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Aluminium based dye lakes from plant extracts for textile coloration

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ABSTRACT

Production of concentrated natural dyes is a pre-requisite for a re-introduction of plant colorant based dyes into modern textile dyeing operations. Aluminium salts such as $Al_2(SO_4)_3.14\text{-}15H_2O$ or $KAl(SO_4)_2.12H_2O$ can be used to precipitate extracted plant dyes from aqueous extracts at pH 5.0–5.5. Onion peel, Canadian Goldenrod and pomegranate peel were studied as representative sources for dye extraction. As an average 5% w/w of the extracted dry plant material could be collected as precipitate. After dissolving these residues in diluted oxalic acid, the quality of the dye lake was characterised by photometric analysis of the total phenol content in the dry using the Folin-Ciocalteau method, determination of the aluminium content and measurement of the absorbance at 400 nm. Representative values of TPH in the dry solid dyestuff range from 20 to 40% and representative values for the aluminium content were determined with 3–5% w/w. Colour strength of the dissolved lakes was determined in dyeing experiments using different substrates and mordants followed by measurement of CIELab coordinates and K/S value according Kubelka-Munk function. Compared to the direct use of plant extracts the colour strength of the lakes is lower, however chroma of the dyeings is higher, as the lake formation also represents a dye purification step.

1. Introduction

Increasing awareness about the sustainability profile of textile dyeing processes led to intensified discussions about the possible use of natural colorants [1–6]. In general two main aspects define the main requirements on natural colorants as to be met by all textile dyes:

- The quality of the dyed goods has to reach at least a minimum level with regard to fastness, levelness and reproducibility [7–9]. For niche products and so called eco-products some flexibility is possible, as for these products higher flexibility for acceptance of lower fastness could be expected.
- In any case the arguments in support of an increased sustainability of natural colorants in textile dyeing operations are based on clear defined savings in resources consumption among them energy, water, chemicals or emission of greenhouse gases, effluents and land-use [10,11].

Production of the plant material for extraction of natural colorants must not compete with farming of crops for food production. This can be overcome by the use of by-products food industry and wastes from forestry.

As a disadvantage, independent of plant source used, with a low concentration of dye present in the plant material allows only the production of extracts with low concentration of dye.

Concentration of extracts by evaporation consumes considerable amounts of energy [10]. Membrane concentration techniques required considerable capital investment, thus direct use of plant extract usually is recommended for natural dyeing procedures. This concept requires the preparation of the extract in the dyehouse, which results in a number of handling problems. The dyehouse has to process rather high amounts of plant material, the disposal of the extracted residues has to be managed and in addition specialised equipment for plant material extraction has to be used [7,8].

The formation of an iron containing dye lake has been reported in the literature, however the addition of iron salts for dyestuff precipitation restricts the use of such products in the following dyeing experiments to applications with use of iron salt mordanting [1,12–15]. Al-based dye lakes are more preferable as dye product. Following to their dissolution in acid, Al-salt based lakes can be used as direct dyes, with Al-salt mordanting and also with Fe-salt mordanting. The higher complex stability of the iron–dye complex favours formation of iron-dye complexes, in presence of iron-ions in the dyebath [1].

Thus for the precipitation of the natural colorant from the plant extract, the use of aluminium salts instead of iron salt would be

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favourable. Only limited amount of information about use of aluminium salts to precipitate dyes from plant extracts for purposes of textile dyeing is available in the literature, the major part being older than 100 years [16–18]. More recently research has been published adressing dye lake production to obtain yellow and red pigments [19,20].

In this work the formation of aluminium based dye lakes has been studied with three different plant sources, namely Canadian Onion (*Allium Cepa*), Canadian Goldenrod (*Solidago Canadensis*) and Pommegranate (*Punica Granatum*). Extraction procedures and formation of dye lake have been performed with low-cost equipment. Characterisation of the aluminium-dye lakes was performed by analysis of their content in total phenolics and aluminium. The colour strength of the products was characterised by UV–Vis spectrophotometry and by standardised dyeing experiments.

The given data draw form a first set of parameters, required as a basis for the future installation of the process at the site of plant farming and harvesting. Parameters useful for quality assessment of aluminium based dye lakes in terms of dye content and color strength in dyeing experiments also are discussed.

2. Experimental

2.1. Chemicals and reagents

Analytical grade chemicals were used for the total phenol analysis and aluminium analysis Na_2CO_3 (Merck, Darmstadt, Germany) gallic acid monohydrate (Riedel-de-Haen, Seelze, Germany) Folin-Ciocalteau reagent (Sigma–Aldrich Chemie, Steinheim, Germany) $Al_2(SO_4)_3.16H_2O$ and Alizarin Red S $C_{14}H_7NaO_7S.H_2O$, $CaCl_2.2H_2O$ (Zeller GmbH, Hohenems, Austria) $KAl(SO_4)_2.12H_2O$, HCl 25 %w/w and sodium acetate 98.5% purity (Roth, Karlsruhe, Germany). For the dyestuff precipitation technical grade $Al_2(SO_4)_3.14\text{-}15H_2O$was used (Deuring, Hoerbranz, Austria). For the dyestuff dissolution technical grade oxalic acid $H_2C_2O_4.2H_2O$ and for the dyeing processes $FeSO_4.7H_2O$ (technical grade, gt; 96% purity, Riedl-de-Haen, Seelze, Germany) were used.

For dyeing experiments bleached wool yarn (metrical number Nm 28/2, Schoeller Bregenz, Austria) was used in form of small hanks. Scoured and bleached cotton jersey, flax fabric, and cotton fabric served as cellulosic substrates.

