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Research Article

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Photofading mechanisms of azo dye in its azo and hydrazone forms under UV irradiation

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ABSTRACT

The aim of this study is to propose a general understanding of the photodegradation mechanism of azo dyes in both azo and hydrazone forms on the basis of reactive oxygen quenching experiments. Results revealed that singlet oxygen and hydroxyl radicals were only observed during the photochemical reaction of azo dyes in the hydrazone form under UV irradiation rather than dyes in azo form. Hydroxyl radicals were the dominant reactive species involved in the photodegradation of hydrazone dyes. Furthermore, the photodegradation mechanisms for azo dye in its azo and hydrazone forms were proposed respectively.

Keywords: photofading mechanism; azo dye; azo-hydrazone equilibrium; singlet oxygen; hydroxyl radical

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INTRODUCTION

Generally, the complex light-induced fading process of azo dyes corresponds to various factors and their chemical structures always play the most important role [1-4]. Many previous works have been done on the effect of substituents on the light fastness of azo dyes. The fading rates of a series of substituted hydroxyazo dyes were firstly quantitatively studied by Kienle [5] in 1946. They showed that electron withdrawing groups accelerated the fading and electron donating ones retarded it. However, Atherton et al. [6,7] observed a reverse relationship, i.e., electron withdrawing groups retarded fading, in a series of benzene azo-naphthylamine dyes. The apparent contradiction was solved by latter investigations on the study of azo-hydrazone tautomerism of hydroxyazo compounds [8]. It was found that the tautomeric equilibrium of hydroxyazo compounds was primarily affected by the nature (electron withdrawing or donating) of substituents. Subsequently, a correlation was obtained between the fading rates of a series of hydroxyazo dyes on polypropylene and the ratio of hydrazone to azo content [9]. Furthermore, Hempel [10] reported that the fading rate of azo dyes in the azo form was increased by electron donating substituents, while that of hydrazone tautomer was increased by electron acceptors. Due to the difficulties in detecting the ratio of hydrazone to azo content [11], many works were not related to the azo-hydrazone equilibrium in discussing the light fastness of azo dyes.

Recently, numerous works have been done on the physical chemistry and reactive species involved in the dye photodegradation. The oxidation involving singlet oxygen generated by the excited states of azo dyes in hydrazone tautomer was proposed [12]. However, Jansen [13] and Yamaguchi [14] suggested that the role of singlet oxygen in the photodegradation of hydrazone dyes was quite weak. The products of both photochemical oxidation and reduction were detected by Kuramoto [15] in the fading of hydroxyazo dyes in methanol. Okada [16] also indicated that both photochemical oxidation and reduction took participate in the fading of reactive azo dyes, and the photooxidation played the dominant role in the presence of oxygen. In 1994, Imada [17] found that hydrazone dyes tended to photooxidation while azo dyes preferred to photoreduction. However, Hihara [18] observed that azo dyes were more susceptible to singlet oxygen than hydrazone dyes (i.e. azo dyes was easier to photooxidation) using the semiempirical molecular orbital PM5 method. In spite of numerous studies on the photofading of azo dyes, an extremely complex picture emerges and the reactive species involved still remain unclear.

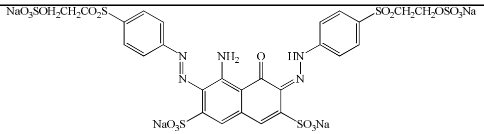
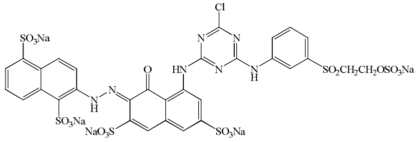
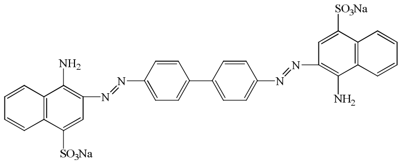
In this present work, we explore the possible photochemical processes, especially reactive oxygen species involved, in the photodegradation of azo dyes in both azo and hydrazone forms using reactive oxygen quenchers. The effects of pH values and different atmospheres on the photofading of hydrazone dyes are also studied in order to fully understand the role of reactive oxygen species.

EXPERIMENTAL SECTION

2.1 Chemicals

Table 1 lists the three dyes used in this study alongside their chemical type. C.I. Reactive Black 5 (RB5) and C.I. Reactive Red 195 (RR195) were provided by Transfar Group Co., Ltd, China and recrystallized from dimethylformamide and diethylether [13]. C.I. Direct Red 28 (DR28) from Sinopharm Chemical Reagent Co., Ltd. was of analytical purity and was used without purification. 1,4-diazabicyclo[2.2.2]octane (DABCO, ≥ 98.0%) was purchased from TCI (Shanghai) Development Co. Ltd. High purity water (resistivity = 18.2 MΩ·cm) made by a Master-S plus UVF ultra pure water system (Hitech Instruments Co., Ltd, China) was used throughout the study.

