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Kinetic study on the sunlight-induced degradation of acid azo dyes on silk

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Abstract

The effects of solar irradiation on the two azo dyes CI Acid Red 1 and CI Acid Orange 8 were investigated both on dyed silk and in aqueous solution at pH 2–4.5. When absorbed on silk, the dyes were more photoreactive, both undergoing photodegradation, though at different rates, and displaying a protective action towards the fibre substrate, as evidenced by viscosimetric analysis. In aqueous solution CI Acid Orange 8 underwent photodegradation, with a quantum yield around 10^{-3} mol einstein^{-1}, while the predominant reaction occurring from CI Acid Red 1 was photocyclization, especially at low pH. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the most important properties of textiles is their light fastness, i.e. the resistance to the action of sun light of fibres and of the dyes adsorbed on them. It is well known that prolonged solar irradiation can induce chemical modifications in the fibres and changes in the hue, intensity and brightness of colours. These processes may be affected by several factors, such as the physicochemical characteristics of the fibres, the chemical structure of the dyes, the wavelength distribution of the impinging radiation and several other environmental conditions.

In the present work, the effects of sunlight irradiation on silk have been investigated kinetically, both in the absence and in the presence of azo dyes absorbed on it, in order to obtain information on the photodegradation mechanisms of this protein fibre and of the dyes absorbed on it. The photochemical behaviour of the same azo dyes has also been investigated in aqueous solution, in order to ascertain how it may be modified by dye absorption and specific interactions with the fibre.

2. Experimental

2.1. Materials

A twill silk (*Bombyx mori*) fabric was degummed by a double treatment in a Marseilles soap solution (7 g dm^{-3}) at 95°C for 30 min, washed twice with distilled water and extracted with petroleum ether. All sericin, representing 23 wt% of

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silk samples, was removed by this treatment. The fabric, thus containing only fibroin, was then stored at 20 ± 2°C and 65 ± 2% relative humidity.

Azo dyes C.I. Acid Red 1 (**1**) and C.I. Acid Orange 8 (**2**) were Aldrich products and were used without purification, in order to reproduce actual dyeing conditions. The employed commercial products contained 60 wt% of pure **1** and 70 wt% of pure **2**, as checked by determining their inorganic content by calcination at 570°C and their content of other organics, after extraction with petroleum ether.

All other reactants were Carlo Erba (Italy) pure products.

2.2. Methods

Aqueous solutions containing 0.5 wt% of dye (ca 10^{-5} M), 10 g dm^{-3} of Na_2SO_4 and different amounts of formic acid, in order to adjust their pH value to 2.1, 3.1 or 4.5, were employed for dyeing the fabric in a Multicolor (Gavazzi, Italy) apparatus. The liquor ratio between silk and solution weights was always 1:100. The following dyeing conditions were adopted: increase of 1.8°C min^{-1} from 40°C up to 90°C, 45 min at 90°C, cooling at 1.0°C min^{-1} down to 40°C. Spectrophotometric analysis (vide infra) of dye solutions after this treatment revealed that higher amounts of dyes (ca 85% of **1** and 98% of **2**) were absorbed on the fibre at pH 2–3, while silk dyeability was much lower at pH 4.5, corresponding to a 25 and 80% uptake of **1** and **2**, respectively. Some blank silk samples were prepared by following exactly the same procedure, in the absence of dye. Aqueous solutions of **1** or **2** ($1–2\times10^{-5}$ M) at pH 2.1, 3.1 and 4.5, obtained by adding different amounts of formic acid, were also employed in kinetic studies.

Irradiation of both silk samples and dye solutions was carried out by means of a Xenotest 150S (Heraeus, Germany) apparatus, at 45 ± 2°C and 65 ± 5% relative humidity. Dye solutions were irradiated in 35 ml cylindrical quartz cuvettes (i.d. 17 mm, height 154 mm). The intensity of the polychromatic radiation on the samples, estimated by means of a Radialux Heraeus instrument, was 94 W m^{-2}.

