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Investigation of the Effect of (Urea + Ammonia + Calcium Oxalate) Mordant Mixture on the Dyeing of Wool, Feathered-Leather and Cotton

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A new development was carried out in the dyeing of wool, feathered-leather and cotton using the root of common madder (*Rubia tinctorum* L.). The mordant effect of the (H_2N—CO—$NH_2 + NH_3 + CaC_2O_4$) mixture was widely investigated using a pre-mordanting method. Samples were mordanted in each chemical and combination of urea, ammonia, calcium oxalate, urea + ammonia, urea + calcium oxalate, ammonia + calcium oxalate and urea + ammonia + calcium oxalate. Selected transition element salts such as $Cu(NO_3)_2·3H_2O$, $MnSO_4·H_2O$, $Ni(CH_3COO)_2·4H_2O$, $Al(NO_3)_3·9H_2O$, $SnCl_2·2H_2O$, $Fe(NO_3)_2·9H_2O$, $Zn(NO_3)_2·6H_2O$ were used as second mordant agents after every combination. Dyeing conditions and colour codes and fastness were determined to obtain repeatable processes. High fastness colours were obtained using the triplex mixture of (urea + ammonia + calcium oxalate). In addition, resolution energies of complexes were calculated using the HyperChem computer programme.

Key Words: Madder plant, Urea, Ammonia, Calcium oxalate, Dyeing, Wool, Cotton.

INTRODUCTION

Because of the authentic importance and long term unfading properties of natural dye, natural products are the preference of humans. Colour retention is an important factor in natural dyeing. For this purpose, several mordants have been used. These are generally metal oxide mixtures, clay soil, juice of some plants, or metal salts such as $CuSO_4·5H_2O$, $AlK(SO_4)·12H_2O$, $FeSO_4·7H_2O$.[1]

According to the literature survey, some animal urine has also been used to obtain fast colours with wool[2]. Animal urine contains mainly urea, ammonia and calcium oxalate[3]. Which component(s) cause this result? This subject was investigated and interpreted according to the experimental results, theoretical approaches and data.

In this study, *Rubia tinctorum* L. was selected as a natural source, which has been used for dyeing textiles since 2000 B.C.[4] it can also be grown easily. In

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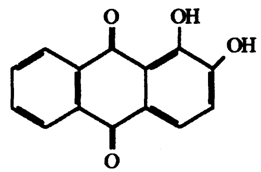
addition, this plant is important with respect to economics and trade. Common madder contains mainly alizarin (1,2-dihydroxyanthraquinone) (1) which is produced by the hydrolysis of ruberythric acid (2), rubiadine (1,3-dihydroxy-2-methylanthraquinone) (3) and purpurine (1,2,4-trihydroxanthraquinone) (4) are other components, which are found to a lesser extent in the roots of madder plant[5, 6].



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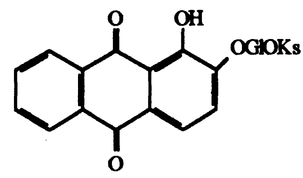

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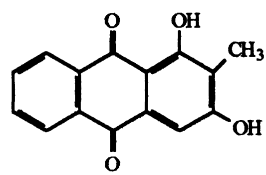

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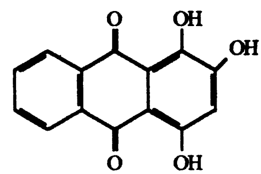

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The amount of the red component (alizarin) increases in October and is darker in May and June. Thus, the concentration of dyestuff changes in summer and autumn[7]. However, the amount of dyestuff is not effective on fastness. On the other hand, it affects only colour strength. Alizarin has two auxochrome group (—OH). This group exhibits dyeing properties for the dyeing of wool.

In this study, 616 numbers of wool, 112 numbers of feathered-leather and 82 numbers of cotton were dyed using the mordanting methods.

EXPERIMENTAL

General: Soxhlet apparatus was used to extract the dyestuff from *Rubia tinctorum* L. The solvent was evaporated using the Buchi RE rotary evaporator at Gaziosmanpaşa University. Light fastness was carried out with an Alas laundrometer LHTP model; crocks fastness was made with a crockmeter 225 model, in the Merinos factory, Bursa, and Se-Na textile factory in Tokat.

Plant Material: Common madder (*Rubia tinctorum* L.) belongs to Rubiaceae family. It was picked in the centre of Tokat in June 2001. It was kept in the herbarium of the Plant Protection Department, Faculty of Agriculture, Gaziosmanpaşa University and identified by Prof. Dr. Zeki Özer. The herbarium number of *Rubia tinctorum* L. is A.E.F. 1571.

