Staphylococcus aureus the most susceptible one with MIC of 0.1 mg/mL for all the extracts [10-11].

This study focused onnon-mordant dyeing with extract from walnut green husks. In this research the dye extract was obtained by means of using green walnut husks, andthe quality of its use a dye with yarn and fiber. Colour coordinates were determined for wool based textile materials. In this way, the property of dyeing yarn of green walnut husks was examined. The colours obtained in conclusion of non-mordant and mordant dyeing were determined numerically by an X-Rite portable spectrophotometer. In conclusion, washing and rubbing fastness values of these dyes which are very important for carpets, rugs, blankets and socks were examined.

2 MATERIAL AND METHOD

2.1 Materials: The research materials are constituted by those below: walnut green husks extract as dyestuff, 2,5Nm loop wool yarn, Potassium double sulfate of aluminum[KAl (SO4)2] and copper sulphate CuSO4 as mordanting material. Distilled water was used at tests.

2.1 Method: Dyeing extract was prepared by walnut green husks. 100 % wool yarn samples were dyed by the programmable dyeing machine by non-mordant and mordant methods, then, L*a*b* measurements of the colours obtained were made by means of E-Rite brand portable spectrophotometer. Dyed samples were tested in accordance with the standards for washing and rubbing (wet-dry) fastness values.

2.2 Preparation of Dyeing Extract: Walnut healthy green husks (figure 1) were manually collected in September 2016 in Edirne, TURKEY.Each sample was carefully washed and dried at air dryer.

Fig. 1. Walnut Green Husk

Walnut green husks were made smaller by means of grinding in the grinder. Later, walnut green husk taken at 200% rate according to wool yarns to be dyed weight were boiled in the water at 1:20 flotte rate for an hour according to the weight of the material to be dyed. At the end of 60 minute, the extract was cooled until it reached to the room temperature, filtered and the dyeing extract was obtained.

2.3 Dyeing machine: Dyeing was performed in an Ataç (model HT 16) brand programmable sample-dyeing machine having 12 steel tubes, and making dyeing at constant temperature by two methods called as mordant and non-mordant. Beforehand, the textile materials to be dyed were steeped and wetted in the water for 60 minute.Ataç laboratory dyeing machine having high temparature, using between 30-135 °C.

2.4 Dyeing with mordant: The prepared extract was taken into the steel tube of the dyeing machine, and the samples to be dyed which were wetted and moistened beforehand were put into it. The mordant determined beforehand was added at the rate of 3% and dyeing was made at 80 °C for 60 minute. At the end of this duration, the samples dyed were washed firstly with water at 50°C, then rinsed with cool water, and dried at a dry machine at 100 °C.

2.5 Non-mordant Dyeing: The prepared extract was taken into the steel tube of the dyeing machine, and the samples to be dyed which were wetted and moistened beforehand were put into it, and dyed at 80°C for 60 minute. At the end of this duration, the samples dyed were washed firstly with water at 50°C, then rinsed with cool water, and dried at a dry machine at 100 °C.

2.6 Determination of the Colours Obtained by Spectrophotometer: The colour also changes according to the view field (viewing angle), due to the relationship with the sensitivity distribution characteristics of the retina. A spectrophotometer measures light intensity as a function of wavelength. By measuring the spectrum of reflected light, it allows a more precise determination of an object's color than with a colorimeter using three sensors (red, green, blue). Colour values of the samples dyed were measured by means of using the spectrophotometer (X-RİTE brand, D65/10). Colour coordinates of wool yarns and ISO test fabric dyed samples by green walnut husks extract are given at Table1-2.

2.7 Colour Fastness: Washing and rubbing fastnesses (wet and dry) of dyed samples were determined in accordance with ISO 105 - C06: 2012 [12]andTS EN ISO 105-X12: 2006 [13] standards respectively. Dry and wet rub fastness of dyed samples were tested using a Crock meter as per Turkish standard TS 717:1989based on ISO 105-X12:2006 Change at colours of samples after the test was evaluated according to ISO 105- A02 by means of using the numerical grey scale rating for change in colour. AATCC Gray Scale for Color Change: The Gray Scale for Color Change is used to visually evaluate change in color due to colorfastness tests as described in Evaluation Procedure 1 which is included [14].