A Lambda 19 Perkin–Elmer apparatus, equipped with a RSA-PE-19 accessory for reflectance measurements, was employed for spectrophotometric analysis. The molar extinction coefficients of dyes **1** and **2** at the wavelengths corresponding to their absorption maxima in water (531 and 491 nm, respectively) were determined using solutions of pH 6 in the concentration range 6×10^{-6}–3×10^{-5} M; their absorption spectra did not vary in the pH interval 2–7.

Intrinsic viscosity of silk samples was determined at 21 ± 1°C by means of a Ubbelohde capillary viscosimeter (Schott Gerät, Germany) according to the SW 195595 procedure, after silk dissolution in a saturated LiBr aqueous solution.

IR analysis of dye solutions was carried out using an FT-IR 1725 Perkin–Elmer spectrometer. Total organic carbon (TOC) determinations were carried out on a TOC 5000 Shimazu equipment.

3. Results and discussion

3.1. Photodegradation of dyed silk

The photodegradation of silk dyed with **1** or **2** was kinetically followed by both spectrophotometric and viscosimetric measurements.

Reflectance spectra of dyed samples, recorded at different times during irradiation by means of the sunlight simulator, show that, in the investigated pH range, dye **2** underwent a much faster fading with respect to dye **1** (see for example, Fig. 1 vs Fig. 2). As expected, a higher increase of percent reflectance (%R) was observed when the amount of dye absorbed on the fibre was low, i.e. in samples dyed at pH 4.5, whereas the smallest increase in %R was noted in samples dyed at pH 2.1, in the case of dye **1**, and in samples dyed at pH 3.1 in the case of dye **2**, in correspondence with the highest dye uptake on the fibre. Irradiation of blank samples induced some photoyellowing in silk, without any remarkable difference attributable to the pH values of the blank dyeing treatment.

Viscosimetric analysis of both dyed and blank samples irradiated for different times evidenced a progressive decrease of intrisic viscosity, as reported in Fig. 3. This fact is indicative of a progressive depolymerization of the fibre. It is worth noting that this process may be due not only to the action

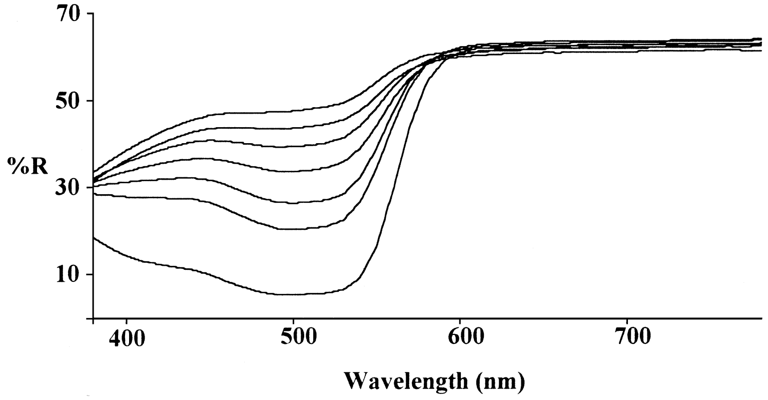


Fig. 1. Reflectance spectra of silk dyed with **2** at pH 2.1, recorded at different irradiation time (from bottom: 0, 40, 60, 100, 120, 160 and 200 h).

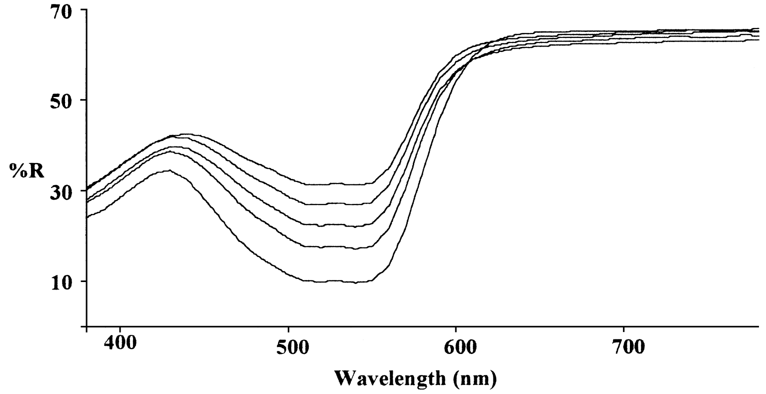


Fig. 2. Reflectance spectra of silk dyed with **1** at pH 2.1, recorded at different irradiation time (from bottom: 0, 50, 100, 150 and 200 h).

