Parameters that affect the photodegradation of dyes and pigments in solution and on substrate – An overview

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A B S T R A C T
It has been known for many years that dyes and pigments are subject to light-induced degradation, or photodegradation, when exposed to light. It is the very reason why some beverages or medicines are wrapped in light-tight packaging materials, and why museums cover their windows with UV-blocking filters. The exact chemistry of light-induced degradation can be quite complex. Why and how are these dyes and colorants affected by light? How fast do these processes occur? Are there ways to prevent this from happening in a straightforward and durable way? These were and are still questions that are relevant to the many fields where colorants are applied.

In order to support these questions, we have tried to provide a broad overview of the research that has already been conducted on photodegradation of dyes and pigments and the analysis of photodegradation products. In those papers, the most important parameters that were discussed are the influence of the irradiation source, intensity and time, the presence or absence of oxygen, temperature, the effects that catalysts have, as well as the dye or pigment concentration. Additionally, we have investigated the differences found for photodegradation in solution and on substrates and specific parameters that may affect the processes in these media.

1. Introduction

Energy in the form of light induces physical and chemical changes to most organic compounds [1–4]. Inks, foods, pharmaceuticals, cosmetic products and polymers are only a few examples of materials that undergo degradation under the influence of light, also called light-induced degradation or photodegradation [5–7]. Among them, organic colorants are of great interest, as they are often used for the decoration of various products, thereby playing a decisive role in marketing and art. Photodegradation can have both a positive and a negative impact. On the one hand it can be responsible for fading colours in (historical) art objects, the loss of colour and valuable nutrients in foodstuffs, the fading of cosmetics, and the degradation of functional active components in pharmaceuticals [3,8–10]. On the other hand, photodegradation can also be implemented as a straightforward way to disinfect and purify wastewater generated from textiles, printing and paper industries [6,11]. A famous example of undesirable photodegradation in historical objects can be found in the painting Sunflowers by Van Gogh, depicted in Fig. 1A, from which it is evident that the yellow colours are fading. Researchers have found that the reason for the darkening of these once bright chrome yellow pigments is through the \( \text{Cr}^{VI} \rightarrow \text{Cr}^{III} \) reduction in the light-sensitive sulphur-rich chrome yellows (\( \text{PbCr}_4 \cdot x\text{SO}_4 \)), depicted as bright red dots in the Raman map in Fig. 1B [12]. The findings of studies like these will eventually result in a more accurate, safe and controlled strategy for the light exposure of historical objects. In addition, it will inform art historians but also the wider public about the original appearance of objects of art which is of relevance to understand the intention of the artist.

To better understand how these photodegradation processes occur or to ensure product quality, light stability testing is often performed using...
accelerated ageing to estimate within a shorter amount of time the long-term effects at the expected light levels. However, most studies focus on the visual effect, i.e., fading, but less on the degradation mechanisms, which are key to a better understanding of photodegradation. Not only for increasing the shelf life of consumer products and preserving artwork, but for example also for reducing the amount of (unknown) chemicals released into the environment.

1.1. Photochemistry of dyes and pigments

Colorants can interact with light in multiple ways. After a molecule absorbs a photon and is brought into the excited state, it can lose the excess energy by following several different pathways. These include physical processes that cause the relaxation of the molecule back to the ground state, as well as photochemical reactions that lead to the degradation of the molecule and the formation of new products [13]. Two main classes of photochemical reactions are distinguished depending on the photon-absorbing molecule and are illustrated in Fig. 2: (i) direct photochemical reactions, i.e. the dye molecules (D) are brought into the excited state (D)* and undergo intra- or intermolecular reactions after absorption of a photon, and (ii-v) indirect photochemical reactions, i.e. photons are absorbed by a photosensitizer (S) after energy transfer (ii) or by a photocatalyst (C) after oxidation (iii) or reduction (iv) of the catalyst, or by photochemically induced hydrogen atom transfer (v), which in turn excites the dye molecule [14].

1.1.1. Direct photochemical reactions

When light is absorbed by the dye itself, several protective pathways may be followed to lose the excess energy: (i) by emitting a photon (fluorescence or phosphorescence), (ii) through non-radiative relaxation e.g., vibrational relaxation, and molecular or atomic collisions, or (iii) by molecular reactions i.e., photoreactions. In the situation where photoreactions take place, two distinct pathways are possible: (a) intramolecular interactions occur, i.e., the photoexcited dye decomposes without further reactions with other substances, or (b) intermolecular reactions, i.e., the dye molecule may react with other substances present in the system. Both mechanisms result in photodegradation [15]. In the first case, the dye molecules must be chemically unstable in their photoexcited form and decompose through dissociation, intramolecular rearrangement reactions, or redox processes [15]. In the second case, the photoexcited dye molecules are chemically unstable only if other reactive substances are present in the

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Fig. 1. (A) Photograph of Sunflowers by Van Gogh (Arles, 1889; Van Gogh Museum, Amsterdam) with sample spots shown. (B) Raman distribution of different types of chrome yellows, with the light-sensitive pigments indicated by LS-CY (red). Adapted with permission from Ref. [12] (Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA).

Fig. 2. An overview of possible direct (i) and indirect (ii-v) photodegradation pathways. D = dye, S = photosensitizer, C = catalyst. Adapted with permission from Ref. [14] (Copyright 2018 American Chemical Society).
system \[15\]. In both cases, the photochemical reactions are initiated from the singlet or triplet excited state \( (^1D^*, ^3D^*) \) of the dye molecules. The lifetime of \(^1D^*\) is much longer (μs) compared to the lifetime of \(^3D^*\) (ns), and for many compounds the former is therefore assumed to be more reactive.

1.1.2. Indirect photochemical reactions

Photosensitizers are generally compounds with high absorption coefficients and low activation energies and are often in the same phase as the compound to be researched \[14\]. When excited, they either react directly with the neighbouring dye or pigment or they react with molecular oxygen \( (^3O_2) \) to create singlet oxygen \( (^1O_2) \), which then becomes the reactive species. It goes without saying that photosensitizers can also include dyes. Examples of dyes that create \(^1O_2\) through \(^3D^*\) and, thus, behave like photosensitizers are Green 8 (a pyrene dye), Chlorophyllin (a chlorophyll dye), Red 22 (a xanthene dye) and Green 5 (an anthraquinone dye) \[16\].

Besides photosensitizers photocatalysts can be used, which are classified as homogeneous or heterogeneous, depending on whether the reactants and the photocatalysts exist in the same or in different phases, respectively. The most commonly employed homogeneous photocatalysts include ozone \( (O_3) \) and photo-Fenton systems with iron \( (Fe) \) and hydrogen peroxide, whereas in heterogeneous photocatalysis transition metal oxide particles, such as titanium dioxide \( (TiO_2) \) and tin oxide \( (SnO_2) \) as well as semiconductors are most often used \[17\]. Pigments and coatings often contain metals that can behave as a catalyst, for example \( TiO_2 \) \[18\], aluminium oxide \( (Al_2O_3) \) \[19\] or iron oxide \( (Fe_2O_3) \) \[20\]. Section 2.4 goes into more detail of the exact reaction mechanisms of photocatalysis.

