Mordanting of Cellulosics with Iron (III) Sodium Tartrate (FeTNa) Complexes for Coloration with Natural Dyes

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Abstract

The effects of cellulose pretreatment with iron (III) sodium tartrate (FeTNa) complexes on subsequent coloration with natural dyes (alizarin, madder root extract, tannic acid) was investigated. The pretreatment leaves iron residues in the cellulose, which functions as a mordant in the subsequent dyeing. The residual iron improves dye uptake and the wash and light fastness ratings of the dyed materials. Thus, pretreatments with FeTNa may be a method of improving cellulose coloration with natural dyes.

Keywords: *FeTNa, viscose, alizarin, tannic acid*

Introduction

Iron (III) sodium tartrate complexes (FeTNa)[1] exhibit strong interactions with cellulose through formation of coordination complexes between the transition metal ion and polymer hydroxyl groups [1]. Stable mixtures of FeTNa are achieved with iron (III), tartaric acid and NaOH in a molar ratio of 1:3:6 respectively [2, 3], but by increasing the relative proportions of tartaric acid and/or NaOH, the degree of FeTNa interaction with cellulose may be varied from swelling up to dissolution. Thus FeTNa formulations have been employed for such purposes as viscometric evaluation of cellulose degree of polymerization [4], structure modifications of cellulosics [5, 6], and the manufacture of membranes and fibers [7, 8].

In our investigations on the effect of FeTNa on structure and morphology of regenerated cellulosics [9-11], it was noticed that the treatments left iron residues in the treated fibers. Iron salts are among the commonly used "mordants" in coloration with natural dyes to improve dye uptake and the wash- and light-fastness of dyed substrates. In this paper, we report on the effect of FeTNa pretreatments on the dyeing of viscose fabrics with alizarin (1,2-dihydroxy anthraquinone), extracts of roots from the madder plant *(Rubia tinctorum)* the main colorant in which is also alizarin, and tannic acid.

[1] The names of these mixtures are abbreviated as "FeTNa" in English language publications and as "EWNN" in German language publications (for Eisen-Weinsäure-Natrium).

Materials

The substrate used in the work was a satin-woven fabric made of viscose fibers, with a mass/area of 79 g/m^2, kindly provided by Lenzing AG (Austria). Of the colorants used, the madder root was obtained from a local farmer, the tannic acid ($C_{76}H_{52}O_{46}$) was of >95% purity, and the alizarin was of microscopy grade (purity ≥ 98%). All other reagents were of purity 95% or higher unless mentioned otherwise, and deionized water (of conductivity less than 10 µS/m) was used in the formulation of solutions.

Methods

Demineralization of fabrics

As calcium in cellulose fibers may influence their dyeability [12], the fabrics were demineralized to remove any residual ions, by treating them with a 0.5% (w/w) solution of HCl at a liquor ratio of 1:40 for 1 hour at 40°C. They were then rinsed with deionized water, neutralized by immersion in 1 g/l CH_3COONa, rinsed again with deionized water, and line-dried.

Preparation of FeTNa solutions

The solutions were prepared as described previously [9, 11] with a basic formulation of $FeCl_3.6H_2O$, tartaric acid, and NaOH in a molar ratio of 1:3.28:9.56. Three variations of this basic formulation were investigated in this work, where the iron (III) concentration was always 0.25 mol/l, but the content of excess NaOH (i.e. in addition to the amount required for the basic formulation) varied between 0.8, 1.25 and 2.5 mol/l.

FeTNa mordanting of fabrics

The demineralized fabrics were padded with the FeTNa solutions at a nip pressure of 1 bar and roller speed of 1 m/min, rested at room temperature for 10 min, then rinsed twice with deionized water for 5 min, neutralized by immersion in 1 g/l CH_3COOH, rinsed again with deionized water, and line-dried.

Determination of iron content in mordanted fabrics

About 0.2 g pieces from FeTNa mordanted fabrics were subjected to extraction in 50 ml of 1 mol/l HCl for 30 min at 90°C, and the Fe content in extracts were photometrically determined with the 1,10-phenanthroline method (DIN 38406–1: 1983-05) as described elsewhere [13]. In brief, 5 or 10 ml of extracts were pipetted into a 100 ml volumetric flask and buffered to pH 5 with ammonium acetate buffer. To this was added 2 ml of 100 g/l $NH_2OH.HCl$ and 2 ml of 5 g/l 1,10-phenanthroline. A colored complex was formed, the photometric absorbance of which was measured at 510 nm. The Fe contents were derived from the measured absorbance using a calibration curve constructed over a concentration range of 0.5–5.0 mg/l Fe with ammonium ferrous sulfate.

Fabric dyeing

The dyeings were performed on 5 cm × 20 cm pieces from the FeTNa mordanted fabrics. In addition, a set of dyeings were performed on pieces from fabrics treated only with 0.8, 1.25 and 2.5 mol/l of NaOH.

