Photofading Mechanism of Reactive Blue Dyes on Cotton against Sunlight and Xenon-arc lamp

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ABSTRACT

The photofading mechanism investigates in this study for dyeing of cotton fabric with five different blue reactive dyes by exposing sunlight and xenon arc lamp. Fading rate has enhanced by prolonging the time period 24 - 120 hr and stabilized at 72 hr of irradiation. Furthermore, a significant color difference obtained with unexposed and exposed cotton fabric dyeing with di fluoro pyrimidine azo ($\Delta E = 5.5$) by irradiating xenon arc lamp. The structural characteristics of both the dye and substrates confirmed by using FT-IR and UV-Vis spectroscopy. Among five reactive blue dyes, the di fluoro pyrimidine and copper metal complex azo dyes appeared most sensitive. However anthraquinone based reactive dyes showed the best stability for sunlight and xenon arc lamp.

Keywords: Photofading, Sunlight exposure, Xenon arc lamp exposure, Reactive dyes, Singlet oxygen, Cotton

Introduction

The photo degradation of reactive dyes undergoes a complex mechanism (Oakes et al. 2001). Moreover, the effect of photofading on reactive dyes has been extensively studied by many factors, such as characteristics of dye structure, substrate effect, atmospheric composition, dye-fiber interactions etc (Hihara at al., 2004; Oda et al., 1986; Dubini-Paglia et al., 1989; Rastogi et al., 2001; Oda et al., 2001). The photo degradation reactions of the terrestrial sunlight spectrum from 3000 to 4000 A$^\circ$ and bond dissociation energies involving carbon chains lie in 70-90 kcal. The xenon arc lamp produces a similar spectral power distribution like terrestrial sunlight than carbon arc. Several researchers explained the photo degradation effects of the different yarns under sunlight behind window glass and xenon arc lamp radiation (Wall et al., 1971). The fading reaction for any dye an exposure of sunlight was shown in scheme 1. The dye destruction was not defined by reactive oxygen species such as singlet oxygen, hydrogen peroxide, superoxide radicals or peroxy radicals. However, many researchers reported the propagation of singlet oxygen $^1$O$_2$, which could be formed by the quenching of excited states of dyes by the triplet ground state of oxygen.
The quenching of excited states of dyes by oxygen, it leads to the formation of superoxide radical and destruction of the dye shown in scheme 2 (Batchelor et al., 2003; Wilkinson et al., 1995). The covalent bond formation between dye and fiber facilitates the transfer of energy from the excited state of the dye to the fiber, which is the resultant of the photo degradation reduction of the dye (Ingamells et al., 1963; Hladík et al., 1979). On the other hand, several studies explained that, dye substrate bond does not affect the light fastness such as Remazol and Lanasol dyes on wool did not show any significant differences in light fastness due to attributable to the dye fiber bond (Krčevsk et al., 1975; Wall et al., 1971; Shah et al., 1976). In addition, bi-functional reactive dye formed crosslink in the fiber, which imparts a fiber protective effect against light and improves better fastness properties (Ball et al., 1986; Rastogi et al. 2001). Furthermore, the catalytic fading of azo dyes and anthraquinoid dyes caused by photo-oxygenation reaction by singlet oxygen mechanism (Rembold et al., 1978; Oda et al., 1986). Studies on photofading mechanism of commercial reactive dyes on cotton both UV and visible light also determined that azo/hydrazone formation of dyes is the most important contributor under normal lighting conditions (Batchelor et al., 2003). The fading rate curves and the characteristic fading curves of seven azo dyes on cellulose acetate and polyamide films were examined and the results obtained that substrates of higher polarity and porosity acted in favor of association of dye molecules impeding fading (Tera et al. 1985). Singlet oxygen is the responsible photo oxidation of vinylsulfonyl (VS) reactive dyes in the absence of substrate (Okada et al. 1991; Choudhury et al. 2019). The absence of oxygen and the presence of substrate, fading occurs by photo reduction mechanism (Okada et al., 1990). The azo linkages seem to be first attacked. Mixed dyes may fade quickly by exposing of light, which is called catalytic fading (Okada et al. 1990). The chemical structure of reactive dyes was greatly influenced by exposing light and perspiration. Vinylsulphone based reactive dyes containing J- or γ-acid azo chromophore exhibited greater fastness to both light and perspiration than H- or K-acid azo chromophores (Imada et al., 1994; Aranyosi et al., 1998). In order to investigate the fading behavior of vinylsulphone (VS) reactive dyes on cotton influence of light and perspiration and concluded the fading mechanism was either photo reduction or photo oxidation, depending on the exposure condition (Zhuang et al., 2007). The fading rate of azo reactive dyeings observed that the photo reductive mechanism under light and perspiration adopted JIS L0888, AATCC and ATTS standard test were greatest extent (Vi´g et al., 2007).