1.2. Aim of the review

Photodegradation is significantly influenced by a number of different factors. These parameters may affect both the kinetics and the photochemical mechanism, thereby affecting the degradation products formed as well as the extent of fading of dyes and pigments. To understand the changes occurring to artworks and to develop proper mitigation strategies, the chemical processes and kinetics should be known. There are many papers published describing these mechanisms including the analytical methods used to obtain them, however, a clear overview of the parameters that influence these mechanisms is still missing. Hence, this work is an attempt to provide such an overview, describing what can be found in existing literature across a variation of application areas and how these processes have been studied using various analytical detection methods. The discussed parameters include the type and the intensity of the irradiation source, the influence of oxygen, temperature, catalysts and dye concentration. This is followed by a comparison between in-solution and on-substrate photodegradation, where we describe the matrix specific parameters as well. Afterwards, an overview of how these photodegradation products are generally analysed is provided, and finally, all findings are discussed and summarized in the conclusions.

2. Parameters influencing photodegradation of dyes and pigments

Photodegradation of organic colorants is a dynamic process that is influenced by a number of different parameters, both internal and external. Internal factors are inherent to the compound under investigation and comprise the chemical structure and the physical state of the dye (e.g., absorption spectrum and polarity), as well as the properties of other substances present in the system (e.g., catalysts). External factors include the spectral distribution and intensity of the light source, presence or absence of oxygen, temperature, humidity, \( \text{pH} \), the type of solvent or substrate, and the concentration of dye. All these parameters are extensively reviewed in this chapter and are also depicted in Fig. 3.

![Fig. 3. Overview and classification of the discussed parameters that influence the photodegradation of dyes and pigments.](image)
reciprocity principle to investigate the sensitivity of colorants as a way of relating the exposure doses (intensity×time) acquired from accelerated ageing to the ones typically encountered in a museum environment [34–37]. These photometric measurements are often extrapolated to estimate the time required to reach a specific degree of damage. A popular approach makes use of a microfading tester (MFT), which can be applied directly on the art object [38,39]. The MFT consists of a probe containing several lenses to focus a high energy light source into a small spot (∼0.3 mm) to induce accelerated light ageing. Advances are still being made to the set-up, indicating that this method is of interest to many [40,41]. The use of an MFT takes little time and the result can be followed in real-time. However, there is concern regarding the validity of the results from MFT studies due to the large difference between the light intensities of MFT (5 Mlx) and those typically present in galleries (<200 lux) [42–44]. According to the reciprocity principle, similar photodegradation efficiencies are caused by the same light dose, i.e., using either high irradiation intensities for shorter periods of time or lower intensities for longer periods of time. This principle is indeed valid for most light stable colorants, however, deviations from the reciprocity principle proportional to the illumination intensity have been observed for organic colorants with a lower lightfastness. This is shown by the work of Hoyo-Meléndez et al. [45], who demonstrated that silk samples dyed with the lightfast dye cochineal followed the reciprocity principle at all light intensities tested (0.5–4 Mlx), whereas the less light stable dyes Pomegranate and Turmeric only followed the reciprocity principle at low light intensities (0.1–0.5 Mlx). Their study showed that reciprocity failure is mainly correlated to the use of high intensity lamps, however, they also state that the physical state of the dye (e.g., aggregate formation) may positively influence the dye’s lightfastness, which seems to be the case for cochineal. Therefore, in the case of photosensitive dyes and pigments, light intensity should be kept at low levels when studying the photodegradation to avoid inappropriately relating the exposure doses of normal and accelerated ageing.

2.1.3. Wavelength

The nature of the incident light plays a major role in the photodegradation of dyes. Unstable dyes typically fade more easily under Visible (Vis) radiation, whereas dyes of high light fastness usually require UV radiation as it is of higher energy [46]. To fully comprehend how photodegradation is influenced by the irradiation wavelength, two main factors should be considered: (i) the absorption spectrum of the dye and (ii) how damaging the light is that is being absorbed. Typically, light of shorter wavelengths provides higher levels of energy capable of breaking bonds, thus leading to higher photodegradation efficiencies and increased reaction rates. This has indeed been observed for several organic dyes and pigments [21,47–50]. Nonetheless, the dependence of the wavelength on photodegradation is also related to the absorption spectrum of the irradiated compound. For photons to be absorbed, the spectrum of the irradiation source should overlap with the absorption spectrum of the dye or the photosensitizer/catalyst [15]. This explains why some colorants experience higher degrees of photodegradation when exposed to light of longer wavelengths if this matches the absorption spectrum better [51]. However, no direct correlation between the fading rate and the colour of the dye has been found, as this also depends on many other factors, such as the medium, binding agent, and other additives [52–54].

Batchelor et al. [57] showed that both UV and Vis light induce the photodegradation of azo dyes and phthalocyanines under solar lighting conditions, however, in the case of azo dyes the Vis fraction was the most important, while for phthalocyanines the UV portion was dominant. This difference can be attributed to the fundamentally different structures of the dye classes, resulting in different photochemistry. Both azo dyes and phthalocyanines absorb UV and Vis light as can be seen in Fig. 4, but the chemical structure of the phthalocyanine is much stronger compared to the azo dye, meaning that more energy (i.e., UV light) is needed to initiate photodegradation. There may be an additional explanation for this difference. Compounds that predominantly absorb light of longer wavelengths, thus lower energy, such as Cu(II)
phthalocyanine, have lower $S_1$ and $T_1$ states compared to compounds that mainly absorb in the UV region. As a result, the lifetime of the triplet excited state is shorter, which also decreases the time for the compound to undergo chemical reactions with neighbouring molecules. Additionally, it was found that oxygen is required in the photodegradation of these specific dyes with Vis light, but not with UV light, again indicating that the photofading mechanism can be different depending on the irradiation wavelength.

The illumination wavelength may not only affect the photodegradation rate, but also the photodegradation mechanism. This is because the absorption bands of a compound may be related to different chemical subgroups of the molecule. Therefore, by irradiating at different wavelengths it is possible to excite different chromophores of the molecule. For example, Ahmad et al. [21] showed that intramolecular photoaddition of riboflavin into cyclolehydroriboflavirn is enhanced under UV irradiation, whereas under Vis light mostly photo-reduction of riboflavin into fomylmethylflavin, lumiflavirn and lumi-chrome takes place. Nevertheless, the measurements in both of these studies were performed only by spectroscopic techniques, therefore, the identification of the various photodegradation products is questionable. Alvarez-Martin et al. [58] used both spectroscopic and chromatographic techniques and demonstrated that by irradiation with wavelengths close to the main absorbance band of the red pigment eosin Y the photodegradation reaction was faster by a factor of $>20$.

