

Colour stability and performance of vegetal dyes on natural fibres

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In the past natural dyestuffs were employed extensively to colour textiles, but their use has been progressively substituted by synthetic colours. Nowadays, we assist to a renewed interest being natural products safer both for humans and environment. The respect of nature and human health underlies the search for low-impact production methodologies and materials; anyway, the choice of colours and fibres should ensure long-lasting and stable visual performance. In this work we investigated the chromatic robustness of some dyestuffs on cotton and silk samples; we also evaluated the colour changes they underwent after repeated washes or exposition to direct sunlight. Vegetal Woad, Weld and Madder, produced at the Museum of Natural Colours in Lamoli (PU, Italy) by non-dangerous traditional techniques, were selected to colour our sample textiles. The results of this investigation would provide useful guidelines towards dyeing processes, in the full respect of the environment.

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Introduction

There is renewed interest in natural dyestuffs and growing attention at their application in the field of textiles, as they are neither toxic nor polluting. As a consequence, several investigations arose aiming at their production and extraction by means of traditional techniques. Woad, Weld and Madder plants are grown, harvested and used to extract colouring matters at the Museum of Natural Colours in Lamoli (PU, Italy) by means of traditional and environmentally friendly procedures.

Woad is a blue European dyestuff extensively used in place of Oriental Indigo, mostly in the textiles. It originates from the fresh leaves of *Isatis tinctoria L.* and derives its hue from the Indigotin molecule. Weld is obtained from the dried plant of *Reseda luteola L.*, found in Central Europe, India and China. Its main colouring matters are Luteolin and Apigenin that, from antiquity, made Weld widely appreciated for the vivid yellow hue, mostly to colour silk and wool. Madder (*Rubia tinctorium L.*) is perhaps the oldest and undoubtedly one of the most used dyes to make red lakes from antiquity up to the nineteenth century, with ample geographical distribution, spanning Eastern and Western cultures. Its main colouring substances are Alizarin and Purpurin that reside in the roots and return an orange-red dyestuff, when fixed on aluminium trihydroxide.

Dyeing textiles with natural substances is far more complex and difficult than with synthetic colours, that is the reason why many researches are in progress with the purpose of optimizing the dyeing of animal (wool and silk) and vegetal (cotton, linen, ...) fibres.

All the samples we investigated have been coloured with different concentrations of both dyes and excipients and with different soaking times and temperatures of the colour bath. We monitored the chromatic stability of the samples through spectrophotometric techniques after washings and after exposition to direct sunlight; in particular, we calculated colour coordinates and chromatic differences as well, from the acquisitions of the Spectral Reflectance Factor (*SRF*).

The final goal is to provide useful hints that can be fruitfully exploited to optimise dyeing procedures.

Experimental

The current work activity supports the evaluation of performance and stability of colour on cotton and silk fibres versus auxiliary substances (alkalizing, precipitants, fixatives, mordants, etc.), colour bath concentration, temperature and soaking time as well, through spectrophotometric analyses. Table 1 summarises the different dyeing conditions.