In recent years, dyers facing lot of problems for lower stability of the blue reactive dyes under simultaneous exposure of sunlight and xenon arc lamp. The studies on photofading of reactive dyes observed contradictory results. There, are no research has apparently been carried out about blue reactive dyes fading on cotton. In addition, there are no significant effects of covalent bonds with dyes and fiber was not analyzed by FT-IR and extraction of dyestuff was not measured by UV-Vis spectroscopy after fading under sunlight and xenon arc lamp.
exposure. This paper deals with the studies related to the fading characteristics of different types of bi-functional and different chromophores of reactive blue dyes on cotton. In order to study the effects of dye fiber interaction, the results compared with unexposed and exposed conditions of sunlight and xenon arc lamp exposure.

**Experimental Materials**

**Dyes**

A series of different functional groups for blue reactive dyes were kindly supplied by Archroma Bangladesh Ltd. Blue reactive dyes used without further purification in this study: Anthraquinone (Dye 1, C. I. Reactive Blue 19), Copper Phthalocyanine (Dye 2, C. I. Reactive Blue 21), Di-azo bifunctional (MCT-VS) (Dye 3, C. I. Reactive Blue 198), Copper metal complex (MCT-VS) (Dye 4, C. I. Reactive Blue 221) & Di-azo bifunctional (DFP-VS) (Dye 5, C. I. Reactive Blue 225).

![Dye 1](image1)

**Dye 1 (M.W. 626.54)**

![Dye 2](image2)

**Dye 2 (M.W. 1155.66)**

![Dye 3](image3)

**Dye 3 (M.W. 1205.38)**

![Dye 4](image4)

**Dye 4 (M.W. 1082.82)**
Fabric & Chemicals
Cotton (100%) tubular single jersey knitted fabrics (Yarn count 36\(\text{\textdegree}\)) with wales/inch 36.92, courses/inch 48 and weighting of fabric 118.80 g/m\(^2\) were used. Prior to dyeing, the single jersey knitted fabrics was scoured and bleached in a solution containing 1 g/L wetting agent (Imerol Blue Liquid, Clarichem Ltd), 1 g/L sequestering agent (REQUEST 2207, Resas chemie), 4 g/L NaOH (50\%) and H\(_2\)O\(_2\) (35\%) 5 g/L for 40 min at 100\(\text{\degree}\)C, at a liquor to goods ratio of 20:1. Subsequently, fabrics were thoroughly washed with peroxide killer (Peroxide Killer RS, Honghao chemical Company, China) 1 g/L at 80\(\text{\degree}\)C for 15 minutes and neutralized with acetic acid for 10 minutes at 50\(\text{\degree}\)C. All the chemicals used in the pre-treatment of laboratory-reagent grade.

Dyeing of cotton fabric
A 50 ml dyebath, suitable for the cotton fabric dyeing with reactive dye (1\%) in laboratory dyeing machine (Starlet dyeing machine, DLS-6000 and infrared). In the dyeing bath, 40 g/l sodium sulphate used for dye exhaustion and 15 g/L sodium carbonate used for fixation with material liquor ratio 20:1 at 80\(\text{\degree}\)C for 50 minutes. Dyed samples were thoroughly rinsed with cold water by soaping 1 g/L solution at the temperature 70\(\text{\degree}\)C for 10 minutes. After treating the soaping agents all the samples were dried.

Irradiation of Dyed fabrics
Cotton fabric dyeing with blue reactive blue was cut into 10 cm \(\times\) 10 cm samples and mounted on strips of white chart paper. Thus samples were prepared for exposing sunlight and xenon arc lamp irradiation.

Sunlight Irradiation
For sunlight exposure, an exposure rack was placed in an open area and confirming no shadow during day time at an angle from the horizontal equal to the latitude (latitude = 22.757\(^\circ\)). The fading of dyed samples under daylight testing was carried out in three successive seasons. The winter season starts from the month of December, January and February during which testing was carried out for continued 24 h, which means 8h for each month. The summer starts from the month of March, April and May during which testing was done for the next 48 h. The test continued for the third season namely rainy season, in the month of June and July for the next 72 hr. Also the fading was performed for the next 96 hr to 120hr from August to November. During the intermediate period, the dyed samples were carefully preserved in a dark place keeping inside the plastic packet to keep away from moisture.