2.2. Oxygen

Different photochemical reactions are observed depending on the presence or absence of free molecular oxygen [59–63]. Under anaerobic conditions, $D^*$ can either be reduced or oxidized, depending on the presence of a reducing or oxidizing agent, respectively. When both agents are present in the system, the reaction mechanism is determined by the nature of the reagents and the environmental or experimental conditions. Under aerobic conditions, interaction between $D^*$ and $O_2$ (the latter normally being in the triplet ground state) takes place through an energy transfer process, resulting in the formation of $O_2^*$, provided that no reducing agent is present. This highly reactive oxygen allotrope leads to further decomposition and fading of the organic dye. Less commonly, $D^*$ may also react with $O_2$ via an electron transfer process, generating radical superoxide ions ($O_2^-$). When a reductant is also present in an aerobic system, competition takes place.

Obviously, the presence or absence of oxygen plays a major role in the photodegradation process of dyes and pigments. Multiple studies have shown that in most cases of organic colorants, a decrease in oxygen concentration leads to lower photodegradation rates, however, a complete halt to the fading process has not been observed [48,57,64–71]. This might be due to other degradation processes occurring simultaneously (e.g., reduction in presence of a reducing agent). The degree of influence that oxygen has on the degradation rate has been found to depend on both the structure of the colorant and the solvent or substrate, which was demonstrated in an extensive study conducted by Arney et al. [61]. In their work, different trends were observed for different samples: some faded at rates that varied linearly with oxygen concentration, whereas others faded at rates that varied linearly with the square root of the oxygen concentration. Additionally, in proteinaceous substrates, where photodegradation mainly proceeds via reduction pathways, oxygen may have less of an influence on photodegradation. Saito et al. [70] observed lower photodegradation rates for six natural dyes on both silk and cotton substrates in the absence of oxygen, however, the overall influence of oxygen was more pronounced in the case of the cotton (cellulosic) substrates, thus confirming this hypothesis.

Contrary to what is typically observed, Schwen et al. [72] showed that diazacyanine blue and diazacyanine yellow dyed textiles degraded quicker under anaerobic conditions. The same trend was observed for Basic Blue 3 on silk and wool, also proteinaceous substrates. Arney et al. [61] demonstrated that the vermillion azo pigment follows the same tendency when applied as an oil pigment onto a glass slide. Blaisdell [73] found that oxygen inhibits the photodegradation of two azo dyes in isopropyl solution, due to a photosensitized oxidation of the solvent.

Furthermore, as would be expected, oxygen can also influence the mechanism of the photodegradation reaction. Alvarez-Martin et al. [58] investigated the photodegradation of eosin Y in aqueous solution under aerobic and anaerobic conditions and found that oxygen affects both the rate and the mechanism of the reaction (Fig. 5). In particular, in the presence of oxygen, photodegradation followed a fast oxidative pathway where the breakdown of the chromophore resulted in complete loss of colour. In contrast, in the absence of oxygen a slower debromination process took place, which led to less pronounced photofading, since the chromophore remained essentially intact. These results combined prove that it is impossible to draw generalized conclusions and detailed investigation of the fading reactions of different dyes and in different media is crucial in order to understand how the reaction mechanisms proceed.

2.3. Temperature

In general, temperature has been found to have relatively little effect on the photofading process of organic dyes and pigments. As would be expected, a rise in temperature increased the fading rate, but to a lesser extent compared to other parameters [24,50,74,75]. The pathways of the photodegradation process have not been found to be altered by differences in the temperature. This is an unexpected observation when considering that an increase in temperature leads to more energy, therefore reactions with higher activation energies could become preferable. However, since the thermal energies involved are small compared to the energies absorbed in the form of photons, the changes are rather insignificant.

Photodegradation of organic colorants on fibre substrates was shown to be influenced by temperature in two different ways. On the one hand, a change in temperature in such substrates almost invariably causes a change in moisture content. In particular, an increase in temperature leads to lower moisture levels in the fibre material, thus reducing the degree of photodegradation. On the other hand, however, it was shown that heat breaks down aggregated dye particles and that this may a reversible process [76]. Giles et al. irradiated dyed cellophane films in a heated atmosphere, but included ‘cooling down’ breaks in between where the sample was stored in a cold and dark environment. They found that the optical density increased linearly with temperature as a result of the breakdown of aggregates when irradiated in a heated atmosphere but saw a decrease in optical density after the cooling down period, indicating reggregation of dye particles. The breakdown of aggregates increases the surface area accessible for photochemical reactions, therefore increasing photodegradation. These opposing effects both depend on the type of the fibre substrate, as some fibre substrates can absorb greater amounts of moisture or promote aggregation to a

Fig. 5. (A) Under anaerobic conditions a relatively slow debromination process takes place from the triplet excited state of eosin Y (EY*), while under aerobic conditions (B) a second, faster process takes place resulting in the breakdown of the chromophore after generation of $O_2$ by EY*. Reprinted with permission from Ref. [58] (Copyright 2017 Elsevier).
higher extent, thereby being more susceptible to temperature than others.

In aqueous solutions, an increase in temperature results in lower concentrations of dissolved molecular oxygen, indicating that the influence of temperature and oxygen may be interrelated. Not many studies have assessed this effect, however, neither the photodegradation pathway nor the fading efficiency have been found to show any change in such systems [24].

In heterogeneous photocatalytic systems, temperature was found to have an indirect effect on the photodegradation of dyes. In particular, low temperatures favour the adsorption of the dye onto the catalyst, which is a spontaneous exothermic process. Nevertheless, in this case the adsorption of the degradation products is also enhanced, thus reducing the number of active sites on the catalyst. In contrast, high temperatures lead to an increase in the mobility of the dye molecules, therefore increasing the kinetic energy. However, the enhanced kinetic energy of the dye molecules may also allow them to escape from the photocatalyst surface, without being subjected to photodegradation. This effect was demonstrated by Barakat et al. [77] who showed that the morphology of the catalyst is very relevant when studying the effect of temperature on the photodegradation of dyes. They compared the photodegradation of rhodamine B at different temperatures with silver nanoparticles, higher temperatures increased the photodegradation rate, whereas a rise in temperature had a negative effect when nanoparticles were used. This was explained due to the super activity of the nanofibre surface compared to the nanoparticles. Unfortunately, very few studies [78–81] have evaluated the effect of temperature on the photodegradation of dyes in such systems.