At washing fastness test, 150 ml solution is prepared by 4 g/lt ECE detergent. Solution and dyed samples are put into the tubes. 10 steel balls are put into the tubes, and the tubes are closed. The temperature is set for 40 ^{o}C and it is washed for 30 minutes. After washing, it was dried and washing fastness value was determined by grey scale.

For rubbing fastness test; dry and wet dyed samples were rubbed on white standard fabric separately by means of using crock meter apparatus, and staining degree of the standard fabric was measured by the numerical grey scale rating for change in colour.

Evaluation method with AATCC Gray Scale; Place a piece of the original, untested fabric and the tested specimen side by side in the same plane and going in the same direction in the Color Matching Cabinet so it can be viewed at a 45^{o} angle. Place the Gray Scale along the edges of the two fabrics, tested and untested. Compare the visual difference between the two fabrics to the differences represented by the Gray Scale. Determine the grade by figuring out the grade that corresponds with the most appropriate change in color. A grade of 5 is given only when there is no perceived difference in color or contrast between the original and the tested

specimen.

2.8 Anti Mikrobiyel Activites: CLSI (Clinical Laboratory Standards Institute) microbial dilution method was used in the study. For this purpose, microorganisms of Gram (+) Staphylococcus aureus ATCC 25923, Gram (-) Listeria monocytogenes ATCC 19115, Gram (+) Bacillus cereus ATCC 11778 and yeast Candida albicans ATCC 10231 were cultured for 24 hours at 37 ° C in Tryptic Soy Broth (TSB) was also enshrined, The MC Farland Scale is set to 0.5.Ampicillin and Gentamycin were used for bacterial cultures and Amphotericin B for yeast culture as antibiotic control. For sterility, antibiotics and solute stock solutions were filtered through a 0.45 µm sterile filter. Substance concentrations were set as dilutions from 2.5% to 0.08%.Bacterial and yeast cultures were inoculated into each well. All microplates were incubated at 37 ° C for 48 hours.Absorbance was measured at 600 nm, and% viability values were determined.

3 RESULTS AND DISCUSSION

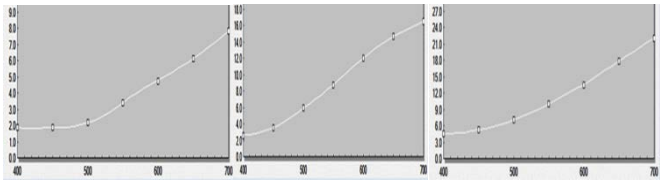
3.1 Colour Data of 100 % Wool Yarn Samples: CIE L* a* b* colour coordinate values that lightness-darkness (L*), green-red (-a, +a) and blue-yellow (-b, +b) colour coordinates of wool yarns dyed by walnut green husksextract fall into are given at Table1.

TABLE 1
L*, A*, B* VALUES OF WOOL YARN DYEİNG BY WALNUT GREEN HUSKS EXTRACT

Sample	L*	a*	b*
Non-mordant	**22.03**	**7.52**	**12.14**
Mordant with potassium double sulfate of aluminium	**38.53**	**8.62**	**18.27**
Mordant with Copper sulphate	**36.93**	**7.13**	**23.55**

According to table1, when L* values (lightness-darkness) of non-mordant and mordant wool yarns dyed by walnutgreenhuskswere examined, L* values increased after mordanting. Therefore, the samples dyed as non-mordant are darker. When a* (red-green) axis values of the samples were examined, it was observed that they took positive values, thus, they were dyed on red hue. The highest* value occurred on the sample mordanted with potassium double sulfate of aluminium. Potassium double sulfate of aluminium increased redness of the mordant colour. When b* (Yellow-blue) axis values were examined, it was observed that they took positive values, thus, the samples had yellowish hue. The highest b* value was obtained on wool yarns dyed by copper sulphate mordant. Copper sulphate increased yellowness of the mordant colour.

