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Research Article

Zirconium Oxychloride as a Novel Mordant for Natural Dyeing of Wool Yarns

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Zirconium oxychloride, a well-known flame retardant, is introduced as a novel mordant for wool dyeing. This has been indicated by mordanting of wool yarns with zirconium oxychloride in different conditions and then dyeing with madder as a famous natural dye. The tenacity, color coordinates, washing, and light fastnesses of the dyed wool confirmed the positive influence of zirconium oxychloride as a useful mordant for wool dyeing with a low impact on the color coordinates. Further, an appropriate washing and light fastness were obtained for the zirconium-oxychloride-mordanted wool yarns. The central composite design (CCD) was used to design the experiments with four variables on the results of tensile strength. Statistical analysis confirmed the optimum conditions obtained through the experimental results.

1. Introduction

Wool with high water absorption, good dye ability, high elasticity, reasonable bulkiness, and fire resistance has been used in clothing and floor coverings [1]. The dyeing of wool also poses a challenge for textile chemists due to its complexity of chemical and physical structure [2]. Wool yarns were initially dyed with natural dyes which then the dyeing process improved and transferred from one generation to the other. Although the consumption of natural dyes is high, it has been decreasing by the invention of synthetic dyes. Natural dyes were replaced by synthetic dyes due to their ability to easily match a desired color, increasing variety, high purity, cheap price, and easy processing. However, through production and application of synthetic dyes, producers and consumers have observed several ecological and biological problems [3].

Recently, an interest of using natural dyes in textile coloration has been growing due to the environmental regulation appearing in response to the toxic and allergic reactions associated with synthetic dyes. However, natural dyes are friendly to the environment and exhibit better biodegradability with higher environment compatibility [4].

Madder is a main source of a natural dye producing a variety of anthraquinone dyes in its roots and rhizomes. The main components are di- and tri-hydroxy-anthraquinones, alizarin and purpurin and their derivatives; ruberythric acid (alizarin-primeveroside), pseudopurpurin, and lucidin-primeveroside. Rubiadin, munjisti, quinizarin (1,4 dihydroxyanthraquinone), lucidin, nordamnacanthal, xanthopurpurin, and 1,8-dihydroxyanthraquinone are also identified from plant tissues [5–7]. Farizadeh et al. [8] determined the amount of alizarin, purpurin, and quinizarin in the Iranian madder. It is an old and famous dye for dyeing wool, silk, and cotton fibers [7] which has been widely distributed in southern and southeastern Europe, the Mediterranean area, and in Asia [9]. The chemical structure of more important coloring compounds is presented in Figure 1.

Finding new natural dye and obtaining easy application process are two considerable facts which are interesting for chemists. These are including dye content in the natural source, combination usage, other unknown properties, effect of mordants and auxiliaries on color, light fastness, improvements in production methods, and the development of alternative sources [2]. Gulrajani et al. studied the colorimetric properties of a range of natural yellow dyes,

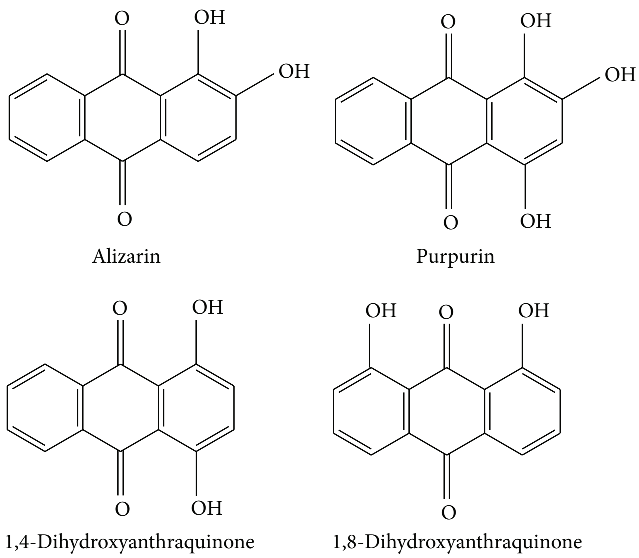


Figure 1: Chemical structure of the main compounds of madder.

Table 1: Central composite design for mordanting of wool with HCl.

