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In-fibre formation of $Fe(OH)_3$—a new approach to pigment coloration of cellulose fibres

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Abstract

In alkaline solution a ligand exchange reaction between dissolved Fe(III)–D-gluconate complexes and cellulose fibres occurs. This reaction can be used to insert Fe(III)-ions in cellulose fibres. During rinsing the complex stability of the Fe(III)–cellulose complex is lowered and precipitation of Fe(III)-hydroxide inside the cellulose fibre occurs. This process permits pigment dyeing of cellulose fibres with in-situ in-fibre formation of the pigment. The impregnation was performed as an exhaust method at 80 °C using solutions Fe(III)–D-gluconate complexes with $c(Fe^{3+})$ 0.25–3.75 mmol l^{-1} and c(D-gluconate) 0.5–7.5 mmol l^{-1}. Due to the higher complex stability of the fibres iron concentrations in the fibre were determined with 2.7–14.8 mmol Fe per kg of fibre. Excellent fastness properties of the dyeings were found with light fastness of 7–8 and wet fastness of 5.

Keywords: Iron-pigment; Pigment dyeing; Cellulose fibre; Complex; D-Gluconate; Textile dyeing

1. Introduction

Insoluble Fe(II/III)-oxide containing pigments might be classified under the first substances used for coloration purposes. When the insoluble pigment is applied for textile coloration, the pigment either is mixed into the polymer prior to the formation of the textile raw material e.g. fibre, or the pigment is fixed on the surface of the textile material by means of binder systems [1–5].

In the case of cellulose fibres the latter of these processes may be preferable however the required binders define technical limits for example with regard to the handle of the product and the rub and wash fastness properties. Use of iron(II/III)-salt containing mordants for dyeing with natural dyes is an important traditional method for dyeing of cellulose fibres [6].

Attempts to precipitate iron hydroxides in cellulose fibres and on the surface of cellulose fibres also are proposed in the literature [7,8]. The dependence of the final result on the conditions of precipitation and pigment formation hinders the application of such processes for coloration of cellulose fibres. However the method has been described to be suited for production of technical products [7,8]. An important aspect to be considered is the low tendency of cellulose fibres to

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bind Fe(II/III)-ions, respectively, affinity of Fe(III)-ions to cellulose fibres is low [9–12].

In a strongly alkaline solution D-gluconate (DGL) is able to form very stable complexes with Fe(III)-ions thus no precipitation of $Fe(OH)_3$ is observed even above pH 14 [11–14].

In the presence of cellulose fibres a ligand exchange reaction proceeds and the Fe(III)-ions are complexed in the fibre [12].

The general reaction scheme is given in Eqs. (1)–(4) in Scheme 1. The reactions in Scheme 1 are given in general form with regard to the H^+ ions because various species can be expected to be presented as a function of pH value [11–13]

As shown recently a distinct capacity to complex Fe(III)-ions in alkaline solution has been determined for different cellulose fibres [Eq. (2)]. Following to the ligand exchange reaction the soluble ligand is released and the Fe(III)-ion remains in complexed state in the cellulose fibre and thus is immobilised.

During the rinse step the pH is decreased and the complex stability is lowered thus precipitation of $Fe(OH)_3$ according to Eq. (3) is induced inside the fibre.

This set of reactions forms the basis for a new procedure of pigment dyeing. In this paper the results of a study to investigate the use of this reaction for in-situ/in-fibre formation of Fe(III)-oxide pigments for dyeing of cellulose fibres are presented. Fundamental results characterising the formation of the pigment dyeings are presented and selected fastness properties are summarised.

2. Experimental

2.1. Chemicals and material

$Fe(NO_3)_3.9H_2O$, $(NH_4)_2Fe(SO_4)_2.6H_2O$, NaOH, NH_4Ac, AcOH, HCl, $NH_2OH.HCl$, 1,10-phenanthroline-hydrochloride were analytical grade chemicals (Merck, Darmstadt, Germany). Na-D-gluconate (DGL) with purity >99% was used. Bleached cotton yarn was used for the experiments (yarn count 63 m g^{-1}).