of light, but also to the acidic conditions employed during dyeing, which cause partial hydrolysis of fibroin [1]. Indeed, dyed and blank samples prior to irradiation could be classified as medium degraded, on the basis of their intrinsic viscosity values [2].

Absorbed dyes displayed a protective action on the silk substrate during irradiation, a higher decrease of polymerization degree being observed in samples with the lower amounts of absorbed dye (e.g. in samples dyed at pH 4.5). Moreover, dye **2** displayed a higher protective action on silk, with respect to dye **1**, allowing a lower degradation of the fibre (Fig. 3), while undergoing itself higher fading (Fig. 1). Thus in the case of dye **2**, the photodegradation process seems to involve mainly the dye, rather than the fibre, while the opposite seems to hold for dye **1**. This can be related to differences in the absorption spectrum of the two dyes, and to the consequent different filtering action at different wavelengths.

3.2. Photochemistry of dyes in aqueous solution

Both investigated dyes are α-phenylazo-naphthols. Thus, two tautomeric structures are possible (Scheme 1), the azo and the hydrazone form [3]. However, it was verified that the shapes of their absorption spectra did not change in the pH range investigated in this present work, indicating that the hydrazone form should be by far predominant, as supported by experimental and quantum mechanical studies [4–9]. In contrast,

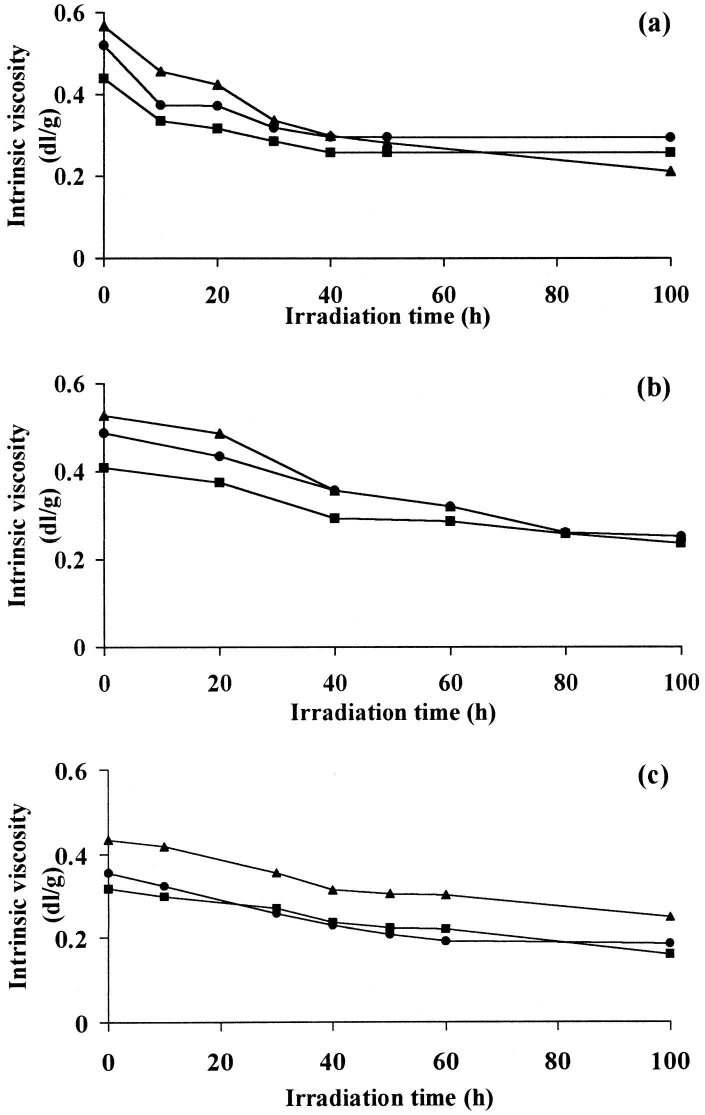
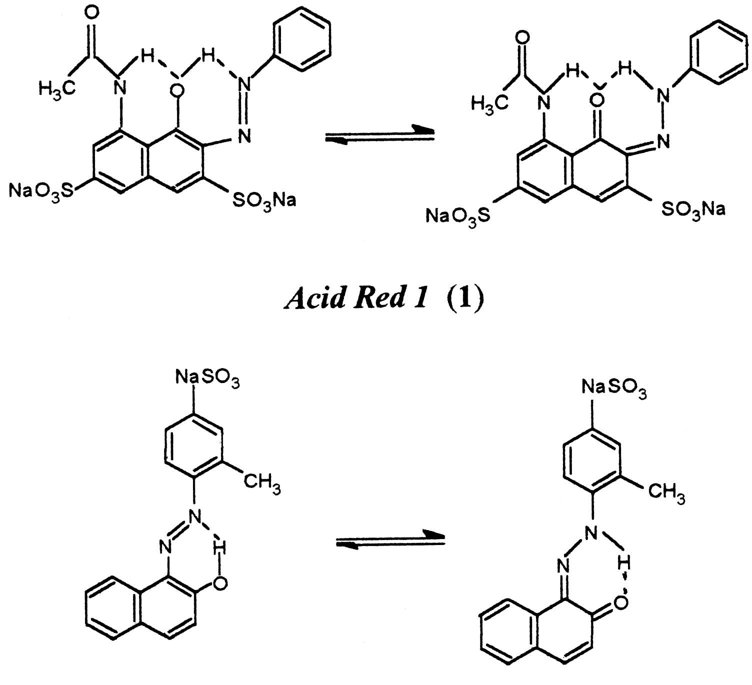