Table 1 Three dyes used

Code	Name	Structure	Type
RB5	C.I. Reactive Black 5		Hydrazone
RR195	C.I. Reactive Red 195		Hydrazone
DR28	C.I. Direct Red 28		Azo

2.2 Photoreactor and light source

The photodegradation of dye solution was conducted in an XPA photochemical reactor (Nanjing Xujiang Electromechanical Plant, China). An immersed 100 W mercury lamp with a characteristic wavelength of 365 nm and light intensity at quartz cold trap positions of 9.3 mW/cm^2 (measured using a UV-340A digital instrument, Lutron Electronic Enterprise Co., Ltd, Taiwan) was equipped as UV source. The lamp was surrounded by a circulating water jacket (i.e. quartz cold trap). The quartz cold trap was positioned inside a 250 ml cylindrical reaction vessel and coaxial with the photoreactor.

2.3 Experimental procedures

All of the light irradiation experiments were conducted in the photoreactor as described above with a circulation water of 298±2 K. The effects of hydroxyl radical ($OH^{\bullet}$) and singlet oxygen ($^1O_2$) were certified by addition of benzoic acid (10 mM) and DABCO (10 mM), respectively. The pH of each dye solution was adjusted to 6.5 with NaOH/ H_2SO_4 solution.

A 200 mL of 20 mg/L dye solution (pH=6.5) was placed into the reaction vessel, and all photoreactions were carried out in air-saturated conditions. At 30 min intervals, about 5 mL dye solution was collected and the UV-vis absorption ranging from 200 nm to 800 nm was measured using UV-3300 Spectrophotometer (Hitachi, Japan). The decoloration percentage of azo dyes was calculated by the following formula:

$$\text{Decoloration (\%)} = (C_0 - C)/C_0 \times 100\% \qquad (1)$$

where C_0 and C are the initial and residual concentrations of azo dyes, respectively.

RESULTS AND DISCUSSION

3.1 Effect of singlet oxygen scavenger

Since oxidation involving singlet oxygen has been studied in previous papers and displayed contradictory results [12,13], quenching experiments were carried out by addition of DABCO, which is well known as $^1O_2$ quencher [19]. The results illustrated in Fig. 1 indicate that the effect of $^1O_2$ on the photodegradation of azo dye depends on its molecular structure.

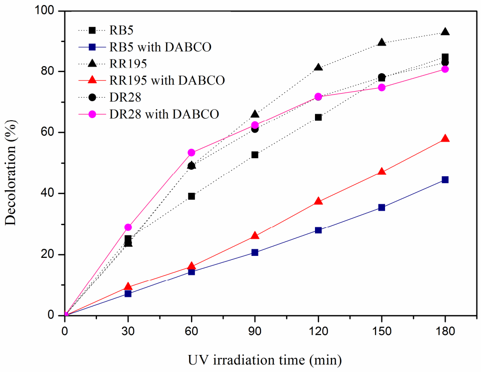


Fig. 1. Effect of DABCO on the decoloration of different azo dyes

It has been proved that both of RB5 and RR195 with a 1-arlazo-2-naphol structure exist in their hydrazone forms in aqueous solution [20]. DR28 is an azo-naphthylamine dye without the azo-hydrazone tautomerism and exists in azo form. The fading rate of DR28 is not slowed down in the addition of DABCO, demonstrating that the $^1O_2$ is lack of importance. On the other hand, marked reductions in the photofading of RB5 and RR195 can be observed respectively after DABCO has been added. Therefore, the $^1O_2$ is only involved in the photofading of hydrazone dyes, that is, the hydrazone form is responsible for the formation of $^1O_2$ rather than the azo one. However, the decoloration of the hydrazone dyes with DABCO is still above 50% after 180 min irradiation, which means that some other reactive species may be involved in the photodegradation mechanism. The formation of $^1O_2$ indicated that the hydrazone dyes have a triplet state with relatively long lifetime. The relatively stable triple-state dye may also abstract a hydrogen atom from water molecular to produce dye radical, which will induce a series of radical reactions.

3.2 Effect of hydroxyl radical scavenger

The above results indicated that $^1O_2$ quencher was unable to completely prevent the decoloration of both azo and hydrazone dyes under UV irradiation. At this moment, a small amount of benzoic acid was added to the solution, and the dye photodecolorations are shown on Fig. 2.