2.2. Preparation of iron containing yarn

A stock solution containing 0.05 mol l^{-1} $Fe(NO_3)_3$ and 0.1 mol l^{-1} DGL was prepared. Yarn (5 g) was mounted on a yarn holder and impregnated in a laboratory dyeing unit (MC-360 Novapretema AG, Schleitheim, Switzerland). The

Formation of complex in solution

$$Fe^{3+} + 2\,DGL^- \rightleftharpoons [FeH_{-x}(DGL)_2]^{(x-1)-} + x\,H^+ \quad (1)$$

Formation of Fe(III)-cellulose complex - Ligand exchange

$$[FeH_{-x}(DGL)_2]^{(x-1)-} + Cell \rightleftharpoons [FeH_{-y}Cell]^{(y-3)-} + 2\,DGL^- + (y-x)\,H^+ \quad (2)$$

Rinse of sample - Decomposition of complex

$$[FeH_{-y}Cell]^{(y-3)-} + 3\,H_2O + (y-3)\,H^+ \rightleftharpoons Fe(OH)_3 + Cell \quad (3)$$

Rinse of sample - Dissolution of $Fe(OH)_3$

$$Fe(OH)_3 + 2\,DGL^- \rightleftharpoons [FeH_{-x}(DGL)_2]^{(x-1)-} + 3\,H_2O + (x-3)\,H^+ \quad (4)$$

Scheme 1. General reaction scheme for the complexation of Fe(III)-ions in cellulose fibres.

samples were treated with 400 ml 0.5 mol l^{-1} NaOH containing a volume of 2–30 ml of the complex stock solution (liquor ratio of 1:80).

The samples were treated in this solutions for 6 h at 80 °C to achieve equilibrium of iron complexation in the fibres. The samples then were rinsed three times with cold water and dried at 40 °C [12].

The composition of the complex solutions are given in Table 1.

After incorporation of the $Fe(OH)_3$ the analytical determination of the iron content in the fibre was performed by extraction with hydrochloric acid and photometry of the Fe(II)–1,10-phenanthroline complex at 510 nm [15]. For this purpose the iron was extracted from the yarn samples with 50 ml 1 mol l^{-1} HCl for 30 min at 90 °C. An aliquot of 5 or 10 ml of extract was used for the photometrical analysis. The extract was pipetted into a 100 ml volumetric flask, neutralised with 5 ml acetate buffer (40 g NH_4Ac, 50 ml acetic acid in 100 ml buffer) and diluted with distilled water. Two millilitres of 1.43 mol l^{-1} $NH_2OH.HCl$ and 2 ml 0.021 mol l^{-1} 1,10-phenanthroline solution were added to form the complex and the flask was filled to 100 ml. The absorbance was measured after a reaction time of 50 min at a wavelength of 510 nm (Hitachi UV 2000, double beam spectrophotometer).

A calibration curve was established using defined amounts of $(NH_4)_2Fe(SO_4)_2.6H_2O$.

The CIE Lab values of the dyeings were measured with a tristimulus colorimeter (Minolta Chroma-Meter CR 210, sample diameter 10 mm).

The K/S values were calculated according the Kubelka–Munk function from the reflectance determined at 413 nm (Pye Unicam SP 8-100 double beam spectrophotometer, diffuse reflectance sphere $0°/d$).

2.3. Fastness properties

The wet-fastness was determined according DIN 54006 [16]. After thorough wetting in distilled water, the samples were treated for 4 h min at 37 °C. After drying the change in colour of the sample and the bleeding to white fabric (cotton, wool) were determined. The light-fastness was determined using artificial illumination with Xenon arc light according to DIN 54004 (Xenotest, Hanau, Germany) and was related to the standard scale of blue dyeings.

3. Results and discussion

An important basis for the reactions according Scheme 1 is the careful selection of the complex used:

- The thermodynamic stability of the complexes formed in solution must not exceed the stability of the cellulose–metal complex to achieve the desired ligand exchange reaction [Eqs. (1) and (2), Scheme 1]. However the precipitation of iron-hydroxides must not occur even at the high pH applied.
- The ligand exchange reaction according Eq. (2) has to proceed with sufficient reaction rate to reach the chemical equilibrium in reasonable time.