Fig. 3. Intrinsic viscosity of silk dyed with (a) **1** or (b) **2** at pH (■) 2.1, (●) 3.1 and (▲) 4.5 and of (c) blank silk pre-treated under the same pH conditions, as a function of irradiation time.

major changes occurred in the absorbance spectra of **1** at pH > 8 and of **2** at pH > 11 (Fig. 4), as a consequence of deprotonation of the naphthol group, the anionic azo form prevailing under alkaline conditions [10].

Dyes **1** and **2**, though having a similar structure, showed a different behaviour when irradiated in aqueous solution in the 2–4.5 pH range. Indeed, while aqueous solutions of dye **2** showed a progressive and uniform decrease of absorbance with increasing irradiation time (see Fig. 5), dye **1** was much less sensitive to irradiation, especially at pH 4.5, as shown in Fig. 6. The decrease of the main absorption band of **1**, characterized by peaks at 506 and 531 nm, was accompanied by a constant increase of absorbance at longer wavelengths, with a sharp isosbestic point at $\lambda \approx 550$ nm. This was more evident at low pH values [Fig. 6(a)].



Acid Red 1 **(1)**

Acid Orange 8 **(2)**

Scheme 1.

The different photodegradability of the two investigated dyes may be a consequence of different shiftings of their tautomeric equilibrium towards the more easily photodegradable azo form. In dye **2**, this should occur to a slightly greater extent [6,9], although the hydrazone tautomer should be strongly prevailing for both dyes [8]. Also, different inductive effects on the azo group, exerted by the sulphomic substituent on the benzenic ring in dye **2**, may be invoked. The sulphuric group plays a role in the photodegradation process and the decrease of pH observed during irradiation of both dyes in the more acidic solutions is a consequence of desulphonation, as confirmed by the precipitation of barium sulphate observed by treating irradiated solutions with barium chloride.