2.2. Plant material - extraction of dye

2.2.1. Onion peel extracts

Loose onion peel is removed during packaging. This part of dried peel from yellow and red onion was collected at local vegetable processing companies (D1 – D5 for yellow; D6 for the red peels). A weighted amount of plant material was extracted in hot tap water. Due to the high amount of soil based impurities, present in the red onion peel sample D6, this material was rinsed with cold tap water immediately before the extraction was started. Temperature and duration of extraction, and total volume of extract, and extract volume obtained per 1 kg of plant material (V_{spec}) are summarised for the individual experiments in Table 1. At the end of the extraction step, the plant material was removed by coarse filtration. Different aluminium salts were used for precipitation of the dye lake (Table 1). The calculated amount of aluminium salt was dissolved in approximately 6–7 times the volume of water to obtain a concentrated solution, which then was added to the extract. pH was adjusted to 3.5–5.5 by addition of diluted NaOH. Experimental details are given in Table 1.

The precipitate was allowed to settle at least for 16 h, then the supernatant was decanted off and the precipitate was concentrated either by centrifugation in a laboratory centrifuge for 10 min at 3000 U/min (Heraeus Multifuge 1L, Kendo, Osterode, Germany) or by filtration through coarse filter paper (commercial coffee filter, MelittaBremen, Germany). The filter cake was dried in a laboratory oven at 60–65 °C for at least 16 h.

2.2.2. Canadian Goldenrod (Solidago Canadensis)

Canadian Goldenrod was collected from wild growth in the western region of Austria, air dried and stored in dark. The full plant was used including buds, upper part of stem and leaves.

For D7 extraction was done with hot soft water, D8 and D9 tap water was used for the extraction. Hot water was used for the extraction, which was then allowed to cool down during the extraction period. At the end of the extraction step the plant material was removed. Pre-dissolved $Al_2(SO_4)_3.14\text{-}15H_2O$ was used to form the dye containing precipitate.

pH adjustment to 5.0–7.1 and isolation of the lake was performed analogous to the procedures described for onion peel.

2.2.3. Pommegranate

Pommegranate purchased from local supermarket was used as source. Dry pomegranate peel (36.3% water content) was extracted with tap water for 45 min at 95 °C. The plant material was filtered off, the extract was adjusted to pH 5.0–5.5 with 1 M NaOH. $Al_2(SO_4)_3.14\text{-}15H_2O$ solution was added and pH was adjusted again 5.0–5.5 with 1 M NaOH. The precipitate was allowed to settle for 3 d in the refrigerator. The clear supernatant was decanted off and the residual precipitate separated in a laboratory centrifuge 12 min at 3000 U/min (Heraeus Multifuge 1L, Kendo, Osterode, Germany). The filter cake was dried in a laboratory oven at 60–65 °C for at least 16 h.

Table 1

Relevant experimental conditions for plant material extraction and lake characterisation: m mass of extracted plant material; temperature and duration of extraction; V collected extract volume; V_{spec} volume of extract collected per 1 kg plant material; temperature and duration of extraction; c(Al-salt) concentration of aluminium salt for precipitation; pH during precipitation: Al-content, total phenolics in the precipitated dyestuff products and absorbance of the lake solution at 400 nm and 450 nm (sd = standard deviation).

Plant source	Dye lake	m g	V L	V_{spec} L kg^{-1}	T°C	t min	c(Al-salt) g L^{-1}		pH	Al-content % w/w	sd	TPH % w/w	sd	Abs. 400 nm	Abs. 450 nm
Onion peel yellow	D1	810	10	12.3	95	45	3.0	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.0–5.5	2.51	0.93	48.1	2.69	1.025	0.370
	D2	366	4.5	12.3	95	45	3.3	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.0–5.5	3.33	0.13	38.2	3.57	0.957	0.272
	D3	2000	40	20.0	80–60	30	4.8	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.2	6.15	0.42	17.1	0.60	0.381	0.125
	D4	258	5	19.4	85–80	30	5.0	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.1	7.09	0.75	22.2	0.93	1.018	0.371
	D5	251	5	19.9	80–60	30	5.1	$KAl(SO_4)_2.12H_2O$	5.4	1.04	0.49	18.0	0.62	0.502	0.188
Onion peel red	D6	1443	30	20.8	80–85	30	4.9	$Al_2(SO_4)_3.14\text{-}15H_2O$	3.5	1.84	0.16	14.8	0.59	0.485	0.171
Canadian Goldenrod	D7	705	10[a]	14.2	80–65	105	3.1	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.0–5.5	2.73	0.22	46.2	1.27	0.518	0.063
	D8	4500	85	18.9	90–60	30	3.2	$Al_2(SO_4)_3.14\text{-}15H_2O$	7.1	4.80	0.32	46.7	2.83	0.543	0.079
	D9	1968	32	16.2	99–95	40	5.0	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.3	11.83	0.42	20.4	2.49	0.245	0.101
Pommegranate	D10	1079	5	4.6	95	45	3.0	$Al_2(SO_4)_3.14\text{-}15H_2O$	5.0–5.5	1.04	0.29	37.1	1.88	0.319	0.032

[a] Softened water.

2.3. Determination of total phenolics (TPH)

Total soluble phenolics (TPH) in the solid precipitate were determined after dissolution of the residue, using the Folin-Ciocalteau reagent according to the method of Slinkard and Singleton and relating the results to gallic acid monohydrate as standard [21–23].