2.4. Catalysts

Catalysts can be added to increase the photodegradation rate and the process is strongly influenced by both the type and amount of catalyst used. A photocatalyst enhances the photodegradation rate by generating reactive radical species on its surface after irradiation with light of energy higher than the bandgap of the catalyst. Upon irradiation, electrons are excited to the conduction band, which generates positive holes (h\(^+\)) and hydroxyl radicals, respectively, which react with and ultimately lead to the decomposition of adsorbed organic dyes [82,83].

In photocatalytic systems, organic colorants may fade completely upon light irradiation, whereas for some photodegradation reactions efficiency levels off after a while [78,84,85]. This is probably due to blockage of multiple active sites on the catalyst surface, which might occur over time and is dependent on the type of catalyst [86].

2.4.1. Type of catalyst

The intrinsic properties of the catalyst significantly influence the photodegradation efficiency of dyes for heterogeneous systems. Such properties include the light absorption range, the redox potential, the charge separation efficiency and the stability of the catalyst. Therefore, some catalysts show higher activity towards the decolorization of organic dyes under identical environmental conditions due to differences in these inherent properties. For instance, zinc oxide (ZnO) was found to be more efficient for the removal of several different organic dyes from water compared to TiO\(_2\) [87–89], which is due to its broader absorption spectrum [85].

Unfortunately, single-component materials, such as ZnO and TiO\(_2\), typically cannot satisfy the requirement of large redox potential and broad light absorption range simultaneously. Therefore, the investigation of new heterostructure systems that can improve the overall photocatalytic efficiency has become increasingly popular throughout the last decades. The outstanding properties of heterostructure catalysts are a result of the synergistic effect, electronic interaction, and strain effect, which will be different from that of pure materials [90]. For instance, Saeed et al. [86] demonstrated that titanium dioxide supported palladium (TiO\(_2/Pd\)) and titanium dioxide supported platinum (TiO\(_2/Pl\)) nanoparticles show higher photocatalytic activity compared to pure TiO\(_2\) nanoparticles, with the effect being more pronounced in the case of TiO\(_2/Pd\). El-Bahy et al. [91] reported that lanthanide ions can enhance the photodegradation efficiency of TiO\(_2\) and found that gadolinium (III) doped titanium dioxide (Gd\(^{3+}/\)TiO\(_2\)) nanoparticles result in a higher photocatalytic activity towards Direct Blue 53. Alzahran [92] showed that the photodegradation of eosin Y was significantly higher when using Ag doped magnetic nanoparticles (Ag–Fe\(_3\)O\(_4\)) compared to pure magnetic nanoparticles (Fe\(_3\)O\(_4\)) and Paul et al. [93] found the same trend for Ag doped graphitic carbon nitride (Ag–g-C\(_3\)N\(_4\)) towards methylene blue, crystal violet and rose bengal. It is evident that advanced technologies have led to the production of new systems, able to transcend difficulties of previous photocatalysts, resulting in more effective and efficient photodegradation.

2.4.2. Catalyst loading

Another factor that has been shown to affect the rate and efficiency of the photofading reaction is the photocatalyst loading. As it would be expected, an increase in the amount of catalyst leads to higher photodegradation efficiencies and increased reaction rates as more active sites are provided for adsorption of dye molecules. In fact, the initial reaction rates were found to increase proportionally with the amount of the catalyst [83,94]. Nonetheless, beyond a certain critical point, both the rate and efficiency of the photodegradation reaction either level off [28,86] or even begin to drop [84,91,95–97]. For heterogenous photocatalysis this can be explained by an increase in the suspension’s turbidity, which leads to more dominant light scattering phenomena, resulting in limited light absorption by the photocatalyst surface. Moreover, Herrmann [83] illustrated that the optimum photocatalyst loading depends on the initial solute concentration, therefore, the higher the initial dye concentration, the higher the optimum amount of photocatalyst required for its photodegradation. Thus, an optimum amount of photocatalyst does exist and should be determined first, not only to ensure efficient photodegradation, but also to avoid unnecessary use of catalyst excess.

2.5. Dye concentration

It was shown that photodegradation is strongly influenced by the amount of organic dye or pigment present in a solution or on a substrate. For dyes adsorbed onto substrates, dye concentration is closely related to aggregation. The higher the dye concentration, the greater the average size of the dye aggregates, thus, the lower the relative surface area accessible to environmental factors that lead to photofading. Therefore, an increase in dye concentration leads to an increase in aggregation, resulting in slower photofading rates. This is indeed evidenced by several studies investigating various organic colorants on paper, textiles and other synthetic materials [57,98–101]. Apart from an increase in aggregation, increased dye concentrations may also lead to higher absorption on the surface and weaker interactions between the substrate and the organic colorant, resulting again in lower reaction rates, which is further elaborated in section 3.2.1 [98,102]. Batchelor et al. [57] investigated the photodegradation of low and high concentrations (light and dark shades) of reactive dyes on cotton fibres and determined the colour change before and after irradiation using a Datacolor SF600 Spectrophotometer. They found that the amount of colour fading due to photodegradation was linear with time for both dark and light shades, but that the percentage of dye lost was greater for the lighter shades.

In heterogeneous photocatalytic systems the initial dye concentration is shown to have a strong influence on the photodegradation mechanism. It was found that an increase in the dye concentration leads to reduced photodegradation efficiencies and lower reaction rates. Numerous experiments have been performed both for different classes of...
organic dyes and with different catalysts, all supporting the aforementioned statement [28-30,86,89,91,103,104]. An explanation for this effect lies in the rate-limiting step of the formation of hydroxyl radicals on the photocatalytic surface. In particular, as the initial dye concentration increases while the irradiation intensity remains constant, fewer photons will reach the catalyst surface due to absorbance by the dye molecules; therefore, fewer reactive radicals are produced by the catalyst, leading to slower photodegradation rates [105].

The effect of dye concentration on in-solution photodegradation in absence of catalysts has been studied less. Research has shown that at low dye concentrations the photodegradation process of xanthene dyes erythrosine and phloxine B follows first-order kinetics, while at higher dye concentrations a more complex reaction mechanism may be involved. In particular, self-catalysis becomes more significant with increased concentration, resulting in higher reaction rates [24,106].

Strongly concentrated solutions also result in slower degradation rates due to high absorption at the top or edges of the sample, resulting in few photons reaching the main portion of the solution. This was demonstrated by Groeneveld et al. when studying the photodegradation of riboflavin in a 12-cm long liquid core waveguide cell [107].