In contrast a remarkable increase in pH (up to pH$\approx$7) occurred during irradiation of solutions having an initial pH value of 4.5. In the case of dye **2**, this could easily be related to the formation of amine species in the reductive photodegradation of the azo group, a process which should prevail at pH 4.5. Unexpectedly, such increase of pH was observed also for dye **1**, even if no major changes in the absorbance spectrum could be detected as a consequence of irradiation. In any case, photodegradation should not proceed much beyond the azo group scission; in fact the formed amine species are able to absorb only a very minor fraction of the incident light. Indeed, the TOC content of irradiated solutions always resulted constant up to 200 h irradiation.

The quantum yield of photodegradation of dye **2** was estimated from spectrophotometric data, under the assumption that photodegradation products do not absorb at $\lambda > 480$ nm. The rate of disappearance of dye **2** can be expressed as:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = -\frac{1}{\epsilon \cdot l} \cdot \frac{\mathrm{d}A}{\mathrm{d}t} = I_0(1 - 10^{-A})\phi \qquad (1)$$

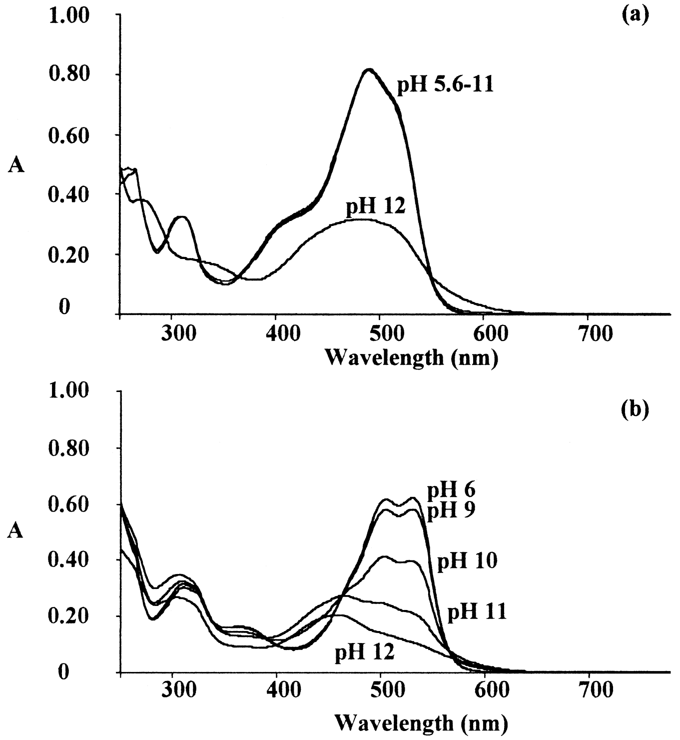


Fig. 4. Absorbance spectra of (a) dye **2** and (b) dye **1** aqueous solutions at different pH values.

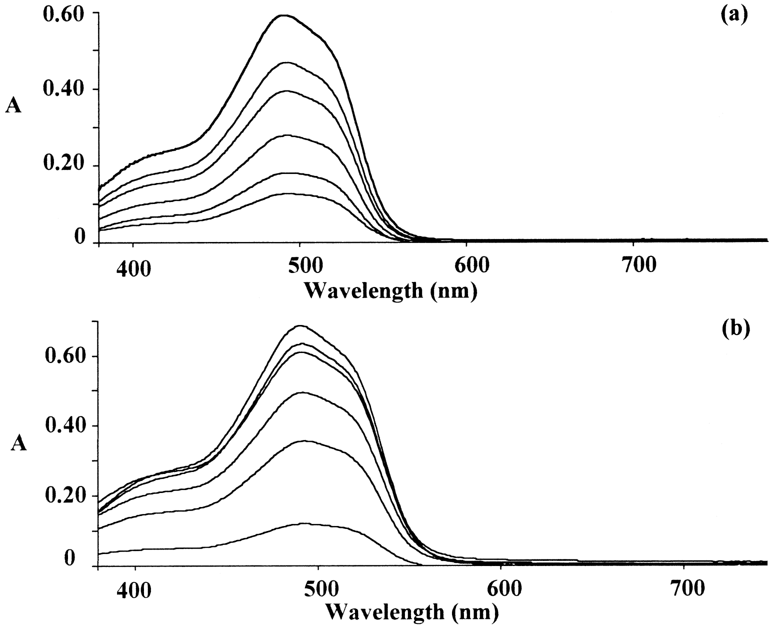


Fig. 5. Absorbance spectra of dye **2** aqueous solutions at (a) pH 2.1 and (b) pH 4.5, recorded at different irradiation time (from top: 0, 40, 60, 110, 160 and 200 h).