Xenon-arc lamp Irradiation
The xenon arc lamp exposure was performed by Q-SUN B 02 xenon light fastness tester (USA). The dyed fabric stripes were irradiated using xenon lamp, which employing 42 W/m\(^2\) in the wavelength range 300 nm to 400 nm in the UV and 343 W/m\(^2\) in the visible wavelength range 400 nm to 800 nm. The effective relative humidity was 35\% in all experiments. The black panel standard temperature was 45\(\text{\degree}\)C. Total exposure time
completed during 24 hr to 120 hr. All the exposed samples preserved inside the plastic packet.

**Color fading evaluation**

The color difference of the sunlight and xenon arc lamp exposed fabrics was measured using a spectrophotometer (X-rite 8000 Series, standard light D65, 10° standard observer, specular component included, \( \lambda = 540 \) nm) interfaced with a personal computer. The CIE 1976 \( L^* \) a* b* (CIELAB) color space were applied by the following equations (1)-

\[
L^* = 116 \left( \frac{Y}{Y_n} \right)^{1/3} - 16, \quad a^* = 500 \left( \frac{X}{X_n} \right)^{1/3} - \left( \frac{Y}{Y_n} \right)^{1/3}, \quad b^* = 200 \left( \frac{Y}{Y_n} \right)^{1/3} - \left( \frac{Z}{Z_n} \right)^{1/3}
\]

Where \( L^* \) is the luminance, \( a^* \) is the red-green axis, \( b^* \) is the yellow-blue axis, where color matching functions for 10° standard observer at each wavelength (ISO 7724/1-1984). The color difference (\( \Delta E_{ab}^* \)) between the unexposed and exposed fabric were measured by the following equation (2)

\[
\Delta E_{ab}^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}
\]

Where \( \Delta L^* \), \( \Delta a^* \) and \( \Delta b^* \) represent the differences in \( L^* \), \( a^* \) and \( b^* \) between the unexposed and exposed samples.

**FT-IR measurement of exposed and unexposed fabric**

Sunlight and xenon arc lamp exposed and unexposed cotton fabric dyeing with reactive dye was measured by FT-IR (300 E system, Jasco Company, Japan). All the samples were placed on ATR mode for the number of scanning was 50 times and the resolution power was 4 cm\(^{-1}\).

**UV-Vis spectroscopic measurement of dye extracted solution**

For extracting the dyes from the unexposed and exposed dyed fabric (0.01 g) was added with chemicals (\( \text{Na}_2\text{S}_2\text{O}_4, 1.5 \, \text{g} + \text{NaOH, 1.5 g} \) in 20 mL of water and heated up at 100° C until the sample become colorless. An extracted solution was kept in 10 mL of vial. The absorption of the wavelength from (\( \lambda_{max} = 400-700 \) nm) of extracted solution from unexposed and exposed fabric was measured using UV-Vis spectroscopy (Agilent 8453, Made in USA).

**Results and Discussion**

**Fading of reactive dyes under exposure of sunlight and xenon arc lamp**

In order to investigate the impact of environment on the fading of cotton fabrics dyeing with different blue reactive dyes such as anthraquinone dye (1), copper phthalocyanine (2), di azo bi-functional (MCT-VS) (3), Cu-complex azo dye (4) and di-azo bifunctional (DFP-VS) (5) dye respectively, were tested under different conditions. The color difference values (\( \Delta E_{CMC} \)) of different reactive dyed cotton fabrics after 24 hr- 120 hr exposure to sunlight and xenon arc lamp were illustrated in Figure 1. It can be observed that the fading rate increases with exposure of time. However, the level off point for faded cotton fabrics were obtained at 72 hr of exposure for sunlight and xenon arc lamp. A comparison for the fading rates of sunlight and xenon arc lamp showed similar trends. The order the rate of fading was as follows: Anthraquinone > (MCT-VS) dye > Copper phthalocyanine dye > Cu-complex azo dye > bi-functional (DFP-VS) dye.
Interestingly, di-azo bifunctional (DFP-VS) dyes shown the highest fading rate than other dyestuffs. It can be explained that a greater absorption of light caused more photo bleaching. On the other hand, Cu-complex azo dyes appeared to be the second most photosensitive under exposure of sunlight and xenon arc lamp. After exposing for 24 hr-120 hr, the color of the cotton fabrics dyed with the two Cu-complex azo dyes was faded to a great extent, and that dyed with even had a color difference value over 4.00. It can be demonstrate that the higher tendency to react with metal Cu-complex reactive dyes because
introducing of Cu ion into the azo group in dye molecules can reduce the electron density of the azo groups, which enhanced the photo reduction process. In sunlight and xenon arc lamp exposure of copper phthalocyanine reactive dyed cotton fabric transfer its energy from the lowest excited triplet states to the acceptor so fading rate were obtained at 1.2 for sunlight and 3 for xenon arc lamp. In addition, diazo MCT-VS reactive dyes shows good stability under exposure of sunlight and xenon arc lamp. The fading rate were obtained at 0.8 for sunlight and 2.2 for xenon arc lamp exposure. The fading rate of the reactive dyes also depends on the stability of covalent bond between the dyes and cellulosic fiber. However, anthraquinone based reactive dyes showed excellent light stability by sunlight and xenon arc lamp exposure. The color difference value of the cotton samples dyed with anthraquinone dyes was 0.5 for sunlight exposure and 1.5 for xenon arc lamp exposure. It is clearly explained that, anthraquinone dyes are photo stable by photo oxidative and photo reductive process.