3. In-solution versus on-substrate

Dye photofading in solution does not always mirror dye photofading on a surface. The properties of substrates (e.g., proteinaceous, cellulosic, synthetic matrix) and those of solvents (e.g., proton accepting or donating) may influence the photodegradation process of dyes significantly. In fact, it has been shown that dye molecules can exist as different tautomers depending on the medium, meaning that interactions between the dye and the medium molecules can lead to different dye structures, even without photoinhibition [108,109]. Nevertheless, solution or gel phase systems can sometimes be used as simple models to evaluate the kinetics and mechanisms of photochemical reactions of organic based colorants in solid samples [59]. Confortin et al. [110] demonstrated that crystal violet produced the same photodegradation products both in solution and on paper (Fig. 6), indicating that it follows the same or a similar photofading mechanism regardless of these media. Sousa et al. [59] found that the major degradation product of indigo in liquids, and in cellulose or collagen gels was isatin, which was in line with the analysis of blues from millenary Andean textiles (200 BC to 200 DC). They propose that the photodegradation rates found for indigo in water could be representative for that in historical artifacts.

Furthermore, it has been found that the rate of photochemical reactions in solution is typically greater due to the enhanced mobility of dye molecules in solution [71,102,111]. However, Abbott et al. [112] reported that the photodegradation of Acid Red 52 and Direct Blue 1 was much faster on paper and cotton (both cellulosic matrices) compared to in-solution degradation. In addition, the UV–Vis absorption spectra showed significant differences when the dyes were dissolved in water or when they were deposited on a substrate. It is worth repeating that the fading rate depends also on the dye concentrations, and this effect was remarkably slower for the substrate compared to the solutions. Other photodegradation parameters that can be related to the matrix are the type of solvent or substrate, the pH of the solution, the presence of mordants in substrates and the humidity of the environment, which are discussed below.

3.1. Solvent

3.1.1. Type of solvent

Properties of the solvent, such as its proticity and polarity, affect the solubility of different compounds through intermolecular interactions with the dissolved substances. Such interactions could eventually result in the formation of products that may lead to incorrect conclusions when used as a model for on-substrate photodegradation. For textile dyes, dimethyl sulfoxide (DMSO) was found to be particularly appropriate for the extraction of dyes that bind to the textile fibre through hydrophobic interactions (i.e., vat dyes and direct dyes) [113]. However, Pirok et al. [114] showed that the presence of DMSO accelerated the photodegradation reaction of eosin Y and carminic acid; it was found to interact with the carboxylic acid groups of all molecules present in the solution. Therefore, the use of DMSO as an extraction solvent of organic dyes from textile for light-induced degradation studies should be investigated as it may affect the composition of the degradation products, which would hamper the use as a model for photofading studies on textiles.

The influence of DMSO on photodegradation reactions as well as ethanol was evidenced by a different study. Ethanol is a common solvent of ink compositions, rendering it very relevant for document dating purposes. Brezová et al. [115] studied the effect of water, ethanol and DMSO on the photodegradation mechanism of six triarylmethane dyes, methylene blue, and eosin Y both under aerobic and anaerobic conditions. The results showed that even under aerobic conditions reactive oxygen species were formed for all dyes dissolved in ethanol and DMSO, indicating that the initial presence of oxygen is less important when these solvents are used for photodegradation studies. However, this may be different for aqueous solutions. It was found that reactive oxygen species were formed by crystal violet, methylene blue, malachite green oxalate and Acid Green 16 in oxygen-saturated aqueous solutions, whereas under anaerobic aqueous conditions these species were only formed by crystal violet.

The polarity of the solution environment also plays an important role in the photostability of photochromic organic dyes. Photochromic dyes

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**Fig. 6.** Comparison of degradation products from crystal violet (peak 1) samples irradiated (A) in aqueous solution or (B) on paper by Confortin using liquid chromatography with photodiode detection (LC-PDA). The same degradation products (peaks 2–12) were found in both media after exposure to UV light, although in higher concentrations and within a shorter irradiation time for crystal violet in solution. Adapted with permission from Ref. [116] (Copyright 2010 IOPscience).
are characterized by a reversible change of colour upon exposure to light, which is a result of a change in chemical structure depending on the environment. In particular, it was found that photodegradation of photochromic dyes in tetrahydrofuran (THF) was faster compared to benzene, due to the higher polarity of THF, which stabilized the unstable open coloured form of the dye molecules, promoting the photodegradation of this specific dye [102]. Furthermore, an increase in the water content of the solvent showed an increase in the fading rate of azo dyes, which may be due to the formation of radical hydroxyl species or may result in an enhanced contribution to the excited state of intra-molecular charge-transfer forms, followed by photoreduction to hydrayzyl radicals, which have a lower stability in water [116]. It is clear that the effect of the solvent in the photodegradation process of organic colorants is strongly associated with the structure of the dye, therefore, to fully comprehend its influence, it is important that future studies evaluate the photofading reactions of different organic colorants in various solvents and media.

3.1.2. pH

Photodegradation in solution may be significantly influenced by the solution pH or other reducing agents. Redox active groups can be protonated or deprotonated in acidic or alkaline pH, respectively, resulting in different forms, which may be less susceptible to photodegradation. Seixas de Melo et al. [117] studied keto and leuco-forms of indigotin derivatives in solution and found differences in the preferred relaxation pathways from the excited state to the ground state. They also suggested a difference in excited-state geometry, which ultimately may lead to a different photochemistry for the two forms.

The effects of the pH are different for many dyes depending on their chemical structure and pKa value. In general, charged molecules are more prone to initiate a photodegradation reaction. Therefore, the photodegradation of acidic dyes, such as carminic acid, alizarin and phycocyanin has been shown to increase at pH values higher than their pKa, where these molecules are mostly negatively charged [47,48,65]. Similarly, the photofading rate of the basic dye methylene blue was found to increase at pH values lower than its pKa, where the molecule exists almost entirely in the cation form [118]. It is also worth noting that changes in the pH leading to protonation or deprotonation may induce alterations in the conjugated system of the organic dyes, thereby changing their absorption spectrum [47,65,119,120], which should be taken into account when performing light-induced degradation studies in solution.

In heterogeneous photocatalytic systems, photodegradation is indirectly influenced by the solution pH, depending on both the solid catalyst and the dissolved dye. In particular, pH affects the electrostatic interactions between the molecules on the surface of the photocatalyst and the dye molecules, thus, the adsorption capacity of the catalyst is altered. Several photocatalytic materials, such as TiO2 and g-C3N4, display amphoteric characteristics [121,122]. Therefore, at a lower pH protonation of the photocatalyst will take place, leading to a positively charged surface, whereas at higher pH values a negatively charged surface will be formed. In the former case, anionic dyes are electrostatically attracted, thus highly adsorbed onto the catalyst surface, thereby being successfully subjected to photodegradation. However, the adsorption of cationic dyes is hindered due to electrostatic repulsion; the reverse is true in the latter case at higher pH. In summary, high adsorption capacities, and therefore high photodegradation efficiencies and reaction rates, are observed when cationic or anionic dyes are adsorbed on the catalyst surface at alkaline or acidic pH, respectively.