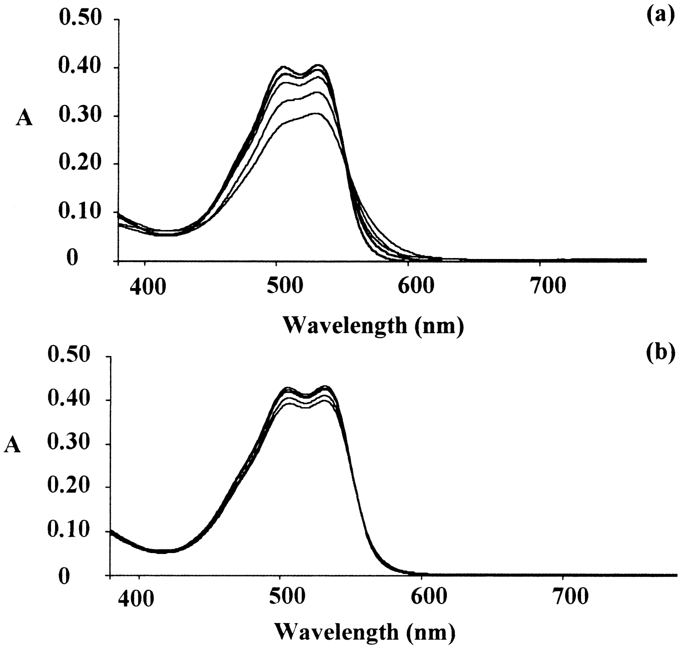


Fig. 6. Absorbance spectra of dye **1** aqueous solutions at (a) pH 2.1 and (b) pH 4.5, recorded at different irradiation time (from top: 0, 19, 35, 55 and 100 h).

A, ϵ and l indicating, as usual, the absorbance of the investigated solution, the molar extinction coefficient of the dye and the optical path length, respectively. ϕ is the mean polychromatic photodegradation quantum yield and I_0 $(1-10^{-A})$ represents the intensity of light absorbed by the dye, which can be evaluated taking into account the emission spectrum of the solar simulator and the absorption spectrum of the dye.

Due to difficulties arising from the presence of photodegradation products, as a first approximation, the absorbance and ϵ value of dye **2** at the absorption maximum ($\lambda = 491$ nm) were employed for evaluating the order of magnitude of ϕ. This probably implies an overestimation of the fraction of impinging light intensity I_0 effectively absorbed by the dye and consequently a certain underestimation of ϕ.

Eq. (1) can be integrated as follows:

$$-\int_{A_0}^{A}\frac{\mathrm{d}A}{1-10^{-A}}=\int_{0}^{t}(I_0\phi\epsilon l)\mathrm{d}t = I_0\phi\epsilon l t \qquad (2)$$

Thus, by plotting the $-\int_{A_0}^{A}\frac{\mathrm{d}A}{1-10^{-A}}$ values, obtained from absorbance data at $\lambda = 491$ nm, as a function of irradiation time, a straight line should be obtained if the quantum yield of the reaction does not vary with time. Such plots are shown in Fig. 7. It is very apparent that, after an initial induction period, the reaction proceeded with constant quantum yield at pH 2.1 and 3.1, whereas a progressive increase in quantum yield, probably consequent to the continuous increase of pH, was observed if irradiation was carried out starting from pH 4.5.

From the slopes of such plots, by taking into account the geometrical characteristics of the cuvettes containing the irradiated solutions and the impinging radiation intensity I_0 (see Experimental), the apparent quantum yield was 0.0018 mol einstein^{-1} for $t > 20$ h at pH 2.1, 0.0013 mol einstein^{-1} for $t > 8$ h at pH 3.1 and 0.0007 mol einstein^{-1} for $8\,\text{h} < t < 20$ h starting from pH 4.5. These quantum yield values are rather low, indicating that photodegradation does not represent an efficient deactivation path of excited **2**, as required for a commercial dye.