An exact mass around 0.15–0.20 g of dried dyestuff containing filter cake was dissolved in 10 mL 0.079 M oxalic acid, after approximately 10 min 40 mL warm deionised water were added. The TPH analysis was performed immediately after dissolution, without further storage of the prepared dyestuff solution.

The solutions were diluted with distilled water to adjust absorbance within the range of the calibration curve. To a volume of 0.2 mL of the diluted extract deionised water (1.4 mL), Folin-Ciocalteau reagent (0.1 mL) and Na_2CO_3 (0.3 mL, 204 g L^{-1} Na_2CO_3) solution were added. After a reaction time of 30 min at a temperature of 40 °C, the absorbance was measured at 765 nm (Hitachi U-2000 double-beam spectrophotometer). Results were expressed as mass % TPH in the dyestuff precipitate, calculated as gallic acid monohydrate equivalents [21–23].

2.4. Aluminium-content in precipitate

Formation of the aluminium-Alizarin Red S complex was used for determination of the aluminium content of the precipitate.

To prepare a calibration curve, a solution of 233.6 mg L^{-1} $Al_2(SO_4)_3.16H_2O$ was prepared as stock solution containing 20 mg L^{-1} Al. The solution then was diluted with water to obtain a 2 mg L^{-1} Al standard solution. Approximately 10 mL of deionised water were dosed into a 100 mL volumetric flask, then a volume of 0–50 mL of the 2 mg L^{-1} standard solution was added. After addition of 10 mL Alizarin Red S solution (80 mg L^{-1}), 10 mL HCl (0.375 M), 10 mL $CaCl_2.H_2O$ solution (1 g L^{-1}) and 20 mL NaOAc solution (0.625 M), the mixture was kept for 30 min at 60 °C. After 30 min cooling down to ambient temperature, the flasks were filled to 100 mL. Absorbance was measured at 490 nm in a 10 mm cuvette (Hitachi, U-2000, double-beam spectrophotometer).

For aluminium analysis an exact mass around 0.15–0.20 g of dried dyestuff containing filter cake was dissolved in 10 mL 0.079 M oxalic acid, after approximately 10 min 40 mL warm deionised water. The dyestuff containing solution then was diluted by 1:50 with deionised water. 10 mL of the diluted dyestuff containing solution were analysed for aluminium in the same procedure as used for the 2 mg L^{-1} aluminium standard. Results given are mean values of double determination.

2.5. Spectrophotometry of dyestuff solution

For spectrophotometric analysis 0.15–0.16 g precipitate were dissolved in 10 mL 0.079 M oxalic acid and 40 mL warm deionised water. The absorbance was measured after appropriate dilution with deionised water using a 10 mm cuvette and a diode-array spectrophotometer (Zeiss CLH 500/MCS521 UV–vis, Carl Zeiss, Jena, Germany). For comparison all values were calculated for a ten times dilution of the initially prepared solution.

2.6. Dyeing experiments

2.6.1. Onion peel/Canadian Goldenrod/pommegranate lake

The required amount of powdered/milled dyestuff was dissolved 0.079 M oxalic acid, and filled to the required dyebath volume with warm deionised water. This solution served as dyebath, the respective experimental details are given in Tables 2–4. The textile samples were placed in the solution and the dyebath was heated to 95 °C for 45 min in open beakers. In comparison to pre- or post mordanting in the case of meta mordanting the mordant is added directly to the dyebath. After dyeing for 10 min at 95 °C, a concentrated solution of $KAl[SO_4]_3.12H_2O$ (25–50 g L^{-1}) or $FeSO_4.7H_2O$ (25–50 g L^{-1}) was added to the dyebath, to achieve the concentration given in Tables 2–4 After cooling down to approximately 60 °C samples were removed from the dyebath and rinsed three times in water at ambient temperature. The resulting CIELab coordinates and colour depth in terms of K/S measured at wavelength of 400 nm are given in Tables 2–4

For experiments 3, 4 and 26, 27 the pH of the acidic dye solution was adjusted to pH 3.62 with addition of 0.1 M NaOH before the dyeing process was started.

For experiments 43–45 the solid dye was dissolved in 10 mL 5% HCl (1.5 M) for approx. 10 min. Then 190 mL warm water was added and the dissolution process was continued for 60 min. Scoured and bleached cotton jersey, flax and cotton fabric were dyed with the dyestuff solution as direct dyeing as described above.

2.7. Reference dyeing with plant extract

Reference dyeing 18 and 19 were dyed with use of the same plant extract as used for production of D9. The extract was applied for wool dyeing at a liquor ratio of 1:20. Dyeing was performed as direct dyeing for 45 min at the boil, in case of meta-mordanting the mordant was added directly to the dyebath. After 10 min at the boil, a volume of 10% of the bath volume $FeSO_4.7H_2O$ solution (0.18 M, 50 g L^{-1}) was added and dyeing was continued for 35 min at 95 °C. Dyebaths were allowed to cool down for 10 min, then samples were rinsed in warm tap water and air dried. The filtrates from dye lake D9 production also were tested in dyeing experiments.

2.8. Colour measurement

The CIELab coordinates were measured with a Konica Minolta Spectrophotometer CM-3610d (sample diameter 8 mm, geometry d/8°, Konica, Japan) and K/S values of the dyeings were calculated from the diffuse reflectance β at 400 nm and calculated according the Kubelka/Munk equation (equation (1)). The L*, a*, b* values were calculate d for illumination D65. Measurements were done in triplicate.

$$K/S = \frac{(1-\beta)^2}{2\beta} \qquad (1)$$

3. Results and discussion

3.1. Extraction and dye lake formation

The major constituents of natural colorants in onion peel and Canadian Goldenrod belong to the group of flavonoids. Representative examples, which are released during the hot water extraction step, are qercetin (C.I. 75670, Natural Yellow 10, 13), quercitrin (C.I. 75720, Natural Yellow 10), isoqercitrin, rutin (C.I. 75730, Natural Yellow 10) and kaempferol (C.I. 75640, C.I. Natural Yellow 13,10) [11,18,24]

For onion peel quercetin has been reported as main component with a content of 4% w/w besides kaempferol and quercetin glycosides as minor constituents [18].