3.2. Substrate

When photodegradation of organic colorants is taking place on a substrate, several different factors need to be considered before evaluating the fading efficiency and reaction mechanism of organic colorants. Such factors include the type of substrate (e.g., synthetic, proteinaceous or cellulosic), its complexity when heterogeneous systems are present and its susceptibility towards photodegradation, interactions with the organic colorant, humidity, and the presence of mordants; a substance used to bind dyes to fabrics and to convert a dye into a pigment.

3.2.1. Type of substrate

The type of substrate may have a strong influence on the photodegradation mechanism. Cumming et al. [123] showed that photodegradation of dyes on proteinaceous substrates (e.g., wool, silk, gelatine) is more likely to follow a reduction pathway with the histidine side chains of the protein substrates acting as reducing agents, whereas on non-protein substrates (e.g., cellulose, cotton, nylon) oxidation is more probable. This observation was further supported by several other studies [70,76]. Nevertheless, this should not be seen as an absolute statement, as oxidation and reduction can both take place on protein and non-protein substrates, as substrate matrices themselves are also susceptible to photodegradation. Proteinaceous substrates can photo-oxidize through specific amino acids after absorbing UV light [124], resulting in significant deterioration and yellowing of the matrix [125]. Cellulosic substrates, on the other hand, such as cotton and paper are found to be less photolabile, therefore, photo-oxidation of these substrates is less common [126].

Additionally, another major factor that may affect the photodegradation of dyes is the hydrophobicity of the substrate. As example, direct dyes show higher lightfastness on hydrophilic substrates (e.g., cotton) [127], whereas disperse and basic dyes are found to have higher lightfastness on hydrophobic fabrics (e.g., polyester) [72,128,129]. Both observations can be easily explained. On the one hand, hydrophilic media have a high porosity and moisture regain, thus, leading to higher levels of aggregation of hydrophobic direct dyes. Aggregation is known to improve the lightfastness of dyes, due to the reduced surface area accessible to environmental parameters that induce photodegradation, as previously mentioned in section 2.5 [130]. On the other hand, hydrophobic substrates cause a decreased rate of photofading due to the low diffusion rate of moisture to the location of the dye, an effect known as the ‘diffusion-restriction effect’ [76]. Therefore, it is evident that the mechanism of photodegradation reactions of organic dyes varies with the species of dyes and substrates and is difficult to be generalized.

3.2.2. Humidity

The humidity of the environment was found to have a significant effect on the lightfastness of dyes adsorbed onto substrates. It has been shown that the fading of textile dyes and inks was faster under damp conditions, therefore, an increase in relative humidity greatly reduces the lightfastness of dyes except for colorants with high dye diffusion, which is predicted to be the case for hydrophilic dyes [50,57,70,75,76,131,132].

Ambient humidity may have a different impact depending on the paint system, i.e. oil vs. watercolour. Rader Bowers et al. [133] found that carminic acid watercolour is more affected by ambient humidity than oil paint. They suggest that this is because of higher mechanical cracking of the watercolour and increased surface area for interactions of the pigment with air. However, it may also be due to differences in absorptivity: water is clearly less absorbed by oils compared to paper. The effect of high relative humidity on oil lakes is observed as an increased formation of dicarboxylic acids and a higher degree of hydroylsis, followed by evaporation of free fatty acids [134]. Harrison et al. [135] observed an increased formation of epsomite (MgSO4·7H2O) crystals on the surface of cadmium yellow and French ultramarine oil paints upon light exposure at 75% relative humidity. This study highlights the importance of minimizing exposure to elevated levels of light and humidity to prevent these types of degradation processes.

Giles et al. [76] demonstrated that a reduction in the relative humidity can decelerate the fading process in two ways: (i) by slowing down the access of moisture to the dye molecules, and (ii) by facilitating the breakdown of large dye aggregates. Additionally, textile fibres are
known to swell due to absorbed moisture, which enables air to penetrate the intermolecular pores more readily and allowing it to participate in the photochemical reactions [136]. Therefore, the influence of humidity may be closely related with the influence of oxygen, although currently no study proves that oxidative pathways are more likely in high relative humidity environments.

Humidity is also closely associated with perspiration, which is a factor to consider for clothing textiles. In humid conditions sweat evaporates slowly due to the inability of the surrounding air to hold more water vapor. Therefore, under high humidity conditions sweat tends to accumulate more. Unfortunately, besides lower lightfastness, photochemical reactions of dyes on garments induced by perspiration could produce potentially harmful substances (e.g., aromatic amines and heavy metals), which could directly contact one’s skin [137]. The extent of influence that perspiration has on the photodegradation of organic colorants depends on their molecular structure and on the pH of perspiration. Several studies were performed on the effect of perspiration on several reactive dyes on cotton fabrics, including anthraquinone, monoazo, disazo and phthalocyanine dyes. Anthraquinone reactive dyes showed the best photostability in both acidic and alkaline perspiration, whereas Cu-complex azo reactive dyes were the most photosensitive [138,139]. Furthermore, structures involving the monochlorotriazine reactive group showed high stability, whereas vinyl sulfone reactive groups were the least photostable [138]. The fading rate of chlorotriazine vinyl reactive dyes was higher in acidic than in alkaline perspiration; the reverse was true for vinyl sulphonyl reactive dyes [139,140]. The fading was caused by interaction with other compounds, such as i-histidine, sodium chloride and glucose, and the pH. The effect of the pH is probably due to changes in the hydrolytic stability of the dye-fibre bonding.

3.2.3. Mordants

A mordant or dye fixative is a material used to bind dyes onto fabrics by creating a coordination complex with the dye, which then attaches to the fabric. The lightfastness of organic colorants is significantly influenced by both the mordant and the mordanting method. In fact, a study on 18 yellow natural dyes concluded that the structure of the dye is not as important as the mordant in determining the lightfastness of coloured textiles [141]. This may be true for structurally similar dyes, however, chemically different structures probably show more pronounced effects. The most commonly used mordants are tannic acid, certain salts of aluminium (Al), chromium (Cr), copper (Cu), Fe and tin (Sn). In general, better lightfastness can be achieved with Cr, Cu and Fe salts used as mordants, whereas a lower photostability is observed for Sn and Al salts [34,141-144]. Additionally, the mordant bath concentration and the dyeing procedure also have an influence on the lightfastness of organic dyes. In particular, the uptake by the fibres is not directly proportional to the mordant bath concentration: at high concentrations the relative amount of mordant absorbed is lower [144]. Moreover, compared to post-mordanting, the pre-mordanting method, where the substrate is first treated with the mordant and then with the dye, leads to fibres with higher amounts of metal ions, therefore stronger colour hues and as a result higher lightfastness [144]. In any case, the overall stability of dyes on fabric substrates strongly depends on the stability of the formed complexes of the dye, the fibre and the mordant.