Run number	A: zirconium oxychloride (wt%)	B: temperature (°C)	C: citric acid (o.w.w.%)	D: HCl (37%) (o.w.w.%)	Tenacity (g/tex)
1	10.60	95.00	12.80	5.65	8.62
2	5.60	77.00	12.80	5.65	8.57
3	8.10	70.86	9.55	8.00	8.86
4	8.10	86.00	9.55	8.00	9.21
5	8.10	86.00	9.55	4.05	8.76
6	10.60	77.00	6.30	10.35	8.86
7	8.10	86.00	9.55	8.00	9.17
8	8.10	86.00	9.55	8.00	8.95
9	8.10	101.14	9.55	8.00	7.65
10	8.10	86.00	9.55	8.00	9.03
11	8.10	86.00	9.55	8.00	9.56
12	12.30	86.00	9.55	8.00	8.57
13	5.60	95.00	6.30	10.35	9.12
14	5.60	95.00	12.80	10.35	9.13
15	3.90	86.00	9.55	8.00	8.95
16	8.10	86.00	15.02	8.00	8.34
17	8.10	86.00	4.08	8.00	8.9
18	10.60	77.00	12.80	10.35	9.5
19	5.60	77.00	6.30	5.65	9.52
20	10.60	95.00	6.30	5.65	9.19
21	8.10	86.00	9.55	11.95	8.38

including henna, dolu, kamala, onion skins, and turmeric, with various mordants.Horrocks investigated the color and fastness properties of natural saffron [2]. There are relatively few papers studying the effect of mordant on color [2].

Zirconium compounds have been used on cotton to improve dye fastness and functional properties and on wool to improve its thermal behavior [10–13]. Zirconium has no known biological role, and its compounds are of low toxicity. The human body contains only 1 mg zirconium, and daily intake is approximately 50 μg per day. Zirconium content in human blood is as low as 10 ppb. 70% of plants have no detectable zirconium content or as little as 5 ppb [14].

Forouharshod et al. investigated the effect of zirconium compounds on the flame-retardant wool indicating higher heat resistance on zirconium-salt-treated wool [11–13]. The optimum conditions of wool flame retardant obtained contain 9.74% $ZrOCl_2$, 9.6% citric acid and 6.3% formic acid, at 95°C and 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C [11, 12].

To the best of our knowledge there is no report on mordanting of wool before dyeing; however, there are some reports on flame-retardant wool with zirconium salts. Here, the bi-functionality of zirconium salt on wool as mordant and flame retardant has been introduced. The flame retardancy properties of zirconium salts have already been reported in our previous papers. In this paper the functionality of zirconium salt as a mordant on wool dyeing was focused on. Also the influence of zirconium oxychloride on the physical properties of the wool yarns at different temperatures and acid concentrations during wool mordanting were investigated. Further the colorimetric properties, light fastness, and washing fastness properties of the dyed wool with madder were reported and discussed.

2. Experimental

2.1. Materials. The coarse wool yarn with 432/2 tex and 144 tpm from Iran, a commercial nonionic detergent for wool scouring from local market (Iran), zirconium oxychloride (35% ZrO_2) from Shanghai Yancui Co., China, hydrochloric acid, formic acid, and citric acid from Merck, Germany, and madder roots from local market (Yazd, Iran) in the powder form were used.

2.2. Scouring. The wool yarns were first scoured with 0.5% nonionic detergent at 50°C for 30 min (L : G = 40 : 1), then washed with tap water, and finally dried at room temperature.

2.3. Mordanting. The mordanting bath was prepared with different concentrations of hydrochloric acid, formic acid, citric acid, and $ZrOCl_2$ with L : G = 20 : 1 according to Tables 1 and 2.

Hydrochloric acid or formic acid was added to the bath solution to maintain a pH = 2 and 3 during mordanting, respectively. The mordanting was started at 40°C, continued for 20 min, and then heated to reach the specified temperature for 30 min followed at the same temperature for 45 min.

2.4. Dyeing. Dye solutions were prepared 24 h prior to dyeing by adding madder powder to water (50% o.w.f., L : G = 50 : 1). The dyeing process was started at 40°C, followed by heating at 85°C within 20 min, and remained at the same temperature for 1 h. The pH was adjusted at 5 by using acetic acid solution.

2.5. Tensile Strength. The tensile strength of the mordanted and unmordanted wool yarns was obtained by using an Instron TE-500 from Farayab (Iran) with gauge of 20 cm and a cross-head speed of 25 cm/min. The samples were conditioned according to ASTM D2256 before testing.