With alizarin and tannic acid: Fabric pieces were immersed in dye formulations at a liquor ratio of 1:40, and agitated at 90°C for 1 h, then rinsed with deionized water and line-dried. The alizarin dye formulation contained 0.25±0.02 g/l of the colorant, 1 g/l CH_3COOH and 1 g/l CH_3COONa. The tannin dye formulation contained only 0.25±0.02 g/l of the colorant.

With madder root extract: The extract was obtained by immersing the plant material in deionized water heated to 90°C at a liquor ratio of 1:20 for 1 hour, and the residual solids were filtered out. The primary colorant in madder root extract is alizarin, and thus the extracts were diluted with deionized water to the extent that the dilutions exhibited the same photometric absorbance at 510 nm as a 0.25 g/l solution of the high purity alizarin. The diluted solutions, along with 1 g/l CH_3COOH and 1 g/l CH_3COONa, were used in the dyeing of fabric pieces, which was performed in the same manner as described above.

Determination of residual colorant content in solutions

Alizarin: A volume of 5 or 10 ml of the residual solution after dyeing was pipetted into a 100 ml volumetric flask containing 50 ml of 0.2 mol/l NaOH, and deionized water was added to make up the rest of the volume. The alizarin content was determined from photometric measurements of these solutions at 510 nm, using a calibration curve constructed with high purity alizarin in the concentration range of 0.001–0.050 g/l. The measurements were performed in triplicate.

Tannic acid: The residual tannic acid content in dye solutions was determined with the Folin–Ciocalteu (F–C) method. A 20 µl volume of residual solution was pipetted into a glass tube containing 1.58 ml deionized water and 100 µl of F–C reagent (Sigma-Aldrich). After a minute, a volume of 300 µl Na_2CO_3 solution was added, and the absorbance of solution was deter-

mined at 560 nm. The Na_2CO_3 solution contained 200 g of the salt dissolved in 800 ml deionized water, boiled, cooled, and then diluted up to 1 liter. The measurements were performed in triplicate.

Measurements on dyed fabrics

The reflectance spectra of the dyed pieces were measured on a d/8 spectrophotometer (Model CM 3610d, Konica Minolta, Japan). The measurement area was 8 mm in diameter and the specular component was excluded. The color coordinates on the CIELAB space were calculated for a D65 illuminant and 10° observer with the onboard software from the measured reflectance. The color depth was calculated with the Kubelka-Munk function from the reflectance measured at the wavelengths of maximum absorbance: 510 nm (samples dyed with alizarin and madder root extracts) and 560 nm (samples dyed with tannin).

The color fastness to washing was determined as per DIN 54014, by evaluating the color change in specimens washed with a detergent mixture containing 1.5 g/l of Ufarol™ NA 30 (30% formulation of sodium lauryl sulfate from Unger Fabrikker AS, Norway) and 1 g/l of Glucopon® EC 650 (50% formulation of C8-C16 alkyl polyglucosides from BASF AG, Germany) at 40°C for 30 min at a 1:50 liquor ratio. The color fastness to daylight was determined as per ISO 105-B01: 1999 by evaluating the color change in samples exposed for 24 h on a XENOTEST Alpha Lm device (Atlas-MTS, USA). The color changes in both tests were evaluated with grey scales as per ISO 105-A02: 1993.

Results and discussion

Table 1. *Iron content and L*, a*, b* coordinates in the CIELAB color space of fabrics pretreated with FeTNa containing different amounts of excess NaOH.*

Excess NaOH (mol/l)	Fe content (g/kg)	L*	a*	b*
0.8	2.2 ± 0.08	80.02	7.52	20.62
1.25	2.4 ± 0.16	79.72	7.25	22.47
2.5	3.4 ± 0.21	76.75	9.11	24.52

The iron content in samples increased with the content of excess NaOH in the FeTNa (see Table I), which may be attributed to the increase in substrate swelling with the change in NaOH amounts. From the CIELAB coordinates shown in the same table, it may be observed that the rise in Fe content coincided with a reduction in the L* value and an increase of the b* value, indicating that the fabrics acquired a dark yellowish hue with rising Fe content.

Table 2: *Residual dye contents in baths (g/l) after dyeing from an initial dyebath concentration of 0.25 g/l, forfabrics pretreated with FeTNa containing different amounts of excess NaOH, and fabrics pretreated with NaOH alone. The values shown in parentheses are the exhaustion percentages calculated from the concentration changes.*

Excess NaOH (mol/l)	Pretreatment[a]	
	FeTNa	NaOH alone
	Alizarin	
0.8	0.11 ± 0.01 (56%)	0.19 ± 0.01 (24%)
1.25	0.11 ± 0.01 (56%)	0.17 ± 0.01 (32%)
2.5	0.15 ± 0.01 (40%)	0.19 ± 0.01 (24%)
	Madder	
0.8	0.14 ± 0.01 (44%)	0.21 ± 0.01 (16%)
1.25	0.16 ± 0.01 (36%)	0.21 ± 0.01 (16%)
2.5	0.15 ± 0.01 (40%)	0.20 ± 0.01 (20%)
	Tannic acid	
0.8	0.06 ± 0.02 (76%)	0.20 ± 0.01 (20%)
1.25	0.06 ± 0.02 (76%)	0.20 ± 0.01 (20%)
2.5	0.06 ± 0.02 (76%)	0.20 ± 0.01 (20%)

[a] The residual dye contents in baths from dyeing of non-pretreated samples with alizarin, madder root extract and tannic acid were 0.17 ± 0.01 g/l, 0.20 ± 0.01 g/l and 0.18 ± 0.01 g/l corresponding to exhaustion percentages of 32%, 20% and 28% respectively.