Table 1
Composition of complex solutions for iron impregnation (blank <25 ppm)

		Solution			Fibre	
No.	Vol. stock sol.	c(Fe^{3+}) mmol l^{-1}	ppm Fe^{3+} mg l^{-1}	c(DGL) mmol l^{-1}	ppm Fe^{3+} mg kg^{-1}	c(Fe^{3+}) mmol kg^{-1}
0	0	0	0	0	<25	<0.5
1	2	0.25	14	0.5	153	2.7
2	2	0.25	14	0.5	218	3.9
3	8	1.00	56	2.0	647	11.6
4	12	1.50	84	3.0	800	14.3
5	16	2.00	112	4.0	829	14.8
6	20	2.50	140	5.0	405	7.3
7	30	3.75	209	7.5	552	9.9

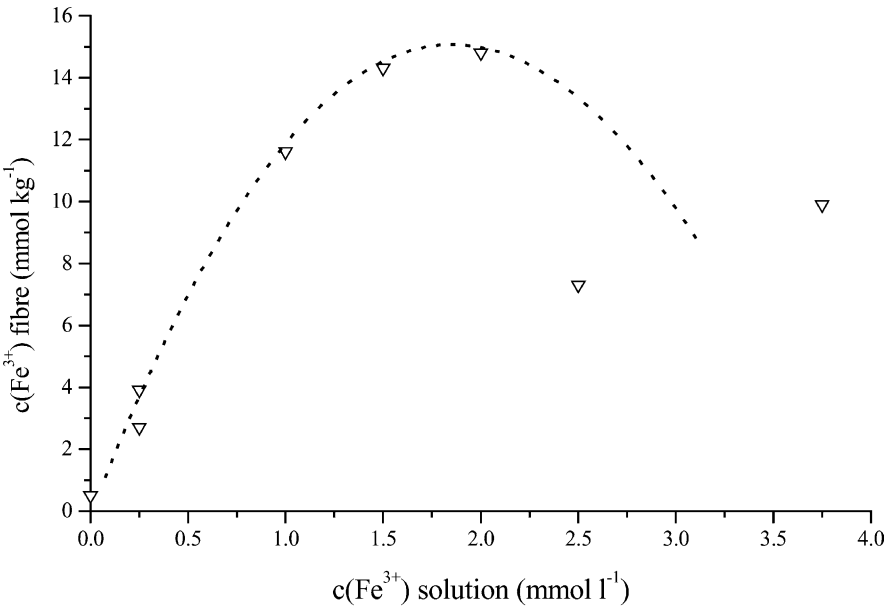

Fig. 1. Concentration of Fe^{3+} analysed in the fibre as function of the concentration of Fe^{3+}–DGL complex in the solution.

Due to the stability of the complexes no precipitation of $Fe(OH)_3$ is observed at the end of the impregnation step. As a result of the high relative volume of dyebath, changes in the Fe^{3+}-concentration in the bath remain low and at the end of the impregnation step the final concentration of the complex in solution can be estimated with approximately 85–90% of the initial value.

The concentration of the Fe(III)–DGL complex in the impregnation bath was varied from 0.25 to 3.75 mol l^{-1}. Due to the ligand exchange reaction the concentration of iron-ions in the fibre increases with the higher concentration of complex in solution. A maximum is observed at a concentration of 1.5–2 mmol l^{-1} Fe^{3+} and a ligand concentration of 3–4 mmol l^{-1} DGL (experiments 4 and 5). At a high concentration of complex a decrease in the analytically determined Fe-concentration in the fibres is observed, which can be explained with higher DGL concentrations present during the rinse operation which then can cause a re-dissolution of the precipitated hydroxide [Eq. (4)] (expts. 6 and 7).

In Fig. 1 the amount of $Fe(OH)_3$ pigment formed as a function of the concentration in the solution.

At the experimental conditions applied, the iron concentration in the fibre can reach approximately 10 times the concentration of Fe(III)–DGL complex present in solution. The CIELab-coordinates and the K/S values measured at a wavelength of 413 nm are shown in Table 2. The most dark colour was reached in experiment 5 at an iron content of 829 ppm showing $K/S = 0.549$, $L = 84.91$ and $b = +19.87$, which corresponds to a yellow-beige colour. The relation between K/S and the iron content is shown in Fig. 2. As expected for a

Table 2
CIELab-coordinates of pigment dyed fibres and K/S as function of Fe(III)-concentration (samples sorted with increasing iron content)

No.	ppm Fe^{3+} mg kg^{-1}	c(Fe^{3+}) mmol kg^{-1}	L	a	b	K/S
0	<25	<0.5	94.28	−2.14	+3.72	0.026
1	153	2.7	87.97	−5.58	+3.84	0.092
2	218	3.9	–	–	–	0.169
6	405	7.3	88.57	−0.81	+13.81	0.259
7	552	9.9	86.07	+0.67	+15.79	0.340
3	647	11.6	86.99	+0.66	+17.61	0.410
4	800	14.3	85.43	+1.66	+19.81	0.559
5	829	14.8	84.91	+2.51	+19.87	0.549