2.6. Reflectance. The reflectance of the dyed samples was recorded by using a GretagMacbeth Coloreye 7000A spectrophotometer integrated with an IBM personal computer. CIELAB color coordinates (L^*, a^*, b^*, C^*, and h) was calculated from the reflectance data for 10° angle observer and illuminant D65.

2.7. Color Fastness. The washing fastness properties and degree of staining on the adjacent yarns of the samples were measured according to ISO 105-C01 using a gray scale with rating from 1 to 5.

The color hue changes of yarn and were measured after exposure to the daylight for 2 and 7 days according to ISO 105-B01. The color fastness of various dyed wool samples was assessed by using a blue scale rating from 1 to 8.

2.8. Scanning Electron Microscopy (SEM-EDXS). Morphology of the samples was observed by scanning electron microscopy (VEGA TESCAN, Czech Republic) as the samples were fixed to SEM holders and coated with a thin layer of gold prior to SEM observation.

2.9. Experimental Design. Central composite design (CCD) was used to obtain experimental plan with four variables according to Table 3. Four variables were zirconium oxychloride, formic acid or hydrochloric acid/citric acid, and temperature with the indicated ranges as indicated in Table 3. Also the influence of the variable on the results of tensile strength (C.L.) based on g/tex was fitted in the following second order polynomial function:

$$\text{C.L.} = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum c_i x_i^2, \quad i \geq j, \quad i = 1, 2, 3, 4. \tag{1}$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i is regression coefficient explaining the influence of the variables in their linear form, b_{ij} is regression coefficient of the interaction terms between variables, and c_i is the coefficient of quadratic form of variables.

3. Results and Discussion

3.1. Tensile Strength. The initial modulus, tenacity, and extension at break of the untreated and zirconium-oxychloride treated wool yarns are presented in Table 4. The extension at break for the treated samples is higher than the untreated one due to that the influence of mordanting with zirconium salt led to producing more elastic wool fibers. Also the sample treated with HCl shows a small decrease in tenacity comparing to the sample treated with formic acid thereby resulting in higher adsorption of zirconium salt. Further, the initial modulus of the treated wool with zirconium salt decreases that is lower for the fabric treated in very low pH (HCl) that can be due to the acid impact on the wool fabric.

Table 2: Central composite design for mordanting of wool with formic acid.

Run number	A: zirconium oxychloride (wt%)	B: temperature (°C)	C: citric acid (o.w.w.%)	D: formic acid (o.w.w.%)	Tenacity (g/tex)
1	10.30	95.00	12.80	5.65	8.97
2	10.30	77.00	12.80	10.35	8.27
3	4.00	86.00	9.55	8.00	8.92
4	5.60	95.00	12.80	10.35	8.36
5	10.30	95.00	6.30	5.65	9.20
6	7.95	101.14	9.55	8.00	8.57
7	5.60	95.00	6.30	10.35	9.16
8	11.90	86.00	9.55	8.00	8.50
9	7.95	86.00	15.02	8.00	9.50
10	5.60	77.00	12.80	5.65	9.23
11	7.95	86.00	9.55	8.00	9.65
12	7.95	86.00	9.55	8.00	9.71
13	7.95	86.00	9.55	8.00	8.95
14	7.95	86.00	4.08	8.00	8.58
15	5.60	77.00	6.30	5.65	9.94
16	7.95	86.00	9.55	8.00	8.37
17	7.95	70.86	9.55	8.00	8.64
18	7.95	86.00	9.55	11.95	8.85
19	10.30	77.00	6.30	10.35	8.68
20	7.95	86.00	9.55	4.05	8.40
21	7.95	86.00	9.55	8.00	8.58

Table 3: Range of variables.

Variable	Lower limited	Upper limited
Temperature (°C)	77	95
Zirconium oxychloride (wt%)	5.60	10.60
Citric acid (o.w.w%)	6.30	12.80
Formic acid (o.w.w%)	5.65	10.35
Hydrochloric acid (37%) (o.w.w%)	5.65	10.35

Table 4: Tensile properties of untreated and zirconium-oxychloride treated wool yarns (SD. was less than 5%).