In Canadian Goldenrod qercetin **1**, quercitrin **2**, isoqercitrin **3**, rutin and kaempferol **4** have been identified, with a total content near 4% w/w [11,18,24]

Pomegranate peel contains up to 28% of their weight tannins, major constituents are gallic acid **5** (3,4,5-trihydroxybenzoic acid),

Table 2

Results of dyeing experiments on wool yarn with $FeSO_4.7H_2O$ meta mordanting, colour depth in % dye (m dyestuff/m of goods), amount of oxalic acid used for dissolution of 1 g of dye lake, liquor ratio (LR, volume of dyebath/mass of sample), type and concentration of mordant used, CIELab colour coordinates and K/S values (400 nm) of dyeings with precipitated dyestuff and reference dyeings with direct use of plant extracts.

Plant source	Dye lake	Dyeing no.	Dye %	Oxalic acid mmol g^{-1}	LR g ml^{-1}	$FeSO_4.7H_2O$ g L^{-1}	L*	a*	b*	K/S
Onion peel yellow	D1	1	5.0	1.6	1:20	4.5	31.94	1.33	18.14	17.76
		2	5.0	1.6	1:20	4.5	36.63	0.74	16.72	12.07
	D2	3	4.2	1.9	1:21	5.2	36.33	0.09	19.17	12.04
		4	4.2	1.9	1:21	5.2	37.44	−0.29	19.41	10.98
	D3	5	5.1	1.6	1:20	4.5	40.82	2.00	19.67	10.22
		6	5.1	1.6	1:20	4.5	43.25	1.57	19.64	8.51
	D4	7	4.1	1.9	1:20	4.7	45.05	0.16	17.35	6.11
		8	4.1	1.9	1:20	4.7	42.67	−0.15	19.45	7.52
	D5	9	4.1	1.9	1:20	4.7	30.07	1.08	16.5	18.13
		10	4.1	1.9	1:20	4.7	32.23	0.93	17.83	16.74
	Extract	[26]			1:20-22	5.0	27.72	0.15	9.24	–
Onion peel red	D6	11	4.9	1.9	1:20	4.5	33.23	1.51	21.38	15.32
Canad. Goldenrod	D7	12	4.1	2.0	1:21	4.5	29.66	−1.40	21.70	32.84
		13	4.1	2.0	1:20	4.5	29.38	−1.47	20.5	30.01
	D8	14	5.2	1.6	1:20	4.5	37.00	−1.76	19.26	16.79
		15	4.4	1.6	1:18	4.5	34.82	−1.28	17.36	18.32
	D9	16	4.8	1.6	1:20	4.5	37.06	−2.62	19.26	17.89
		17	4.8	1.6	1:18	4.5	35.58	−2.26	18.34	19.12
	Extract	18	–	–	1:20	4.5	16.33	0.12	5.13	35.55
	Extract	19	–	–	1:20	4.5	15.67	−0.12	5.40	40.41
	Extract	[1]			1:20	5	27.05	−0.75	8.43	–
	Extract	[25]	–	–	1:20	4.5	21.90	0.53	7.05	–
Pommegranate	D10	20	4.4	2.0	1:22	4.6	43.12	−0.53	2.36	4.98
		21	4.4	2.0	1:22	4.6	41.78	−0.51	3.01	5.84

Raw wool L* 85.26, a* −0.55, b* 10.12.

ellagic acid **6** (2,3,7,8-tetrahydroxy [1]benzopyrano-[5,4,3-*cde*] [1] benzopyran-5-10-dione, C.I. 75270), and flavogallol **7** [18].

The dyestuff content in the available plant sources is low and the natural colorant has to be extracted from a much higher amount of plant material, which has to be handled before and after the extraction step.

Thus in ideal case the extraction of the plant material is performed at the site of farming or plant material collection. Long distance transportation of huge amounts of plant material should be avoided. Attention also has to be paid to the addition of chemicals or solvents during extraction, as the major part of the plant material will be released in form of the extracted residue, which must not be contaminated with hazardous substances [1,10].

The plant material extraction step and the precipitation of the extracted dye lake thus can only be based on inexpensive and robust techniques which easily can be implemented at sites of farming or vegetable/fruit processing.

The dye lake formation was built up from the following main steps:

- Extraction of the plant material with tap water and heating to the boil (D1, D2, D10) or addition of hot water (experiments D3 - D9). From previous experiments the minimum duration of extraction required for reach equilibrium had been determined with 30–45 min, thus the majority of extractions were performed within this period [25].

Table 3

Results of dyeing experiments on wool yarn with alum ($KAl[SO_4]_3.12H_2O$) meta-mordant, colour depth in % dye (m dyestuff/m of goods), amount of oxalic acid used for dissolution of 1 g of dye lake, liquor ratio (LR, volume of dyebath/mass of sample), type and concentration of mordant used, CIELab colour coordinates and K/S values (400 nm) of dyeings with precipitated dyestuff and reference dyeings with direct use of plant extract.