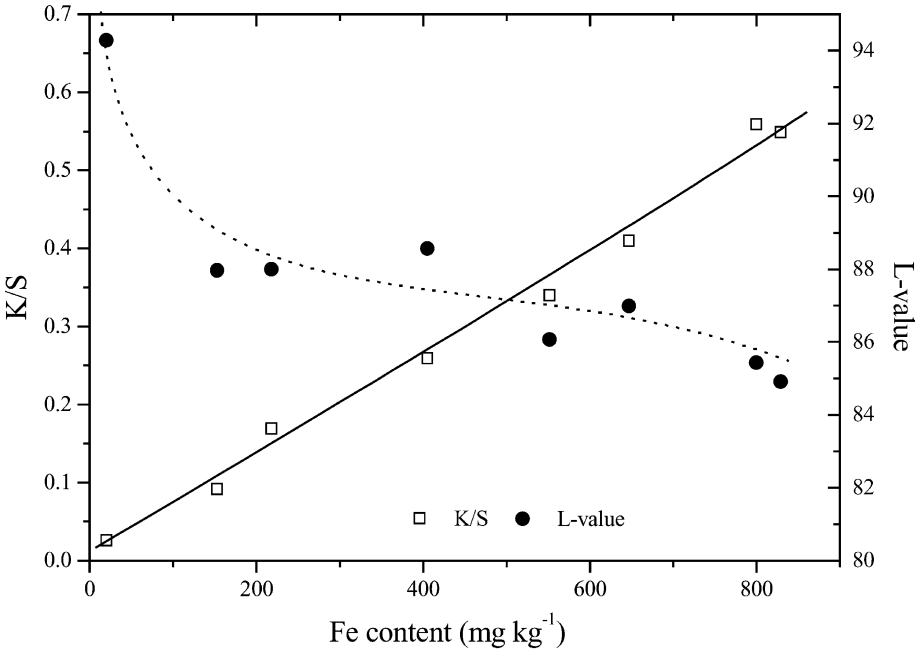

Fig. 2. K/S-values and L-value of the dyed material as function of Fe^{3+}-content analysed in the material.

pigment dyeing a linearity relationship between K/S and Fe-content of the fibre is found. The L-values as function of iron content also are shown in Fig. 2.

The CIELab-coordinates given in Table 2 prove that the colour of the dyeings is within the expected shades typical for Fe(III)-oxide pigments applied at low concentration which then range from yellow to light brown shades.

The fixation of the pigments inside the fibres should result in excellent fastness properties because removal is possible only after dissolution of the insoluble pigment. Excellent light fastness of 7–8 and wet fastness with marks of 5 were found (Table 3). The slight change in colour during the light fastness experiments can be attributed to changes of the cellulose fibre itself rather than to changes of the iron-pigment.

4. Conclusions

The in-situ in-fibre formation of iron-containing pigments by ligand exchange reactions in alkaline solutions could be found to be a useful technique to form coloured cellulose material with excellent

Table 3
Selected fastness properties of pigment dyeings on cotton (samples sorted with increasing iron content)

No.	ppm Fe^{3+} mg kg^{-1}	c(Fe^{3+}) mmol kg^{-1}	K/S	Light fastness	Wet fastness	Staining of cotton	Staining of wool
0	<25	<0.5	0.026	7–8	5	5	5
1	153	2.7	0.092	7–8	5	5	5
2	218	3.9	0.169	7–8	5	5	5
6	405	7.3	0.259	7–8	5	5	5
7	552	9.9	0.340	7–8	5	5	5
3	647	11.6	0.410	7–8	5	5	5
4	800	14.3	0.559	7–8	5	5	5
5	829	14.8	0.549	7–8	5	5	5

fastness properties. The formation of the insoluble Fe(III)-oxide pigments inside the fibre permits to combine the advantages of a homogenous dyeing process permitting fixation without binder with the high fastness properties of a pigment dyed material. In a single step treatment Fe(III)-concentrations of more than 800 ppm can be introduced into the fibre. The obtained yellow–beige shades exhibit excellent fastness values of 7–8 and wet fastness values of 5.

The presented results describe a general method to insert coloured metal oxides into a cellulose fibre on condition that the cellulose in the fibre exhibits a certain tendency to form complexes with the metal ion and that suited ligand systems for the metal ion to be inserted are available. An important requirement is the stability of the dissolved complex, which has to be stable enough to prevent precipitation of metal hydroxides in alkaline solution but also is sufficient weak to undergo the desired ligand exchange reaction with the cellulose fibre.

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