Samples	Initial modulus (g/tex)	Extension at break (%)	Tenacity (g/tex)
Raw wool	49.93 (0.3)	16.20 (4.4)	10.52 (0.9)
Scoured wool	42.47 (0.6)	15.75 (2)	8.70 (0.7)
$ZrOCl_2$-formic acid[a]	33.93 (0.5)	20.33 (2)	8.97 (0.4)
$ZrOCl_2$-hydrochloric acid[b]	27.67 (0.6)	24.75 (4.4)	8.90 (0.9)

[a] Wool treated with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C.
[b] Wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C.

3.2. Statistical Analysis. The variance analysis has indicated that all of the expression models are meaningful (Tables 5 and 6). Also, the suitable P value test, which did not pass 0.050 for samples treated with formic acid and HCl, showed the suitability of the models.

Table 5: ANOVA for response surface quadratic model for samples treated with formic acid.

Source	Sum of squares	df	Mean square	F value	P value Prob > F
Model	0.000	0			
Residual	4.75	20	0.24		
Lack of fit	3.31	16	0.21	0.58	0.8081
Pure error	1.43	4	0.36		
Cor total	4.75	20			

Table 6: ANOVA for response surface quadratic model for samples treated with HCl.

Source	Sum of squares	df	Mean square	F value	P value Prob > F
Model	0.000	0			
Residual	4.02	20	0.20		
Lack of fit	3.80	16	0.24	4.31	0.0839
Pure error	0.22	4	0.055		
Cor total	4.02	20			

According to the ANOVA, suitable models for each treatment are

(i) tenacity = 8.98 (for treated wool with formic acid),

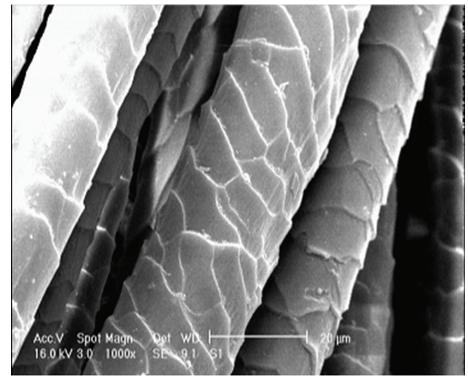
(ii) tenacity = 8.91 (for treated wool with hydrochloric acid).

3.3. Color. The color coordinates of zirconium-treated wool yarns dyed with madder are shown in Table 7. A small decrease is indicated in a^*, b^*, C^*, and L^* for the treated wool with HCl in comparison with the treated samples with formic acid in the two different processes (filtered dye solution and unfiltered dye solution). The treated wool yarn with zirconium oxychloride in the presence of hydrochloric acid showed a higher adsorption of zirconium on the wool and higher metallic complex formation with wool [11, 12] led to the lower L^* comparing to the treated wool with formic acid.

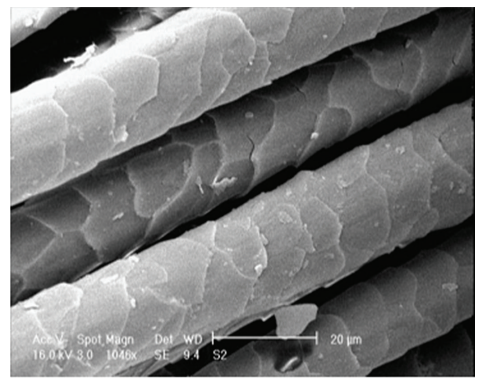
These results are in accordance with the results reported by Montazer and Parvinzaden on dyeing of wool premordanted with alum [3]. Therefore, zirconium oxychloride can be used as a commercial mordant in dyeing of wool with multifunctional purposes.

Also the filtration has a good influence on the lightness of the dye as the filtered dye indicated a higher lightness on the wool yarns. The samples dyed with unfiltered dye showed half lightness comparing to the filtered dye samples due to the higher dye uptake. The color changes in Table 7 indicated the same results.

3.4. Color Fastness. The results of washing and light fastness tests are reported in Table 8. The appropriate washing fastness was obtained on the samples treated with zirconium oxychloride with two diverse methods. Also the samples treated with formic and hydrochloric acids showed appropriate light fastness comparing to untreated wool after 2 days of the daylight exposure. Zirconium oxychloride and hydrochloric acid led to increased dye penetration into the wool fiber and produced darker shades. Hence, they are less vulnerable to the light [15, 16]. Further, no more fading has been observed on the samples exposed to the daylight for 7 days. Thus, the color fading of the samples was limited to a certain period of the daylight exposure. The results are similar to the results of light fastness obtained on the dyed wool with madder pretreated with alum reported by Montazer and Parvinzaden. Overall, zirconium oxychloride premordanting helps to obtain higher fastness properties [3]. Further, filtration of the madder dye led to higher fastness properties as some impurities removed from the dye assisted better fastness features.