Woad	Cotton	WOc1	colour bath (25°C): 10% Woad, 5% caustic soda, 10% sodium hydrosulphite; dyeing time 1h
		WOc2	colour bath (50°C): 20% Woad; dyeing time 2h
		WOc3	colour bath (50°C): 10% Woad; dyeing time 2h; + 3 teaspoons of casein glue
	Silk	WOS1	colour bath (25°C): 10% Woad, 5% caustic soda, 10% sodium hydrosulphite; dyeing time 1h
		WOS2	colour bath (50°C): 20% Woad; dyeing time 2h
		WOS3	colour bath (50°C): 10% Woad; dyeing time 2h; + 3 teaspoons of casein glue
Weld	Cotton	WEc1	colour bath (100°C): 100% Weld; mordant 25% potassium alum; dyeing time 1h
		WEc2	colour bath (100°C): 100% Weld; mordant 25% potassium alum; dyeing time 1h; + 2 teaspoons of sodium sulphate
	Silk	WES1	colour bath (80°C): 100% Weld; mordant 25% potassium alum; dyeing time 1h
		WES2	colour bath (80°C): 100% Weld; mordant 25% potassium alum; dyeing time 1h; + 2 teaspoons of sodium sulphate
Madder	Cotton	Mc1	colour bath (100°C): 100% Madder; mordant 20% potassium alum, 6.2% cream of tartar (C ₄ H ₄ K ₂ O ₆); dyeing time 2h
		Mc2	colour bath (100°C): 100% Madder; mordant 20% potassium alum, 6.2% cream of tartar (C ₄ H ₄ K ₂ O ₆); dyeing time 2h; + 2 teaspoons of sodium sulphate, + 3 teaspoons of casein glue
	Silk	MS1	colour bath (80°C): 100% Madder; mordant 20% potassium alum, 6.2% cream of tartar (C ₄ H ₄ K ₂ O ₆); dyeing time 2h
		MS2	colour bath (80°C): 100% Madder; mordant 20% potassium alum, 6.2% cream of tartar (C ₄ H ₄ K ₂ O ₆); dyeing time 2h; + 2 teaspoons of sodium sulphate, + 3 teaspoons of casein glue

Table 1: Dyeing procedures for cotton and silk samples.

Investigations were performed onto twin groups of samples: the first group was cyclically washed with a neutral commercial soap, whereas the second was continuously exposed to sunlight for a month. Spectral measurements were performed both before and after treatments, in order to infer chromatic alterations.

Colour coordinates and chromatic changes were monitored with a contact spectrophotometer (Minolta CM-2600d, 10 nm spectral step, d/8° illumination-collection geometry with integrating sphere) returning *SRF* spectra in the 360–740 nm range. All the spectra are reported in the specular excluded (*SPEX*) mode, because only negligible differences were observed in comparison with the specular included (*SPIN*) mode.

Colour data were calculated under the standard illuminant D65 and with the colour-matching functions associated with the standard 10° observer [1], in accordance with the recommendations of the Commission Internationale de l'Éclairage (CIE).

For each sample, five spectra were recorded from different areas; every single spectral acquisition was the result of an average over five sequences of illumination to limit the effect of the instability in the emission of the flash lamps and to estimate the statistical fluctuations of colour coordinates. The percent uncertainties of colour coordinates and differences are less than the unity [2-4].

SRF spectra are interpreted in the CIELAB 1976 [5,6], whose axes describe the lightness L^* (from 0-black to 100-white), redness-greenness component a^* and yellowness-blueness component b^* (both unbounded).

However, our results are reported with cylindrical coordinates, where the perceptual attributes of chroma, C^* , and of hue, h , substitute for a^* and b^* in a constant lightness plane.

The coordinate indicating the colourfulness, C^* , is defined as follows:

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (1)$$

The hue angle, expressed in degrees, is:

$$h = \left(\frac{180}{\pi} \right) \cdot \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad (2)$$

and ranges from 0° to 360°.

Hue differences ΔH^* is:

$$\Delta H^* = \sqrt{(\Delta E^*)^2 - (\Delta C^*)^2 - (\Delta L^*)^2} \quad (3)$$

where ΔE_{ab}^* is the Euclidean distance providing the metric for colour differences:

$$\Delta E_{ab}^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (4)$$

Results and discussion

At the beginning, *SRF* spectra were taken from blank coloured samples (Figure 1) to highlight the spectrophotometric properties as a function of the different fibres and dyeing procedures.



Figure 1: Coloured samples (WO: Woad; WE: Weld; M: Madder).

Regardless of the particular colour bath, *SRF* spectra acquired from any Woad dyed fibres show similar behaviour. Cotton samples exhibit a stronger peak in comparison with silk dyed ones, centred about 450 nm (Figure 2a). Weld spectra seem to be insensitive both to colour bath and hosting fibre (Figure 2b). The peak encountered in Madder spectra from cotton samples (centred at 425 nm) is not found in silk dyed samples where the plot is quite smooth (Figure 2c).