Dyeing Material: Wool, feathered-leather and cotton are the most important textile materials, which are used in the textile sector. In this work, fowl wool and feathered-leather and pure white cotton samples were used as dyeing materials.

Extraction of Dyestuff from *Rubia tinctorum* L: Shadow dried madder roots were powdered using grinding machine. For the extraction process, a more polar extraction solvent was required; therefore ethanol was selected as the most appropriate solvent. 100 g of powdered sample was extracted at boiling point of extraction solvent, deionized water-ethanol (1 : 1) in soxhlet apparatus until colourless, approximately 15 times and all the extracts were combined before use in order to minimize variation in extracts. After the evaporation process, the total dyestuff was found to be 29.30%. 20 g of dyestuff was submitted on a silica gel column and eluted with $CHCl_3$—CH_3OH (4 : 1). Two components were separated (red and yellow). The red one was determined as alizarin (m.p. 289°C) which was already known[5]. The yellow component containing purpurine and rubiadine were not used in dyeing.

Dyeing of Wool (General Procedure): After allowing for 12 h of dyeing materials (for wool, feathered-leather and cotton) in 100 mL 0.1 M of urea + ammonia + calcium oxalate combinations, the mordanting methods were applied as given below:

1. Pre-mordanting, which means that the mordant was applied before dyeing.
2. Together mordanting means that the mordant was applied in the dye bath.

1. **Pre-mordanting:** White woollen strips (1 g) were heated in 100 mL 0.1 M of mordant solution for 45 min at 90°C. After cooling, the dyed samples were rinsed with distilled water and dried. This method was applied at pH: 2, 4, 6 and 8 for each mordant.
2. **Together mordanting:** Mordant (equivalent to 0.1 M concentration value), 100 mL of dyestuff solution and 1 g of woollen strips were mixed in a 250 mL Erlenmeyer flask. This mixture was heated for 50 min at 90°C. After cooling, it was filtered, rinsed with distilled water and dried. This method was also carried out at pH 2, 4, 6 and 8 for each mordant. pH was adjusted using acetic acid and sodium hydroxide for pre-mordanting and together mordanting.

Dyeing of Feathered-Leather (General Procedure). For this purpose, only together mordanting method was applied as given below.

Together mordanting: The white feathered leather (feather length 1 cm, area 16 cm^2), 100 mL of dyestuff solution and mordant agent were mixed in 250 mL beher glass. This mixture was shaken at frequent intervals for 50 min at 45°C using a mechanical shaker. Finally, the dyed feathered-leather was filtered, washed with distilled water and dried. This procedure was carried out at pH 2, 4, 6 and 8 for each mordant.

Dyeing of Cotton (General Procedure). The same mordanting method (together mordanting) in dyeing of woollen strips was used for dyeing of cotton.

RESULTS AND DISCUSSION

As mentioned in the experimental section, the purpose of this work is to determine the effect of the triplex mixture (urea + ammonia + calcium oxalate) in dyeing of wool, feathered leather and cotton. For this purpose, urea, ammonia, calcium oxalate and combinations of urea + ammonia, urea + calcium oxalate, ammonia + calcium oxalate and urea + ammonia + calcium oxalate were used before dyeing. After these procedures, each of the materials was dyed using the mordanting methods.

Based on the fastness analysis[7] results for light washing, crocking and hypochloride, the best pre-mordanting agent was determined. The average fastness data are given in Table-1 and Table-2 for each combination.

TABLE-1
THE AVERAGE FASTNESS VALUES (WASHING, LIGHT, CROCKING, HYPOCHLORIDE) FOR THE DYED WOOLEN SAMPLES

Mordant	pH 2		pH 4		pH 6		pH 8	
	Pre mordant	Together mordant	Pre mordant	Together mordant	Pre mordant	Together mordant	Pre mordant	Together mordant
Ammonia	4.84	4.79	4.78	4.65	4.73	4.62	4.74	4.62
Urea	4.54	4.11	4.48	4.36	4.45	4.33	4.44	4.33
Calcium oxalate	4.38	4.02	4.37	4.01	4.31	4.00	4.30	4.00
Ammonia + Calcium oxalate	5.19	5.07	5.19	5.03	5.04	4.92	5.01	4.90
Urea + Calcium oxalate	4.55	5.07	4.36	5.02	4.94	4.81	4.94	4.81
Urea + Ammonia	4.86	4.72	4.76	4.84	4.82	4.68	4.78	4.64
Ammonia + Oxalate + Urea	5.39	5.24	5.34	5.21	5.42	5.28	5.40	5.24

Fastness values have been calculated average of the washing, crocking, light and hypochloride tests. For this purpose, the arithmetic average was applied. When we examine these fastness results we conclude that the best pre-mordanting agent is the triplex mixture ($NH_3 + CaC_2O_4 + H_2NCONH_2$) for dyed woollen strips and feathered-leather. According to the average fastness analyses results given in Tables-1 and 2, mordant combinations are not effective in the dyeing of cotton. It is mainly related to the chemical structure of cotton molecule. It is known that cotton consists of glucoside unit and differs from wool or feathered-leather. Thus, we can say that the treating of cotton with ammonia, calcium oxalate and urea is not important.