(a)



(b)

Figure 2: SEM of (a) wool treated with 9.74% ZrOCl2, 9.6% citric acid, and 6.3% formic acid at 95°C and (b) wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C.

3.5. SEM. The SEM was used to show the effect of mordant on the surface of the fabric. Surface morphology of the treated wool samples is shown in Figure 2. There are no significant changes on the fiber surface of the mordanted wool; however, presence of some particles on the fiber surface may be related to the loaded zirconium mordant. It has been already shown that the adsorption of zirconium is higher with hydrochloric acid in comparison with formic acid [12].

Presence of zirconium and other elements on the wool-treated surfaces is investigated by EDXS analysis and results are reported in Table 9 following the analysis of one particle observed in Figure 2. The treated wool with hydrochloric

Table 7: Color coordinates of zirconium treated madder dyed wool with filtered and unfiltered solution dye.

Sample	a^*	b^*	C^*	h	L^*	ΔE
$ZrOCl_2$-formic acid[a]	29.80 (1.2)	15.64 (1.0)	33.66 (1.1)	27.69 (1.8)	24.68 (1.0)	20.8
$ZrOCl_2$-formic acid[b]	28.22 (0.8)	17.98 (1.0)	33.46 (0.4)	32.51 (0.5)	45.29 (0.7)	
$ZrOCl_2$-hydrochloric acid[c]	26.39 (0.7)	12.02 (0.4)	29.00 (1.5)	24.48 (0.9)	21.00 (0.7)	24
$ZrOCl_2$-hydrochloric acid[d]	27.69 (0.4)	16.56 (0.1)	32.27 (0.8)	30.88 (0.8)	44.56 (0.4)	

[a]Wool treated with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C and dyed with unfiltered madder dye solution.
[b]Wool treated with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C and dyed with filtered madder dye solution.
[c]Wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C and dyed with unfiltered madder dye solution.
[d]Wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C and dyed with filtered madder dye solution.

Table 8: Wash fastness and light fastness properties of zirconium-treated madder dyed wool yarns with filtered and unfiltered solution dye.

Sample	Wash fastness			Light fastness	
	Wash fastness	Staining on wool	Staining on cotton	After 2 days	After 7 days
$ZrOCl_2$-formic acid[a]	4-5	4-5	4-5	5	4-5
$ZrOCl_2$-hydrochloric acid[b]	4-5	4-5	4-5	5	5
$ZrOCl_2$-formic acid[c]	5	5	5	5	4-5
$ZrOCl_2$-hydrochloric acid[d]	5	5	5	5	5
Untreated wool	3-4	3-4	3-4	3-4	3-4

[a]Wool treated with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C and dyed with unfiltered madder dye solution.
[b]Wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C and dyed with unfiltered madder dye solution.
[c]Wool treated with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C and dyed with filtered madder dye solution.
[d]Wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C and dyed with filtered madder dye solution.

Table 9: Elemental analysis of treated wool (normalized) (wt%).

Sample	Zr	S	Cl	Au	Total
$ZrOCl_2$-formic acid[a]	4.97	2.94	0.27	91.82	100
$ZrOCl_2$-hydrochloric acid[b]	6.74	2.13	0.46	90.68	100

[a]Sample was obtained with 9.74% $ZrOCl_2$, 9.6% citric acid, and 6.3% formic acid at 95°C.
[b]Sample was obtained with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92°C.

acid is capable to absorb more salts comparing to the wool treated with formic acid as the more zirconium measured on hydrochloric-treated wool.

4. Conclusion

Zirconium oxychloride, a well-known flame-retardant compound for wool, is introduced as a new mordant for wool dyeing with madder with reasonable properties. This is a colorless mordant for natural dyeing of wool with dye adsorption enhancement properties and light/washing fastness characteristics improvement. Further, using hydrochloric acid in dyeing process produced a darker shade property comparing to formic acid as reported elsewhere. Finally, the optimum mordanting conditions were obtained through using statistical models.

Conflict of Interests

The authors do not have a direct financial relation with the commercial identity mentioned in their paper.

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