Plant source	Dye lake	Dyeing no.	Dye %	Oxalic acid mmol g^{-1}	LR g ml^{-1}	Alum g L^{-1}	L*	a*	b*	K/S
Onion peel yellow	D2	22	2.4	39.5	1:22	4.5	62.55	11.64	65.23	25.79
		23	4.4	19.8	1:22	4.5	64.12	10.72	69.02	27.18
		24	6.6	13.2	1:22	4.5	66.62	7.35	71.29	25.78
		25	8.8	9.9	1:22	4.5	68.76	8.59	74.49	24.63
		26	4.3	1.9	1:21	4.3	69.30	8.88	73.91	18.64
		27	4.3	1.9	1:21	4.3	68.24	9.59	72.65	20.81
	Extract	[26]			1:20-22	5.0	42.80	7.57	31.20	–
Onion peel red	D6	28	5.0	1.9	1:20	4.5	64.57	3.07	56.47	11.29
Canad. Goldenrod	D9	29	4.9	1.6	1:20	4.5	77.48	−1.08	74.03	19.41
	D9	30	4.8	1.6	1:20	4.5	78.32	−2.21	69.40	15.14
	Extract	[1]			1:20	5.0	69.93	−3.02	57.63	–
Pommegranate	D10	31	4.3	2.0	1:21	4.7	79.75	−6.49	42.53	4.37
	D10	32	4.3	2.0	1:21	4.7	79.15	−5.79	41.15	4.11
	Extract	[27]			1:22	4.5	66.88	0.98	40.55	–
Onion peel red	D6	33	4.8	1.9	1:19	–	64.89	7.83	66.85	10.55
Canad. Goldenrod	D7	34	4.1	2.0	1:20	–	72.01	−2.52	76.00	28.61
		35	4.1	2.0	1:20	–	71.23	−1.81	77.80	30.60
	D8	36	5.3	1.6	1:20	–	71.07	3.64	71.89	20.98
		37	5.3	1.6	1:20	–	72.39	3.40	72.54	19.70
	Extract	38	–	–	1:20	–	57.05	1.38	26.51	23.80
	Extract	39	–	–	1:20	–	58.69	0.90	27.59	23.57

Table 4

Results of dyeing experiments, colour depth in % dye (m dyestuff/m of goods), amount of oxalic acid used for dissolution of 1 g of dye lake, liquor ratio (LR, volume of dyebath/mass of sample), type and concentration of $KAl[SO_4]_3.12H_2O$ mordant used, CIELab colour coordinates and K/S values (400 nm) of dyeings with precipitated dyestuff and reference dyeings with direct use of plant extracts.

Plant source	Dye lake	Dyeing no.	Substrate	Dye %	Oxalic acid mmol g^{-1}	LR g mL^{-1}	Alum g L^{-1}	L^a	a^a	b^a	K/S
Onion peel yellow	D3	40	Co Jersey	5.1	1.6	1:20	–	65.10	4.29	42.63	4.40
		41	Flax fabric	4.8	1.6	1:19	–	70.01	3.13	50.30	4.35
		42	Co fabric	5.8	1.6	1:23	–	72.79	3.05	48.10	3.38
		43	Co Jersey[a]	5.5	27.4	1:22	–	62.83	7.64	47.33	6.36
		44	Flax fabric[a]	5.0	27.4	1:20	–	62.31	8.66	48.19	8.94
		45	Co fabric[a]	5.5	27.4	1:22	–	68.77	7.44	51.68	6.11
	Extract	[10]	Flax fabric			1:20	–	68.02	8.14	22.73	–
Canad. Goldenrod	D8	46	Flax yarn	4.5	1.6	1:18	–	79.01	−0.35	51.29	3.34
	Extract	[1]				1:20	–	83.27	−1.10	16.43	–
		47	Flax yarn	4.2	1.6	1:17	4.5	77.55	0.61	58.95	5.21
	Extract	[1]				1:20	5	80.73	6.74	33.75	–

[a] Dissolved in HCl 5%.

- The extracted plant was removed from the extracted material by simple coarse filtration.
- After formation of dye lake by addition of the Al-salt the precipitate was allowed to settle down and the sediments were collected by centrifugation or more simply by sedimentation.

Dependent on the conditions of precipitation and ageing of the settled precipitate the filtered residue contains approximately 95% w/w water before drying. Typical values for the yield of dry dye lake were determined between 3 and 5% of the weight of extracted plant material.

For quality determination and product standardisation simple photometric procedures were chosen. The dry residues were dissolved in diluted acid and analysed for their Al-content, the total phenolic content calculated as gallic acid monohydrate, and the absorbance of the solution was measured in the wavelength interval between 400 and 700 nm (Table 1).

Higher TPH content and lower Al-content were found in the precipitate when lower volumes of water for extraction of 1 kg plant material and 3 g L^{-1} Al-salt were used. Higher TPH content e.g. 38–48% and Al content of 2.5–3.3% was determined for the lakes D1 and D2. $V_{spec} = 20$ L yields products with lower TPH content of 18–22% and higher Al content of 6.2–7.1% (D3, D4). Lowest content of Al and TPH was found in the D5, where alum was used for precipitation and in red onion peel extraction (D6). The red onion peel contained a considerable amount of impurities, mainly adhering soil, which caused a decrease in TPH content.

Similar dependency of Al and TPH content of the lake on the concentration of added Al-salt can be observed in experiments with Canadian Goldenrod extracts, where precipitates obtained with 3 g L^{-1} Al-salt contain 2.7–4.8% Al and 46% of TPH, while at higher concentration added Al-salt, the Al content in the residue increased and the TPH content decreased. This indicates that higher additions of Al-salt just increase precipitation of Al-hydroxide, while precipitation of TPH compounds already had been completed.