It is known that wool and feathered-leather consist of keratin molecule, which has helix form.[8] Here, NH_3 helps to relax the helix form of keratin molecule and thus the dyestuff influences can more easily bond with the keratin of wool or feathered-leather. Urea is widely used in textile industry to increase the solubility of dyestuff. For this research, urea was used as a pre-mordanting agent but we can say that it is not as effective as NH_3.

However, the best results had been obtained from the mixture of ($NH_3 + H_2NCONH_2 + CaC_2O_4$) in dyeing of woollen strips and feathered-leather. The fastness analyses of this mixture are better than others. These results show that calcium oxalate is the most important compound of these mordant mixtures. Otherwise, the fastness analyses wouldn't give good results. The effects of the fastness results of the combinations of triplex mixture for wool and feathered-leather can be given in the following sequence: ($NH_3 + CaC_2O_4 + H_2NCONH_2$) > ($NH_3 + CaC_2O_4$) > ($NH_3 + H_2NCONH_2$) > NH_3 > H_2NCONH_2 > CaC_2O_4.

TABLE-2
THE AVERAGE FASTNESS VALUES (WASHING, LIGHT, CROCKING, HYPOCHLORIDE) FOR THE DYED WOOLEN SAMPLES

Mordant	pH 2		pH 4		pH 6		pH 8	
	F.L.	Cotton	F.L	Cotton	F.L.	Cotton	F.L	Cotton
Ammonia	4.82	3.75	4.75	3.75	4.55	3.75	4.57	3.75
Urea	4.35	4.10	4.25	4.20	4.25	4.10	4.25	4.10
Calcium oxalate	3.92	3.23	3.92	3.23	3.87	3.23	3.87	3.23
Ammonia + Calcium oxalate	5.05	4.10	5.05	4.10	4.85	4.10	4.85	4.10
Urea + Calcium oxalate	4.77	4.00	4.67	4.00	4.75	4.00	4.75	4.00
Urea + Ammonia	4.75	3.70	4.67	3.70	4.70	3.70	4.82	3.70
Ammonia + Oxalate + Urea	5.35	4.40	5.25	4.40	5.30	4.40	5.30	4.40

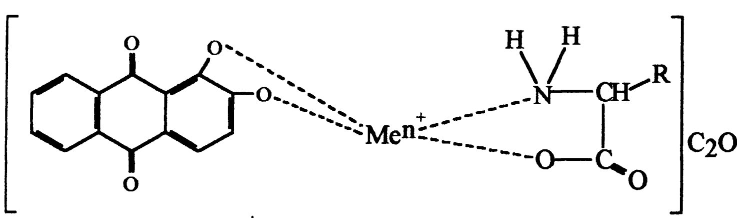
F.L.: Feathered-leather.

Based on the theoretical values, the most resolution complex has to be formed from Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+} and Sn^{2+} follow this metal cation (Cu^{2+}). The resolution energies of Ni^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+} are similar to each other.

In the dyeing of feathered-leather (at 40–45°C) and wool (at 90°C), the better pH values were determined at 6 and less. In dyeing of feathered-leather at higher pH values (pH > 6 and 8) at 40–45°C, desirable dyeing cannot be obtained because of considerable chemical bonding is not occurring. This subject is related to the formation of chemical bond between the structure of feathered-leather and chemical structure of dyestuff. That is, the repulsive forces are present instead of attractive forces between feathered-leather and dye.

Dyeing mechanism

Alizarin molecules have two auxochrome groups. These groups produce stable complex compounds on the woollen strips. These are known as inner complexes. We can say that the oxalate anion, $C_2O_4^{2-}$, has been increasing the resolution of these complex compounds. Urea and ammonia have been helpful in fixing the dyestuff to the amino acid molecule as well as transition metal salts. The dyeing mechanism can be considered as given in **Scheme-1.**