3.2.4. Lake pigments

Lake pigments are pigments that are synthesized by precipitating a dye with a coordination metal also called a substrate. Both the type of the coordination metal and the metal to dye ratio can result in different colours compared to the uncoordinated dye [71,145,146]. Anselmi et al. demonstrated this in their work on geranium lakes where they studied the colouring properties of mono- and hemimetal eosin Y lakes with Al and Pb as the coordination metal [147]. A difference in perceived hue of colour means that a slight shift in the absorbance spectrum has taken place, therefore, possibly altering the photodegradation mechanism as explained in section 2.1.3. The eosin Y-metal coordination was also proven to be different for Al or Pb [148]. This was explained by Beltran et al. who showed that Pb-lakes show unidentate or bidentate bridging coordination, while Al lakes mostly presented a bidentate bridging coordination with eosin Y. These different interactions may determine the reactivity of the complexes, thus also their lightfastness.

The type of metal used for lake pigments may also influence oxidation behaviour of the chromophores in the paint layers leading to the degradation of the substrate. This was shown by Thomas et al. who studied the photodegradation of watercolour drawings based on madder lake pigments applied on paper. They found a strong correlation between the degradation of the paper substrate and the presence and type of the coordination metal. The relationship between the metal content and the colour change was less clear, although the presence of oxygen may play an important role there. The work by Liu et al. suggests that the photodegradation of iron gall ink and other iron-containing pigments is increased in the absence of oxygen, because these anaerobic conditions interrupt an important charge transfer transition from Fe⁷⁺ to Fe⁶⁺ in the coordination process with the dye [60]. However, Bowers et al. [71] showed that the photodegradation of carmine Al lakes stabilized under anaerobic conditions, which strengthens the conclusion that the effect of the coordination metal depends very much on the type and the coordination with the dye.

The paint medium, i.e. oil or watercolour, may also affect the photodegradation of lake pigments in different ways. Watercolours are known to be particularly sensitive to light, however, it was found that this is dependent on the type of mordant used [145]. Rader Bowers et al. [133] compared the photodegradation of carminic acid in water solutions, and in oil and watercolour lake pigments. They found that carmine watercolours were less sensitive to oxygen than oils. Another interesting outcome of this study was that the photodegradation rate of carminic acid in solution closely resembled that of oil paints under anoxic conditions, suggesting that in-solution photodegradation could be used as a model system to study photodegradation in oil paints. The similarity in effects was attributed to the fluid nature of partially dried oil paints, representing a comparable gas permeability as in-solution degradation. It would be interesting to see whether the photodegradation mechanisms in oil and watercolour paints show the same trends amongst other dyes as well.

4. Analytical methods applied to the analysis of photodegradation products

The effect of different parameters on the photofading process of organic colorants, as well as the characterization of their degradation products can be assessed using various analytical techniques. However, the selection of the most beneficial and suitable method depends both on the application field and the aim of the study. For instance, research in the field of cultural heritage faces practical issues due to the complexity and varying levels of degradation as well as the extremely low amount of sample material available. Furthermore, dyes and pigments used in cultural heritage objects are generally deposited on paper or textiles, therefore, minimally invasive analytical methods are required for their analysis. In contrast, studies on the photodegradation of organic dyes for the purification of wastewater are always performed in aqueous solutions and large sample volumes are usually available. Ideally, the selected analytical method should be sensitive enough to measure low concentrations of both the organic colorants and their degradation products and should also be rapid and robust to allow for the large number of measurements needed to evaluate the various parameters that affect photodegradation. Therefore, in this section the benefits and weaknesses of the most applied analytical methods are reviewed and discussed.

The assessment of colour change or fading due to photodegradation is often performed using colorimetry or lightfastness test standards as is depicted in Table S1 [34,46,48,49,68-70,72,75,76,99,126,129,
Colorimetry is a technique used to quantify a colour perceived by the human eye. This is achieved by deriving spectra to physical coordinates of colour perception, which correlate human colour vision with wavelengths in the Vis electromagnetic spectrum. The derived spectra are then used to calculate colour differences (ΔE) prior to and after photoirradiation of the coloured samples, thereby facilitating the evaluation of the photofading degree. Lightfastness test standards, on the other hand, are used to assess the extent of photodegradation for dyeing of textile fabrics, plastics or other materials and manufacturing paints or printing inks. The most commonly used standards are the Blue Wool Scale, the Grey scale and the scale defined by the American Standard Test Measure (ASTM). Testing is typically performed by exposing the dye samples and the standards to controlled sunlight or artificial light generated by a Xenon arc lamp followed by a comparison among them to identify the degree of colour fading. Unfortunately, both colorimetry and lightfastness test standards provide information only about the extent of colour change and results may be subject to interpersonal error; additional analytical tools must be applied for acquiring data on the kinetics or the characterization of degradation products.

As it can be clearly seen from Table S1, UV–Vis spectroscopy is the golden standard for analytically measuring the light stability of organic colorants. Most often, absorption and reflectance spectroscopy are being implemented to evaluate the effects of different parameters as the amount of light absorbed or reflected is indicative of the amount of colouring matter present in the sample. In addition, such methods are generally fast and easy to replicate. However, the absorption and reflectance spectra of organic molecules are strongly dependent upon the matrix composition and the optical absorption wavelength may shift as the chemical structure of the dye is changing during photodegradation [47,119,120]. Other spectroscopic techniques, such as Raman, fibre optics reflectance spectroscopy (FORIS) and fluorescence spectroscopy have also been applied for dye analysis, especially in works of art and cultural heritage artifacts due to their capability of acquiring structural information in a non-invasive way [65,71,110,149,150]. Nevertheless, the relatively low sensitivity of these techniques as well as the distortion of the signal caused by such complex mixtures render the identification of photodegradation and by-products extremely difficult. Additionally, even in samples with sufficiently high dye concentrations and no contaminants present, the degradation products often cannot be distinguished from the parent molecule, as they show very similar spectra. Hence, for the unambiguous identification of the degradation products, which allows for the elucidation of the mechanism of the photochemical reactions, mass spectrometry (MS) is usually a requirement. Indeed, MS provides information on the mass-to-charge ratio of both the molecular ion of the dye and its fragments, resulting in more reliable identification, while simultaneously offering very high sensitivity and selectivity. Direct MS methods, such as laser desorption ionization (LDI), matrix-assisted laser desorption ionization (MALDI), direct analysis in real-time (DART) and surface acoustic wave nebulization (SAWN) have been implemented as straightforward tools for the characterization of organic colorants on textiles and paper [50,98,151–154]. These techniques are minimally invasive due to the small sample sizes, require limited sample pre-treatment, and allow for the rapid determination of photodegradation products. Nevertheless, the lack of separation prior to the introduction of the sample in the MS leads to very complex mass spectra and may induce severe ion suppression effects, thus obstructing proper identification. To overcome these issues, separation techniques such as liquid chromatography (LC), gas chromatography (GC) or capillary electrophoresis (CE) coupled to MS have been extensively applied [51,58,65,71,114,124,144,155]. Most natural and synthetic colorants are non-volatile organic compounds; therefore, GC methods have rarely been implemented, due to the extra time-consuming derivatization step required for their analysis, even though excellent repeatability and reproducibility can be achieved [156]. On the contrary, CE and especially LC techniques constitute the most exploited separation methods for dye analysis. CE provides high resolution analysis while requiring very small sample sizes and low running costs, whereas LC-MS is a very robust combination that allows for the reliable characterization of almost any complex mixture. However, these separation techniques require that the analytes are extracted from the original materials using a solvent, which ideally should not intervene with the photodegradation process of the organic colorants.