The residual dye contents in baths after the dyeing experiments, and the calculated exhaustion percentages (i.e. the percent change in dye concentrations) are shown in Table 2. It may be observed that the FeTNa pretreated fabrics exhibited significantly greater dyebath exhaustion than the fabrics treated only with NaOH, which behaved similar to the non-pretreated samples. Thus, the residual Fe in the FeTNa treated fabrics exerted a positive uptake on the colorant uptake. Among the FeTNa treated fabrics, the exhaustion levels were greater with tannic acid as compared to the alizarin and madder extracts, which correlates with the significantly high propensity of tannic acid to form iron complexes [14]. Madder root extracts contain other components in addition to alizarin [15] that may interfere in alizarin complexation with iron, which may explain the lower exhaustion levels as compared to with pure alizarin.

Table 3: *L*, a*, b* coordinates in the CIELAB color space of fabrics dyed after pretreatment with FeTNa containing different amounts of excess NaOH and with NaOH alone.*

Excess NaOH (mol/l)	Pretreatment								
	FeTNa					NaOH alone			
	L*	a*	b*	K/S		L*	a*	b*	K/S
	Alizarin								
0.8	52.86	6.73	2.23	1.88		91.16	–1.10	11.39	0.05
1.25	50.65	7.12	4.66	2.40		91.26	–0.99	11.04	0.06
2.5	52.12	6.98	7.01	2.55		91.24	–1.02	11.18	0.07
	Madder								
0.8	54.36	10.89	1.10	2.22		75.28	12.11	19.33	0.33
1.25	52.95	11.28	1.23	2.14		76.18	11.85	19.14	0.35
2.5	53.89	10.59	0.88	2.63		75.70	11.94	18.90	0.41
	Tannic acid								
0.8	50.27	2.06	–1.59	1.84		—	—	—	—
1.25	50.06	2.05	–2.98	1.88		—	—	—	—
2.5	47.33	2.02	0.75	2.22		—	—	—	—

In Table 3 are listed the color coordinates and the shade depth (K/S) measured on fabrics after dyeing. The samples after dyeing were rinsed, whereupon all colorant was lost from the fabrics dyed with tannic acid after pretreatment with NaOH alone. Thus, their color coordinates and K/S values are not reported. From the other results, it may be observed that the FeTNa pretreated samples exhibit greater K/S values as compared to fabrics pretreated with NaOH alone, which is consistent with greater dye exhaustion values. Within the FeTNa pretreated samples, the K/S generally increases with the content of excess NaOH, and that is consistent with the rising Fe content in the samples. A rise in Fe content corresponded with a darker fabric color after the FeTNa pretreatment, and this is reflected even in the color after dyeing. The trends in L* values parallel those in the K/S. The differences in a* and b* coordinates between the FeTNa pretreated and NaOH pretreated fabrics reflect the color changes that occur on complex formation between the colorant and mordant. And the differences in a* and b* between the alizarin and madder root extract dyed samples reflect contributions of other components in the root extract in addition to the alizarin.

The wash- and light fastness ratings of the dyed samples are shown in Table 4 (1: poor to 5 and above: excellent). The wash fastness levels were consistently better in samples dyed after the FeTNa pretreatment, and the light fastness levels were generally better after the FeTNa pretreatment.

Table 4. *Wash and light fastness grades of fabrics dyed after FeTNa pretreatment and pretreatment with NaOH alone.*

Excess NaOH (mol/l)	Pretreatment			
	FeTNa		NaOH alone	
	Wash	Light	Wash	Light
	Alizarin			
0.8	3	>5	1	>5
1.25	2/3	>5	1	>5
2.5	2	>5	1	>5
	Madder			
0.8	3	>5	1	3
1.25	3	>5	1	3
2.5	3	>5	1	3
	Tannic acid			
0.8	3	3	—	—
1.25	3/4	3	—	—
2.5	3/4	3	—	—

Conclusions

It was observed that FeTNa pretreatments of cellulosics were effective in functioning a pre-mordanting treatment for the coloration of cellulosics with natural dyes (alizarin, madder and tannic acid). The pretreatment improved dye uptake and the light and wash fastness values. It is likely that apart from the Fe residues after the pretreatment, the swelling effect of FeTNa also contributed to the improved dye uptake and fastness levels, and thus such pretreatment may be useful in improving the performance of natural dyes.

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