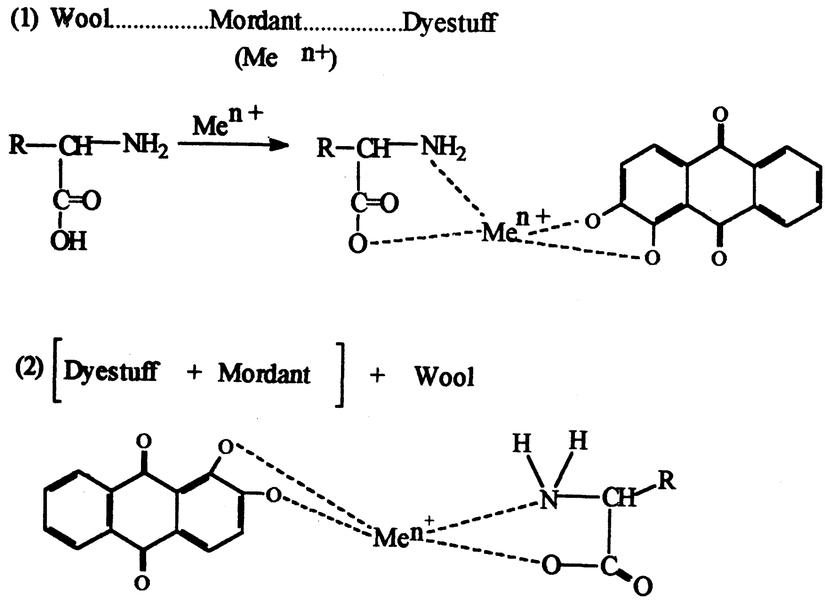


Me^{n+} = metal cation

Scheme-1

Molecules of wool can be considered as an amphoteric compound. During the dyeing of wool, inter molecular hydrogen bonding and coordinative bondings occur between the dyestuff and the amino acid groups of the wool.

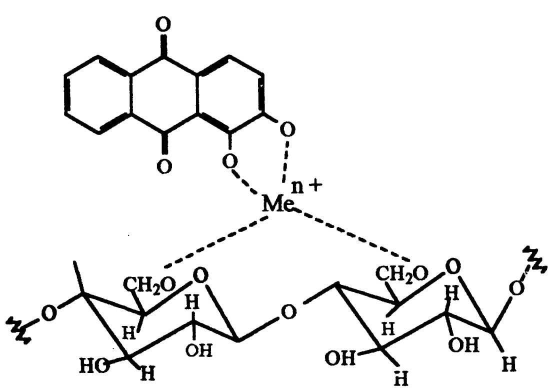
The mechanism of the pre-mordanting (1) and together mordanting (2) can be considered as given in **Scheme-2.**



Scheme-2

In the dyeing of cotton, the most effective pH value was determined at 8. However, the dyeing occurred at other pH values (pH = 6, 4, 2). The effective pH values were determined from the fastness analyses results and penetration rate of dye to fibre.

The dyeing mechanism of cotton[9] can be considered as below **(Scheme-3)**:



Scheme-3

The second purpose of this work is to determine the resolution complex occurring on woollen strips. This was carried out using the HYPER CHEM. Program as theoretical (Fig. 1).

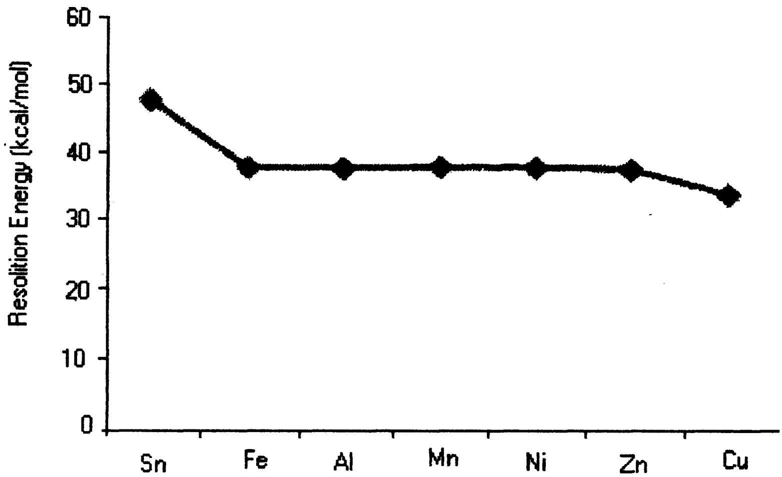


Fig. 1 Resolution energies of some transition elements with alizarin.

Conclusion

1. In this study, a lot of colour tones were obtained.
2. This study is very cheap, reliable and repeatable.
3. These processes can be used by wool and leather industry.
4. To obtain unfading colours, wool or feathered-leather can be mordanted with (urea-ammonia + calcium oxalate) mixture before the dyeing processes.

Generally, these results open new ways to dye natural fibres, especially wool and feathered-leather and help to expand the field of application of natural dyeing technology.

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