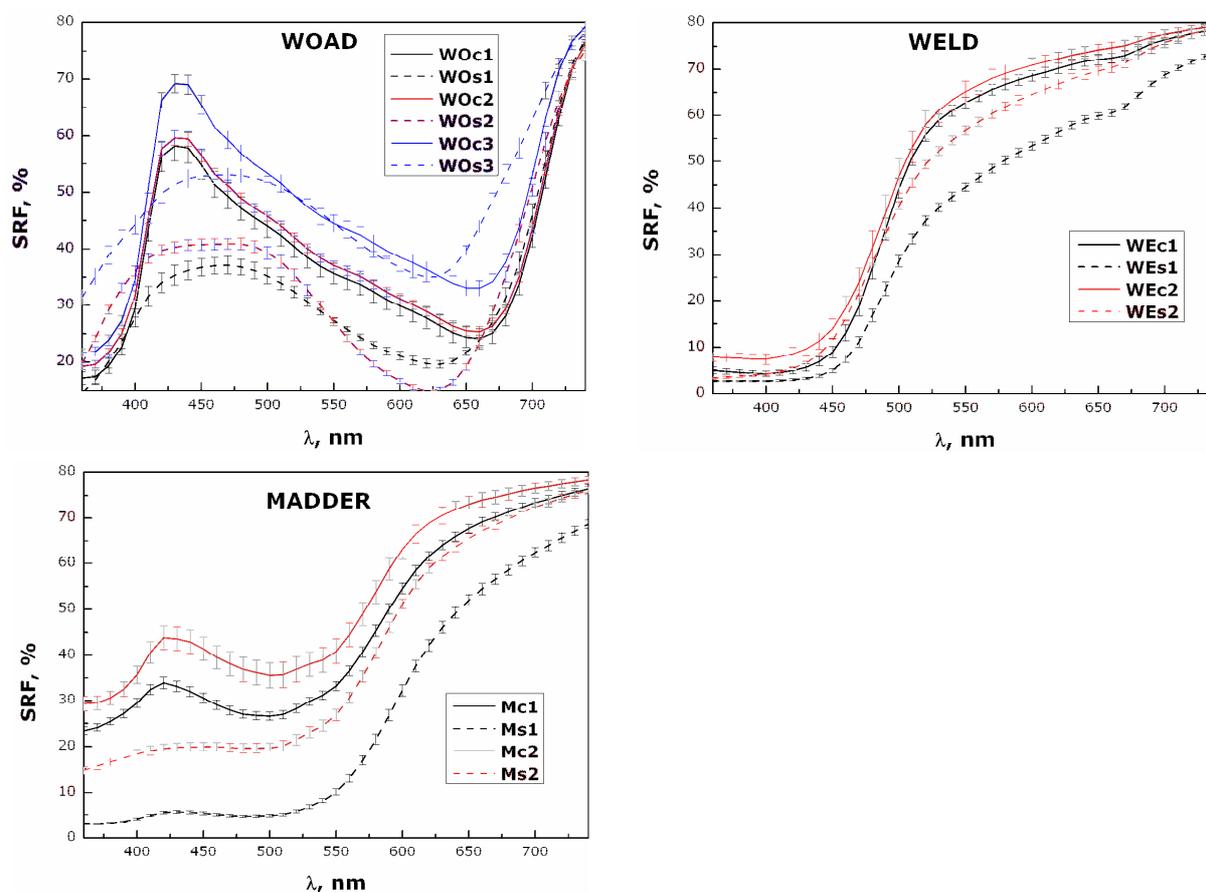


Figure 2: % SRF of (a) blank Woad dyed samples – top left, (b) blank Weld dyed samples – top right, and (c) blank Madder dyed samples – bottom left.

Colour coordinates calculated from *SRF* spectra are reported in Table 2.