Highest TPH content was observed for residues where extraction experiments had been performed at temperatures above 90 °C (D1, D2, D8-D10) or with prolonged extraction time (D7).

In the majority of the experiments the increase of Al-content in the residue also goes parallel with a decrease in the TPH content. Thus in case of $Al_2(SO_4)_3.14\text{-}15H_2O$ concentrations above 3 g L^{-1} unproductive precipitation of $Al(OH)_3$ increases. Further systematic investigations will be required, to determine the optimum concentration for dyestuff precipitation for the individual plant sources.

From V_{spec} and the concentration of Al-salt added an estimate of the Al-content in the residue can be calculated, considering an average yield of precipitate of 5% w/w of the extracted plant mass. In the example where 12.3 L of extract were obtained from extraction of 1 kg of plant material ($V_{spec} = 12.3$ L kg^{-1}) and 3 g L^{-1} $Al_2(SO_4)_3.14\text{-}15H_2O$ were added for precipitation (e.g. D1, D2), a total amount of 36.9 g $Al_2(SO_4)_3.14\text{-}15H_2O$ had been added. This corresponds to 3.3 g aluminium which could precipitate with the lake. Assuming that 1 kg of plant material yields 50 g (5% w/w) precipitated lake, then a theoretical maximum Al-content of 6.6.% w/w Al can be expected. From $V_{spec} = 21$ L kg^{-1} and an addition of 5 g L^{-1} $Al_2(SO_4)_3.14\text{-}15H_2O$ a higher Al content is of 18.8% w/w Al can be calculated as maximum value in the dyestuff precipitate. This reduces to half of the value when a higher amount of dry precipitate is obtained, e.g. 10% w/w of the extracted plant mass. Then the maximum possible Al-content decreases to 9.4% w/w Al.

The Al-content in the residues remains below these theoretical values, which indicates that under the conditions used only an incomplete precipitation of Al occurs.

After dissolution of the dyes in oxalic acid the absorbance curves of solutions were determined by photometry (Fig. 2). In Table 1 the absorbance of the dyestuff solution at 400 nm and 450 nm is given.

As shown in Fig. 1 phenolic groups are present in all colorants extracted from the plant material and will contribute to the TPH content and the absorbance at 400 nm at the same time. Assuming a similar pattern of phenolic compounds is precipitated during lake formation, a correlation between TPH content and absorbance could be expected.

In Fig. 3 the relationship between TPH and absorbance at 400 nm is shown for the dissolved precipitates D1 – D10 obtained from the different plant sources. A correlation between TPH content and absorbance of the solution at 400 nm can be recognised for dye lakes from onion peel and Canadian goldenrod. Variability can be explained by differences in composition, but also is influenced by particle size and dissolution behaviour of the residues in oxalic acid.

In previous studies no significant correlation between the absorbance of dye solution at 400 nm, TPH content of extracts and colour depth of dyeings obtained with Fe-based mordants was found. This was explained with the simultaneous extraction of coloured compounds which also contribute to the TPH content, however these components do not adsorb on the textile fibres and thus are not of value as textile dyes [15,25].

3.2. Dyeing experiments

To determine the coloristic potential of the dye lakes, the dyestuff content in the lakes was determined by standardised dyeing experiments on wool with iron mordanting (Table 2), with use of alum mordanting and as direct dye (Table 3), and on cellulose fabric (Table 4).