Ref % Ref % Ref %



Wave length (nm)Wave length (nm) Wave length (nm)
(a) (b) (c)

Fig. 2. Anti microbial a-b-c. Graphics Between Ref % and Wave Length (nm),Dyeing as (a) Non-Mordant, (b) With Potassium Double Sulfate of Aluminium, (c) With Copper Sulphate Mordant

When the graphics infigure2 were examined, it was seen that potassium double sulfate of aluminium and copper sulphate mordants increased reflection properties of colours. At 700nm wave length; it became ref 22.5 % at dyeing with potassium double sulfate of aluminiummordant, ref 17 % at dyeing with copper sulphate mordant, ref 8 % at non-mordant dyeing.

Colour Fastness Results. Fastness values, one of the significant parameters for textile industry, were examined in terms of washing and rubbing. Sharma and Grover [15] who examined washing, rubbing and light fastnesses of cotton fabrics dyed with walnut shell determined that the samples dyed for FeSO4 and AlK(SO4)2mordants had washing fastness values between 3/4-5, rubbing fastness values between 3/4-5 and light fastness values between 6-7. Mazeyar [16] who examined wool dyeing potential of aubergine shells on FeSO4 and[AlK(SO4)2] presence obtained washing fastness values between 4-5 for both mordants, on the other hand, he obtained '5-6' light fastness value for FeSO4 and '5' for [AlK(SO4)2]. When dyeings made by alder leaves were examined in terms of fastness, light fastness values between 4-7, rubbing fastness values between 3-5 and washing fastness values between 3/4-5 were obtained in the presence of FeSO4 for wool fabric.

In this study, colour fastnesses were found as washing and rubbing on samples yarns dyed as with green walnut husks and the values were given in Table 2.

According to Table 2, washing and rubbing fastness values of 100 % Wool non mordant dyed yarn was found 4/5-5. These values are defined as very good .Washing and rubbing fastness values can be increased by using potassium double sulfate of aluminium and Copper Sulphatemordants dyeing technology.

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TABLE 2
COLOUR FASTNESS VALUES OF DYED SAMPLES

Sample	Washingf astness	Rubbing fastness (dry)	Rubbing fastness (wet)
Non-Mordant dyed wool	4 /5	5	4/5
$KAl(SO_4)_2$] mordant	5	5	5
$CuSO_4$ mordant dyed wool	5	5	5

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3.2 Anti Mikrobiyel Activites:

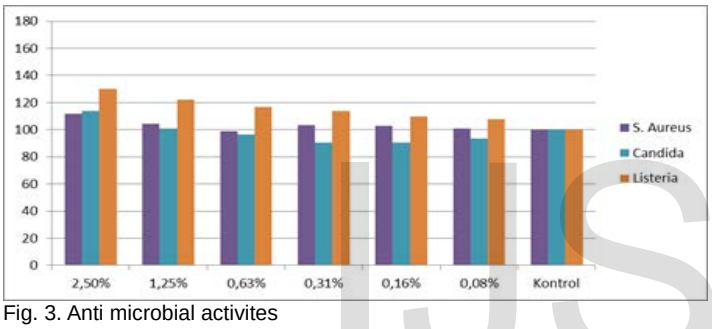

Fig. 3. Anti microbial activites

The non-mordant dying extract obtained from the green walnut husks is effective against reducing **the microorganisms of Gram (+) Candida albicans ATCC** 10231. It was no effective against reducing the microorganisms of gram (-) Listeria monocytogenes and Gram (+) Staphylococcus aureus.

4 CONCLUSION

It is so clear that walnut green husks a rich dye which doesn't require a mordant and affinity of wool based textile materials. Non- mordant dyeing processing parameters;walnut green husk taken at 200% rate according to fabric weight, the dyeing temperature is 80℃ and dyeing time is 60 minute.

Affinities of wool on dyeing with walnut green husks were high.It was seen that wool were dyed on dark brown hues at non-mordant dyeing made by using walnut green husks extract. It was determined that 100% wool yarns were able to be dyed with walnut green husks extract as non-mordant and without using metal salts.

The natural green husk color could be changed into different colors, by applying potassium double sulfate of aluminium,copper sulphate as various mordants.

The result shows that wool dyed with walnut green husks yarn can obtain good dyeing fastness degrees according to the grey scale and can be increased by using mordant dyeing technology.The antimicrobial effect should be investigated for different bacteria and concentrations.

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