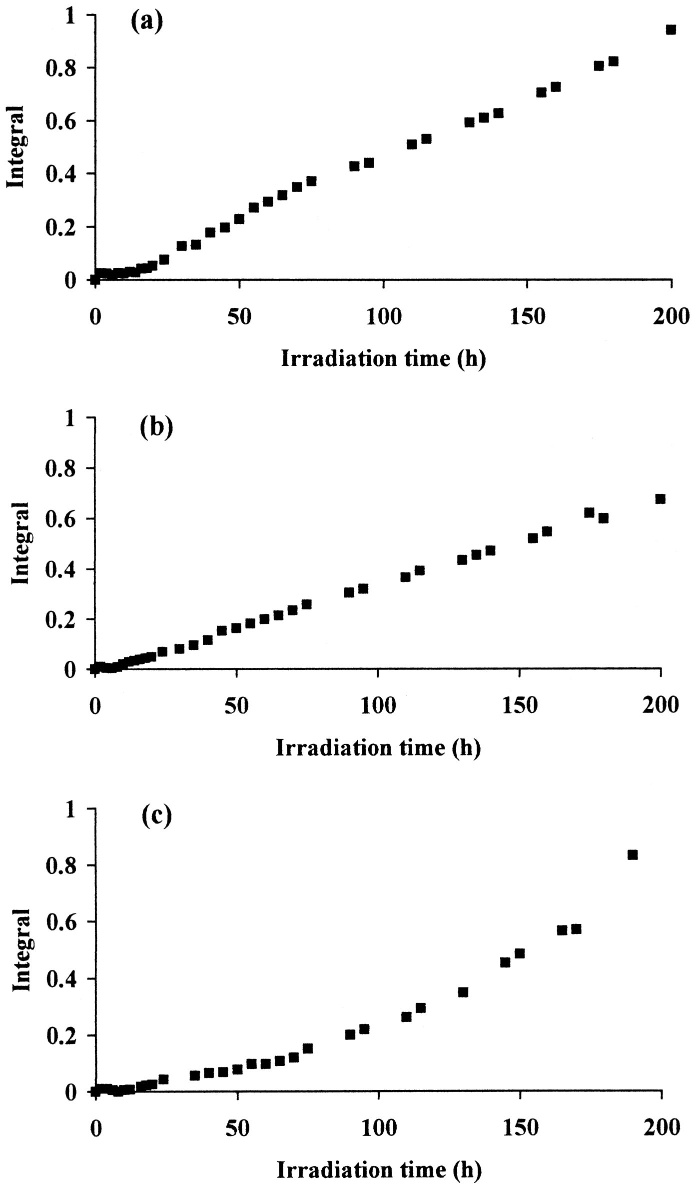


Fig. 7. Photodegradation of dye **2** in aqueous solutions at (a) pH 2.1, (b) pH 3.1 and (c) pH 4.5. Integral $= -\int_{A_0}^{A} \frac{dA}{1-10^{-A}}$ (see Eq. (2)).

Finally, concerning dye **1**, the increase in absorbance al $\lambda > 550$ nm observed during the irradiation of this dye, especially at low pH [Fig. 6(a)], can be explained by taking into account that *trans-cis* photoisomerization represents the main deactivation path of the excited states of azo dyes. The *cis* isomer can easily cyclize at low pH values, i.e. when it is in the protonated form [11]. The sharp isosbestic point at 550 nm indicates that cyclization is the main photochemical route for dye **1** under these conditions. Photodegradation represents a minor reaction path in this case, at least for relatively short irradiation times.

This is in agreement with the results of FT-IR analysis. Indeed, the sharp absorption band, due to the aromatic rings system, appearing at 1500 cm^{-1} in the IR spectrum of dye **1**, undergoes a decrease in intensity after irradiation, while a new band appears at 1530 cm^{-1}, indicating a more extended aromatic conjugation.