	L^*	C^*	h (degree)
WOc1	66.9	18.9	260.2
WOc2	68.0	18.8	259.5
WOc3	73.2	17.9	261.7
WOs1	59.6	14.6	234.9
WOs2	59.4	22.5	232.7
WOs3	72.4	11.1	230.1
WEc1	80.9	64.7	93.9
WEc2	82.2	56.7	93.9
WEs1	71.0	63.7	88.2
WEs2	78.3	56.1	91.4
Mc1	68.4	24.8	27.2
Mc2	74.1	20.8	20.5
Ms1	47.0	50.6	42.3
Ms2	64.0	33.0	40.4

Table 2: Colour coordinates of dyed samples.

From the chromatic point of view, L^* , C^* and h coordinates confirm the different visual conclusions that can be drawn with respect to colour baths and fibres. To be more precise, Weld WEc1 sample is more vivid than WEc2, as well as WEs1 is more vivid than WEs2. Moreover, WEs1 is darker than WEs2. Madder dyed cotton sample Mc1 is slightly more vivid and darker than Mc2; on the silk these differences are stressed as Ms1 is far more vivid and darker than Ms2. Finally, baths #1 and #2 darken Woad samples more than bath #3 does, no matter what the fibre is. Furthermore, cotton samples do not experience any alteration in chroma, whereas silk sample WOs2 does.

In order to monitor the stability of dyes, spectrophotometric acquisitions were systematically repeated after 1, 2 and 10 washings with a common commercial soap. For each sample the colour distance ΔE^*_{ab} (along with the percent variations of ΔL^* , ΔC^* and ΔH^*), from the respective blank one, has been calculated. Figures 3-5 show the plots of ΔE^*_{ab} versus the number of wash, N , for every single sample.

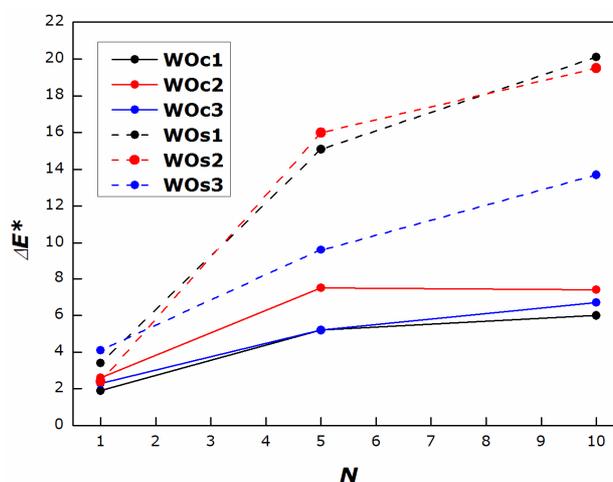


Figure 3: Colour difference ΔE^*_{ab} versus number of wash N for Woad samples.

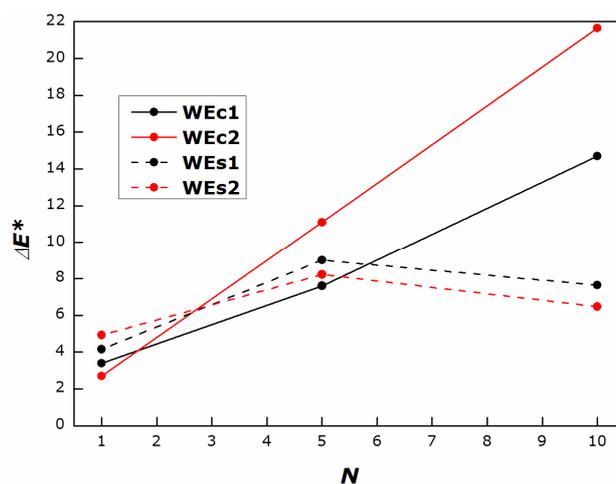


Figure 4: Colour difference ΔE^*_{ab} versus number of wash N for Weld samples.