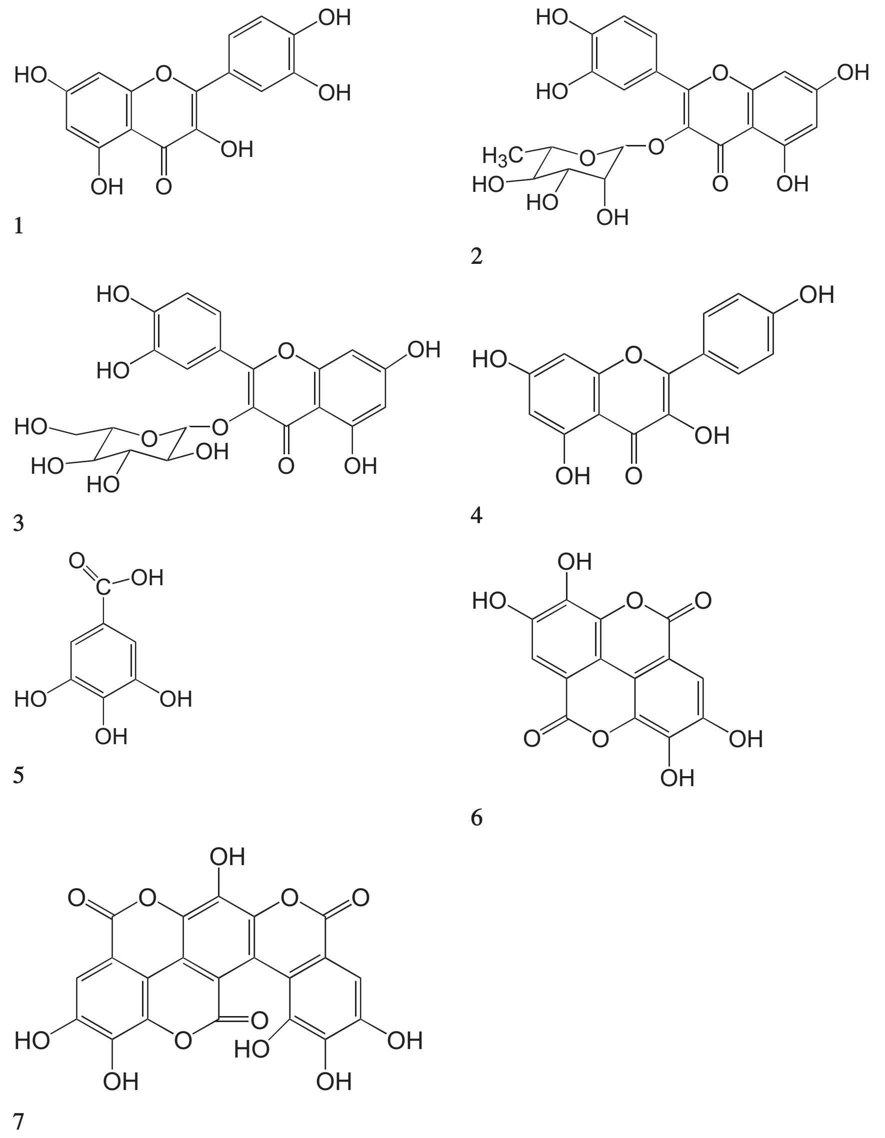

Fig. 1. Representative structures of natural colorants present in Canadian Goldenrod: quercetin **1**, quercitirin **2**, isoquercitrin **3**, kaempferol **4**, gallic acid **5**, ellagic acid **6**, flavogallol **7** [18].

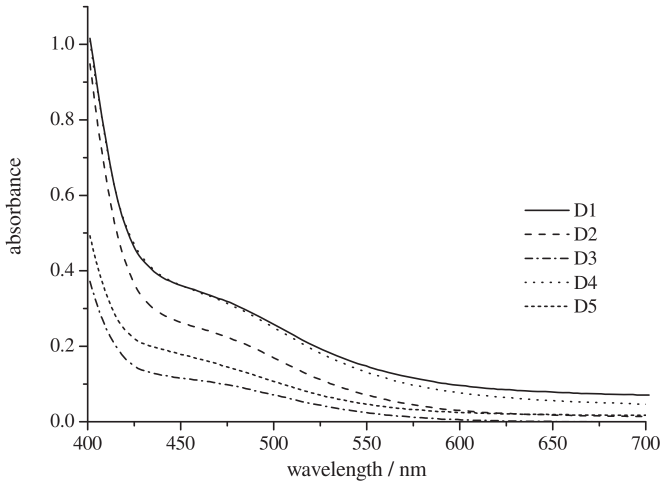

Fig. 2. Absorbance of dyestuff solutions from onion peel lakes D1 – D5 in the wavelength interval of 400–700 nm.

The dyeings shown in Table 2 were performed under similar conditions, using a colour depth of 4.1–5.2% of solid dyestuff, a mordant concentration of 4.5–5.2 g L^{-1} $FeSO_4.H_2O$ and a liquor ratio of 1:18–1:21. Colour depth was assessed by determination CIELab coordinates and K/S values at 400 nm.

For comparison of the colour strength comparable dyeings with direct use of the plant extracts are given at the respective position in the Tables 2–4.

For iron mordanting no significant correlation between the K/S value and TPH content of the dye was observed (Fig. 4) and similarly dependency of K/S value on the absorbance of the dye solution is low (Fig. 5). In case of iron mordanting coloured iron complexes also can be formed with other phenolic compounds e.g. tannins which do not contribute to the absorbance in the visible part of the spectrum. This could explain the low correlation between analytical results and colour depth of the test dyeing. Additional variability can result from incomplete dissolution of the precipitate in oxalic acid and in-homogenities present in the dry dye lake.

Reference dyeings with direct use of the extract using comparable amounts of plant material, showed darker dyeings. Under the

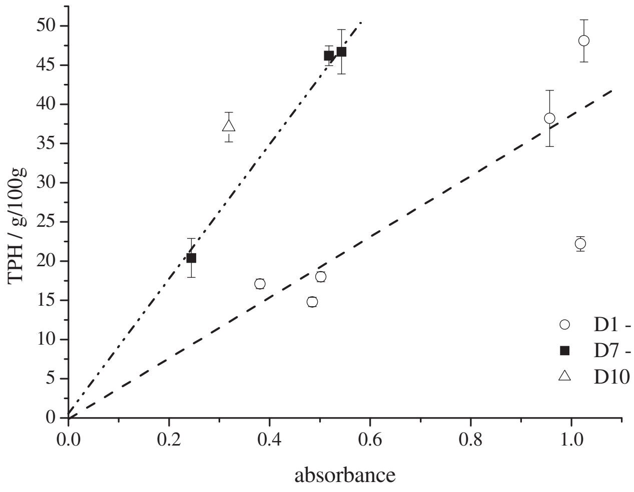

Fig. 3. Correlation between TPH content of the dye lake and the absorbance of the dissolved dye at 400 nm; (○) onion peel (D1 – D6); (■) Canadian Goldenrod (D7 – D9); (△) pomegranate (D10).

experimental conditions used, colour depth with use of dye lakes can be estimated with 50–70% of the plant extract.

Compared to the reference dyeings, the CIELab coordinates of the dyeings with use of solid dye indicate more brilliant colours, as the higher b* coordinate was observed. Most probably the lake production also represents a purification step, which causes losses in colour depth, but in parallel increases chromacity.