**Effect of covalent bond stability of reactive dyed cotton fabric under exposure of sunlight and xenon arc lamp**

The mechanism of photofading also influenced by substrates. The covalent bond between reactive dye and cellulosic fiber has undergoes excitation and participate in electron transfer and hydrogen abstraction or bond dissociation mechanisms. The excitation of substrates containing carbonyl groups which can mediate hydrogen atom abstraction from other functional groups of the substrate or even the dyes themselves. Radicals such as R₂C-OH are extremely good one-electron reductants, schematically illustrated in figure 2.
The effects of covalent bonding between the reactive dye and cotton fiber on the fading behavior were determined by FT-IR analysis. The study was monitored on dyed cotton to get an insight into the role of the substrate on photofading of reactive dyes. The FT-IR (ATR) spectra of different reactive blue dyed cotton fabrics for unexposed and exposed fabrics was revealed in figure 3, using transmittance (%) versus wavenumber (cm⁻¹). It is very hard to detect any differences between the spectrum of unexposed and exposed of dyed fabric by exposure of sunlight and xenon arc lamp.

Figure 2. Photofading mechanism of reactive dyes with different functional groups on cotton fabric under exposure of sunlight and xenon arc lamp.
Figure 3. Photofading effects of reactive dyes with different functional groups on cotton fabrics under exposure of (a) Sunlight (b) Xenon arc lamp

The transmittance (%) of hydrogen bonded of OH stretching in cellulose absorbs (3000-3600 cm⁻¹) and also observed a broad peak centered 3300 cm⁻¹ corresponding to O-H stretching. However, an unexposed fabric illustrates the broad peak at 3000-2800 cm⁻¹ region C-H stretching. Although cellulose has -CH₂ groups in their structure, so the peaks correspond to the symmetric and asymmetric stretching modes shows extra peaks at 2918 and 2849 cm⁻¹. The stretch of -C≡N is a sharp absorption near 2250-2400 cm⁻¹ observed for (dye 5) reactive dyed cotton fabric under unexposed conditions. The C=O stretching would show up at around 1750 cm⁻¹ and C-OH stretching at 1200 cm⁻¹. The carboxylate (COO⁻) ions showed two peaks at 1600 and 1400 cm⁻¹ for the asymmetric and symmetric stretching of COO⁻ ion respectively. The characteristic peaks eliminated observed at -C≡N near 2250-2400 cm⁻¹ for reactive dyed under exposed conditions. However, no
significant differences were obtained for unexposed and exposed fabric. It can be explained that, the covalent bond of reactive dyed cotton fabric formed free radical by xenon arc lamp exposure.

**Multi-step for photo reduction of reactive dyed cotton fabric under exposure of sunlight and xenon arc lamp**

In order to examine the degradation of five different blue reactive dyes bond with cotton were extracted so the UV- spectra were obtained after considerable fading shown in figure 4. Very limited changes in the absorption spectra of anthraquinone dyes (Dye 1) was observed on repeating the treatment of sunlight and xenon arc lamp exposure. The absorption spectrum of the dye 1 showed the absorption band at $\lambda_{max}$ 575 nm, the absorbance peak observed quite lower in exposed condition.