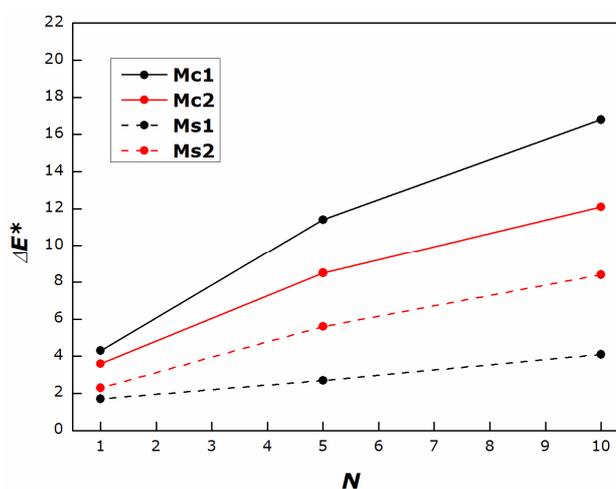


Figure 5: Colour difference ΔE^*_{ab} versus number of wash N for Madder samples.

From this analysis it is clear that, in the majority of cases, ΔE^*_{ab} increases with N ; in particular, in Woad the main contribution to colour variation can be ascribed to lightness, with the exception of some samples where chroma dominates; in Weld, chroma loads the total difference; in Madder, it is lightness to make the difference, although significant percent variations of chroma and hue are noticed, too.

Figure 3 demonstrates that dyeing with Woad is more stable on cotton, whereas the alterations induced on silk are restrained by the action of the casein glue added to the colour bath. Colour is less prone to fade away from Weld and Madder dyed silk samples; it must be pointed out that colour bath has opposite effects on the different fibres (Figures 4–5).

Anyway, an anomalous behaviour is exhibited by Weld dyed silk samples (WES1 e WES2) as shown in Figure 4, because ΔE^*_{ab} decreases after 10 washings and this could be explained with the presence of surface colour inhomogeneity and/or with the impossibility to re-match exactly the same area with the spectrophotometer.

For the sake of quantifying sunlight induced chromatic changes, non-irradiated samples (Table 3) served as reference for colour differences. Weld on cotton is the most sensitive dyestuff and chroma reduction dominates the ΔE^*_{ab} values both on silk and cotton. The net effect of sun irradiation on

Madder samples is essentially some kind of discoloration. Considerations cannot be made for Woad samples as a whole, because the situation is rather complex since WOc1, WOc2 and WOs2 experience discoloration and chroma reduction, whereas discoloration dominates in WOs1 and WOs3 and chroma reduction in WOc3.

	ΔE^*_{ab}	ΔL^* (%)	ΔC^* (%)	ΔH^* (%)
WOc1	15	<u>41</u>	<u>49</u>	10
WOc2	13	<u>39</u>	<u>48</u>	14
WOc3	13	34	<u>52</u>	14
WOs1	18	<u>63</u>	33	4
WOs2	20	<u>50</u>	<u>43</u>	7
WOs3	15	<u>48</u>	36	16
WEc1	38	1	<u>97</u>	2
WEc2	33	1	<u>97</u>	1
WEs1	7	1	<u>75</u>	24
WEs2	11	2	<u>96</u>	1
Mc1	20	<u>66</u>	33	2
Mc2	13	<u>62</u>	31	7
Ms1	7	<u>79</u>	0	21
Ms2	10	<u>70</u>	27	3

Table 3: Colour difference ΔE^*_{ab} and percent photo-induced ΔL^* , ΔC^* and ΔH^* for every single sample.

Underlined values represent major contributions to colour difference.

Conclusions

On the one hand the manufacturing of textiles demands that both the environment and the human health must be preserved and this can be achieved with the use of natural fibres and dyeing procedures, on the other hand it is mandatory to produce goods that are long-lasting, high-performing, simple and cheap when possible.

In this framework, the stability of vegetal dyestuffs used to colour cotton and silk fibres was evaluated through spectrophotometric analyses. Measurements were carried out on samples dyed with different methodologies, to quantify colour alterations after a number of washings or sunlight irradiation.

It can be concluded that particular attention must be paid to the selection of the most suitable dyeing procedures, alkalizers, precipitants, fixatives, mordants, colour bath concentration, temperature and time for each particular fibre and dyestuff, without disregarding the final field of application. The results of this work will be exploited by specialists to revise their dyeing processes for the combinations of dyestuffs and fibres.

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