Considering the advantages and disadvantages of the various analytical tools currently available, it becomes clear that a complete light-induced degradation study of organic colorants must incorporate complementary analytical techniques. Indeed, a more recent approach combines spectral information with MS data to achieve a better understanding of the photodegradation process [50,58,65,71,98,110,113,124,157,158]. This way the advantages of the two methods are enhanced, leading to more reliable results. An example of this approach can be found in the implementation of LC coupled to both photodiode array detection (PDA) and electrospray ionization MS (ESI-MS) [113]. PDA allows for the simultaneous acquisition of multiple absorbance spectra across the UV to Vis wavelength range, rendering it very efficient for light absorbing samples. The application of LC hyphenated with a combination of PDA and MS as detection systems led to improved separation of similar sample components and increased the detection limit, resulting in a more comprehensive understanding of the dye compositions. We have shown an example of such hyphenated systems for studying photodegradation mechanisms in a previously published article where a light reactor cell based on a liquid core waveguide (LCW) with in situ absorption spectroscopy was coupled on-line to LC-PDA [107]. Later, the same light reactor cell was coupled to 2D-LC, where the first LC separation was used to separate and isolate riboflavin from a multivitamin B complex inside the light reactor cell, after which the degradation products of the light exposed riboflavin were subjected to the second LC separation with PDA detection [159].

5. Discussion and conclusions

Degradation by light is a ubiquitous phenomenon that affects a wide range of materials, organic colorants being among them. A more comprehensive understanding of the photodegradation process is needed with the constant development of new synthetic dyes. In the present literature study, we have extensively reviewed the influence of different experimental and environmental parameters on the photodegradation of organic colorants across a variation of work fields. The wide variety of parameters and structurally different organic colorants that are evaluated under different experimental conditions applied in each study make it extremely difficult to render reliable comparisons. Additionally, most photodegradation studies focused on the effect of a limited number of parameters on a selection of organic dyes and pigments. We did not find a single study taking into consideration the entirety of the different parameters that influence photodegradation on a wide range of structurally different organic colorants. Such a study – even though rather complex – could allow for more universally applicable conclusions and a more complete understanding of the photofading process.

Based on the currently available literature, several conclusions can be drawn concerning the effect of the different parameters affecting the photodegradation process:

- An increase in the dose (intensity ’ time) leads to more pronounced photodegradation due to a higher photon input. The effect of the wavelength is associated with the structure of the dye and the absorption spectrum of the absorbing photosensitizer, catalyst or dye and has a strong influence on the mechanism of the photochemical reactions taking place.
- Oxygen is of paramount importance, as it strongly affects the pathways of the photodegradation reaction. A decrease in oxygen concentration usually leads to lower photofading effects, however, the
extent of influence is closely related with the chemical structure of the dye and the matrix. In situations where $^3\text{D}$ is quenched by oxygen to create $^3\text{O}_2$, the photofading rate may actually decrease under aerobic conditions (e.g., riboflavin).

- Temperature increase influences the photofading efficiency of organic colorants, however, to a lower extent compared to other parameters. A rise in temperature may reduce the degree of photodegradation by reducing the moisture content of the substrate or increase the degradation rate by breaking down dye aggregates, providing more surface area for irradiation. In solution an increased temperature may lead to more movement, thus higher kinetic energy of the dye molecules, leading to faster reaction rates, while photocatalysis is preferred at lower temperatures since this increases adsorption to the catalyst’s surface, although this strongly depends on the photocatalytic activity of the catalyst.

- In heterogeneous photocatalytic systems, enriched photocatalysts show higher catalytic activity compared to single-component materials. There is an optimum amount of catalyst that leads to higher photodegradation efficiencies and increased reaction rates.

- A rise in dye concentration leads to aggregated dye molecules adsorbed onto substrate matrices, which reduces photofading. Increased dye concentrations result in more pronounced dye-dye interactions in the absence of a catalytic system, however, it also results in more absorption at the surface, meaning that less light reaches deeper lying molecules. In-solution photocatalytic degradation is also impeded by an increase in dye concentration.

- Dye photodegradation in solution is not always identical with dye photodegradation on a substrate as the reaction mechanisms may differ. The rate of photochemical reactions in solution is usually greater than that on substrate, because of the increased mobility of e.g., dye molecules, catalysts and oxygen and due to the fact that the light distribution in a solution is more homogenic assuming proper mixing.

- The effect of solvent is strongly associated with the structure of the dye. Both the type of solvent and the pH can affect or temporarily change the chemical structure of the dye, thereby altering its susceptibility towards light. Solvents such as DMSO may also act as oxidizing agents. The effect of the pH is mostly dependent on the pKa of the dye or pigment.

- The type of substrate has a strong influence on the photochemical reactions taking place. Where proteinaceous substrates mostly lead to reduction processes, non-proteinaceous substrates favour oxidation reactions. A rise in relative humidity promotes photodegradation and might also be closely related to the influence of oxygen, whereas mordants improve the lightfastness of organic colorants on solid substrates. On the other hand, mordants or metals present in lake pigments may act as photocatalysts or oxidizing agents, which increases the photofading process.

Regarding the analytical methods that have been implemented for the assessment of the effect of the different parameters, a clear trend was observed. The use of MS for the identification of the photodegradation products, as well as the incorporation of separation techniques, such as LC, which allow for the chemical analysis of complex mixtures, have become increasingly popular in recent years. An even more recent approach combines the advantages of two orthogonal techniques, thereby leading to an improved understanding of the photofading process [358]. Other approaches often include spectroscopic techniques, colorimetry, and lightfastness test standards, which are relatively easy to implement, but provide less specific information. Hence, further work in this field could focus on the simultaneous evaluation of the influencing factors and the characterization of the degradation products, which allow for the more detailed elucidation of the photochemical processes.

Declaration of competing interest

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Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.dyepig.2022.110999.

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