![Figure 4. Absorption spectra of extracted reactive dye from dyed cotton fabric under 72 hr exposure of (a) Sunlight (b) Xenon arc lamp](image-url)
It can be explained that anthraquinone dyes are more stable by the fused membered benzene ring structure. The dissociation of dyes require more energy, so it follows more steps to dissociate shown in figure 5. On the other hand, the absorption spectra of copper phthalocyanine (Dye 2) dyes after exposing in sunlight and xenon arc lamp showed a broad band absorption peak at $\lambda_{\text{max}}$ 625 nm. Copper phthalocyanine are efficient singlet oxygen generators. The quenching of an excited state of dyes by oxygen has been led to the formation of the superoxide radicals and the destruction of dyes by scissoring effect shown in figure 5.
There has no significant changes were observed in the absorption spectra of an unexposed condition of sunlight and xenon arc lamp exposure. However, in exposed condition in figure 4, it is clearly shows that dye 2 was catalytically faded by the exposure of sunlight and xenon arc lamp. Interestingly, bi-functional (MCT-VS) reactive dyes displayed higher reactivity to cotton and could be reactive to singlet oxygen by sunlight and xenon arc lamp exposure. However, the extensively delocalised triazine contains electron-rich nitrogen centers, which tend to be efficient physical quenchers of singlet oxygen. The photochemical pathway was found to proceed by means of singlet oxygen attack on the hydrazone form of the dye and dye dissociates in three fragmented parts shown in figure 5. The absorption spectra of dye 3 on cotton and photodecomposition after the exposure an absorption band at λ_max 650 nm shown in figure 4. No changes were obtained by (MCT-VS) dyes under exposure of sunlight and xenon arc lamp. In principle, the photo-oxidation of copper complex azo dyes was mostly affected by xenon arc lamp. It can be explained that, xenon arc lamp experiment was carried out by maintaining appropriate moisture management rather than natural sunlight conditions. Cu-complex azo dyes quenched by \(^1\text{O}_2\) and appeared second most photosensitive after exposure of light. It have a great tendency to react with Cu-complex groups and separate Cu ion from azo cleavage, also reduce the electron density from the bridge group and make the dye more easily photo reduced shown in figure 5. The absorption spectra for the dye 4 in an unexposed and exposed conditions showed characteristics band at \(\lambda_{\text{max}}\) 680 nm in figure 4. The little changes of an unexposed and exposed absorption peak in both conditions were observed, which indicates marginal fading because of the higher polar structure of dyestuff and less stronger covalent bond with cotton. In order to further elucidate the dye 5 showed the strongest covalent bond with cotton. In order to appropriate moisture management rather than natural sunlight conditions. Cu-complex azo dyes was mostly affected by xenon arc lamp.

**Figure 5. Mechanism of oxidation for different reactive blue dyes by singlet oxygen**

![Figure 5. Mechanism of oxidation for different reactive blue dyes by singlet oxygen](image-url)
interestingly, dye 5 (DFP-VS) showed two characteristic peaks at 550 nm and 620 nm for sunlight and xenon arc lamp exposure accordingly shown in figure 4. The absorbance peak was shifted because of its higher absorption and dyes of solvatochromic effects. The highest range of photofading were observed in xenon arc lamp exposure. It can be explained that, the two fluorine and one chlorine group of pyrimidine ring enhanced the electronic steric congestion. On the other hand, Griffiths and Hawkins (Griffiths et al., 1977) reported that singlet oxygen oxidizes the hydrazone form of azo dyes to break the azo group and formed oxophenyl derivatives. Figure 5 shows the mechanism of dye 5 react with singlet oxygen and formed three fragmented parts. From the figure 4, the order of fading rate was conclude that Anthraquinone > (MCT-VS) bifunctional azo > Copper phthalocyanine > Cu-complex azo dye > (DFP-VS) bifunctional azo dyes.

Conclusions

The photofading effect of blue reactive dyes on cotton fabric under an exposure of sunlight and xenon arc lamp were influenced by the nature of dye structure and the degree of interaction with cotton fiber. Anthraquinone based reactive dyes shows the highest photo stability on sunlight and xenon arc lamp exposure among all the selected blue dyes. In addition, di-fluro pyrimidine vinyl sulphone based azo dyes were shown most sensitivity to exposure of sunlight and xenon arc lamp exposure. The covalent bond improves better photofading effects due to a more efficient transfer of energy from the excited molecules to the fiber, which was confirmed by FT-IR analysis and photo reduction mechanism of dye with cotton fiber. In addition to the formation of photo oxidation of reactive blue dyes approximation was explained with UV-Vis absorption spectroscopy.

Disclosure statement

No potential conflict of interest was reported by the authors.

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