3.3. Photodegradation of dyed silk vs photochemistry in aqueous solution

The absorption spectra of dyes **1** and **2** absorbed on silk were practically coincident with those exhibited in aqueous solution, as shown in Fig. 8. Thus, also in the solid state the dyes should be present prevalently in the hydrazone form, and particular conformations or specific interactions with the solid fibre do not significantly modify their absorption characteristics.

However, a different photochemical behaviour was observed. In fact, when absorbed on silk, dye **1** also underwent photodegradation, especially in samples which had been dyed under more acidic conditions. In any case, its photodegradation rate was lower with respect to dye **2**. No remarkable

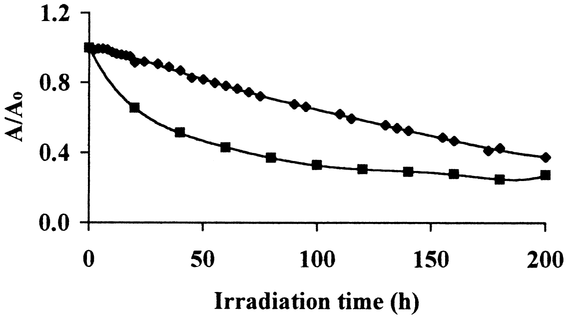


Fig. 9. Absorbance values A of dye **2** at 491 nm (maximum absorbance), normalized with respect to A_0, the absorbance at the beginning of irradiation, (■) on silk dyed at pH 3.1 and (◆) in aqueous solution at the same pH value.

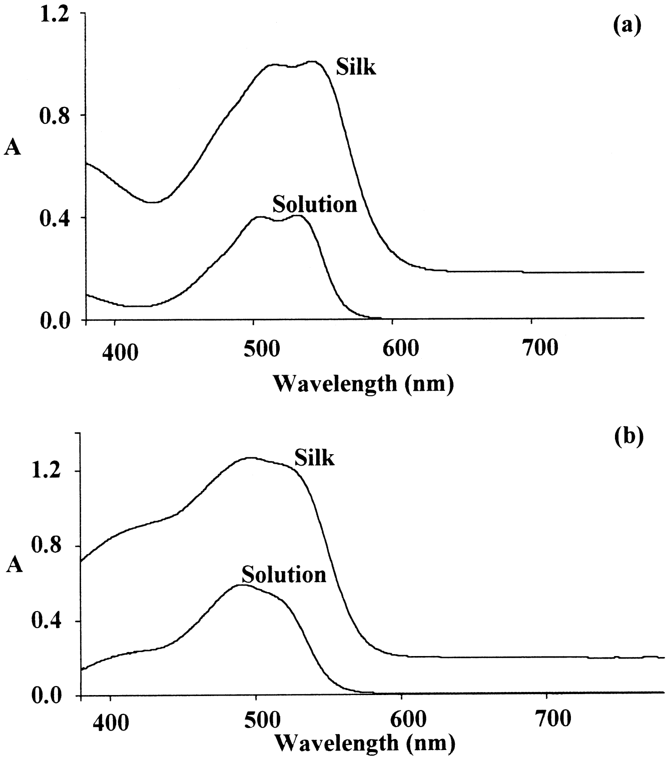


Fig. 8. Absorbance spectra of (a) dye **1** and (b) dye **2** on silk and in aqueous solution.

shifts or variation in shape were observed in the absorption spectra of both absorbed dyes during irradiation.

Moreover, the photodegradation of **2** was faster if the dye was adsorbed on silk, especially for short irradiation times (see for example Fig. 9). Different degradation mechanisms, probably involving hydrogen abstraction from the protein fibre, may thus be operative, facilitating the reductive photodegradation of the dyes. However, the quantum yield of such a reaction path, which was initially higher in the solid state with respect to the same process taking place in solution, continuously decreased with irradiation time when the dye was absorbed on silk, as a consequence of the reduced diffusion processes in the solid state. In contrast, dye solutions underwent photodegradation at an almost constant rate.

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