To test for completeness of precipitation, dyeing experiments with the filtrate after filtration of D9 were performed as direct dyeing and with iron-mordanting. Only light dyeings were obtained (direct dyeing L* 79.75, a* –7.58, b* 34.95; iron mordant L* 51.82, a* –2.55, b* 11.93), which proved that the major part of natural dye had been removed from solution in form of the precipitated lake.

Wool dyeings given in Table 3 were performed with use of aluminium mordanting or as direct dyeings. Representative dyeings with use of plant extracts also are shown. Similar to the results with iron mordant the colour depth of the dye lake is lower than the colour depth of reference dyeings, but again higher b* values indicate higher chromacity.

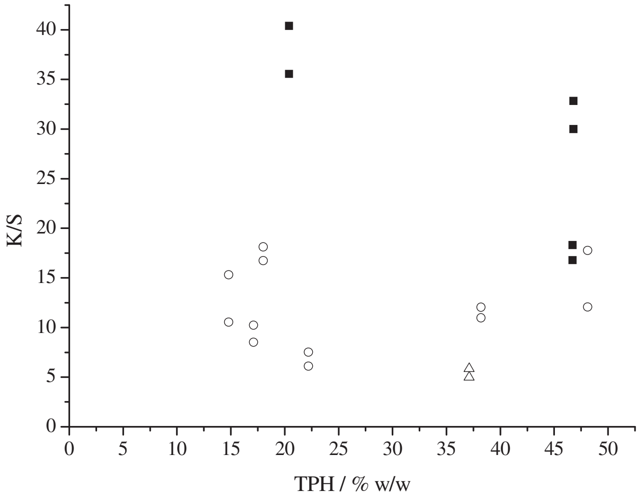

Fig. 4. K/S of the dyeings (1–19, and 20–21) on wool using 4.5–5.2 g L^{-1} $FeSO_4.7H_2O$ mordant, as function of TPH content; (○) onion peel; (■) Canadian Goldenrod; (△) pommegranate.

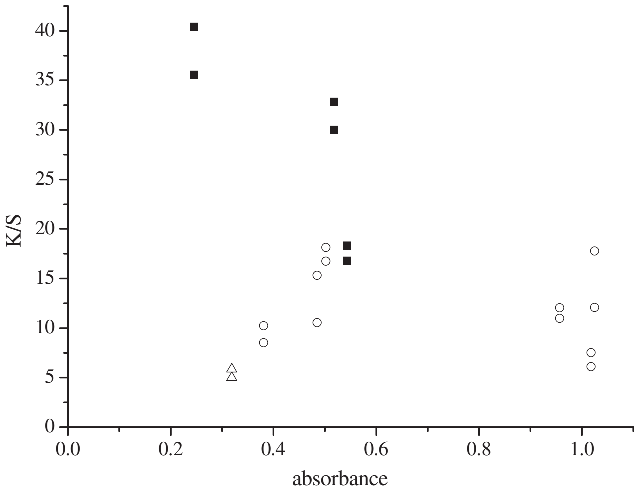

Fig. 5. K/S values of the dyeings (1–19, and 20–21) as function of absorbance of the dye solution wool with 4.5–5.2 g L^{-1} $FeSO_4.7H_2O$ mordant; (○) onion peel; (■) Canadian Goldenrod; (△) pommegranate.

The build up of colour depth was assessed with use of increasing amounts of dye applied under similar conditions (Expt 22–25). Similar colour depth was found independent on amount of dyestuff used. This indicates that a level of saturation in dye uptake already was achieved at a colour depth of 2% dyestuff.

In Table 4 selected dyeings on cellulosic substrates are presented. The dye solutions were applied without pH adjustment to avoid precipitation of dye lakes at higher pH. Also on cellulose fibres the dyeings with solid dyestuff showed higher b* coordinate and higher brilliance compared to standard dyeings with direct use of plant extracts. When diluted HCl is used to dissolve the dyestuff higher colour yields were obtained in comparison to the results with use of oxalic acid (Table 4). This indicates that further research and improvement will be required to optimise finishing and solubility of the powdered solid dye.

4. Conclusions

Implementation of natural colorants into technical textile dyehouses still is hindered by the fact that huge amounts of plant material have to be processed at the site, where the dyeing is performed. The formation of solid dye lakes can offer a promising strategy to overcome this barrier. Aluminium salts can be used to precipitate dye lakes, which then can be used as concentrated dyestuff product. Onion peel, Canadian Goldenrod and pomegranate were studied as representative examples for plant sources. A concentration of 3 g L^{-1} $Al_2(SO_4)_3.14\text{-}15H_2O$ was found to be sufficient to precipitate the natural dyes at pH 5.5. As an average a mass of 5% of the plant weight can be collected as dry plant lake. Typical concentration of total phenolics (TPH) in the dry solid dyestuff range from 20 to 40% and representative values for the aluminium content are between 3 and 5% w/w.

After dissolution of the aluminium lake in diluted acid this solution can be used for textile dyeing in procedures similar to the application of synthetic dyes.

For a given plant source a correlation between the TPH content and the absorbance of the dissolved lake could be found. However correlation between TPH content or absorbance at 400 nm and colour depth in terms of K/S was not sufficient, to recommend these parameters for colour depth prediction. Determination of the coloristic properties of a dye lake thus always should include laboratory scale dyeing tests.

Compared to results with the direct use of plant extracts, lower colour strength was observed when solid dye lakes were used. A distinct increase in b* value indicates more brilliant colour for dyeings based on dye lakes. This result most probably is due to the precipitation step, which also can be understood as a purification step. The improvement of the coloristic quality of the dye in terms of chromacity is demonstrated in the test dyeings, however further analysis would be required to clarify the chemical background in detail.

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