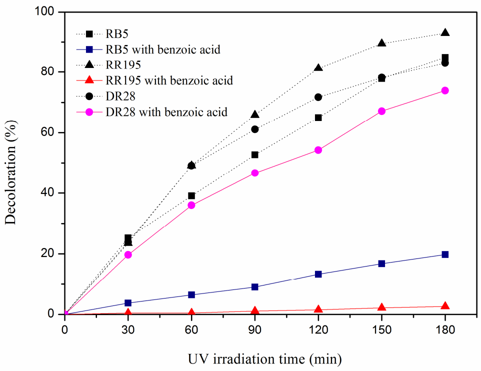


Fig. 2. Effect of benzoic acid on the decoloration of different azo dyes

Benzoic acid is a common quencher used for indirect detection and quantification of $OH^{\bullet}$. The reaction rate of $OH^{\bullet}$ with benzoic acid is reported to be 5.9×10^{12} $M^{-1}s^{-1}$ [21], which is much higher than that between $OH^{\bullet}$ and dye [22]. As shown in Fig. 2, the addition of benzoic acid dramatically inhibits the decoloration of RB5 and RR195, whereas little inhibitory effect of benzoic acid is detected on the fading of DR28. The fact that the decoloration of RB5 and RR195 is roughly linear with time demonstrates that the photofading mechanism does not substantially change with time. Thus, the $OH^{\bullet}$ is the dominant reactive species involved in the photodegradation of hydrazone dyes. Besides, the $OH^{\bullet}$ produced in RB5 solution under light irradiation has been detected using an ESR spectroscopy. However, little reduction in the fading of DR28 with addition of DABCO and benzoic acid are shown in Fig. 1 and Fig. 2, respectively. Consequently the fading of DR28 is not induced by reactive oxygen species and the photoreduction may be the main photobleaching process occurring for DR28. The photoreduction mechanism has been well proposed [23], and we mainly discuss the role of reactive oxygen species in this paper.

3.3 Effect of pH

To further understand the role of reactive oxygen species, the decolorization of RB5 was investigated under pH of 2.0, 3.5, 5.0, 6.5, 8.0, 10.0 and 12.0 respectively. The results are shown in Fig. 3. It can be seen that the photostability of RB5 is the best around neutral pH. At extremely high (≥ 10.0) or low (≤ 3.5) pH, the decoloration rate accelerates much faster.

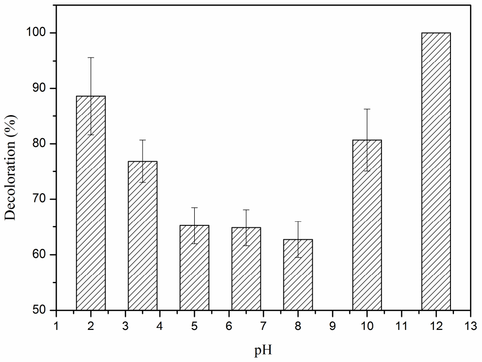


Fig. 3. Decoloration of RB5 with different pHs after 120 min irradiation

In acid condition, it is easier for triple-state RB5 to obtain a hydrogen atom from neighbor molecule to produce RB5 radicals, which may further produce $OH^{\bullet}$ and $^1O_2$. The RB5 radicals also can form hydrazyl intermediates, which causes photoreduction decoloration of RB5. It is considered that both oxidation and reduction may contribute to the decoloration of RB5 at the low pH. Nevertheless, the oxidation by $OH^{\bullet}$ and $^1O_2$ is considered to be the main decoloration pathway, because the hydrzone form of hydroxyazo compounds is more favored in acid condition [8]. The azo form which predominates at higher pH cannot be observed by detecting the maximum absorption wavelength of RB5. Besides, increasing the pH of the dye solution is beneficial to the production of $OH^{\bullet}$. Therefore, the decoloration of RB5 is also increased with increasing the pH in alkaline solution. Interestingly, Okada [24] reached a similar conclusion for the fading of RB5 on the cellulose.

3.4 Effect of atmospheres

Different gases (i.e. oxygen, air and nitrogen) were bubbled into the RB5 dye solutions to research the influence of oxygen on the dye photodecoloration. The results are displayed in Fig. 4. There is no difference between the photofading process of RB5 solution purged with oxygen and that with air. While a reduction can be realized in the photofading of RB5 solution purged with nitrogen. However, the reduction is not as significant as we expected. The effect of oxygen on the photofading of RB5 may be underestimated as dissolved oxygen cannot be removed completely by bubbling nitrogen gas.

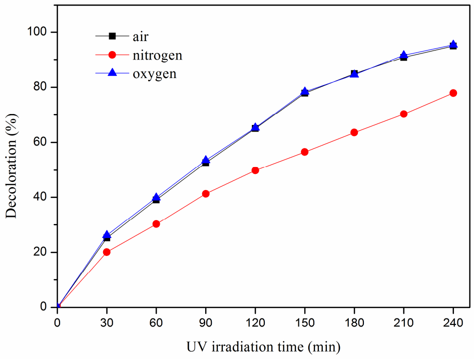
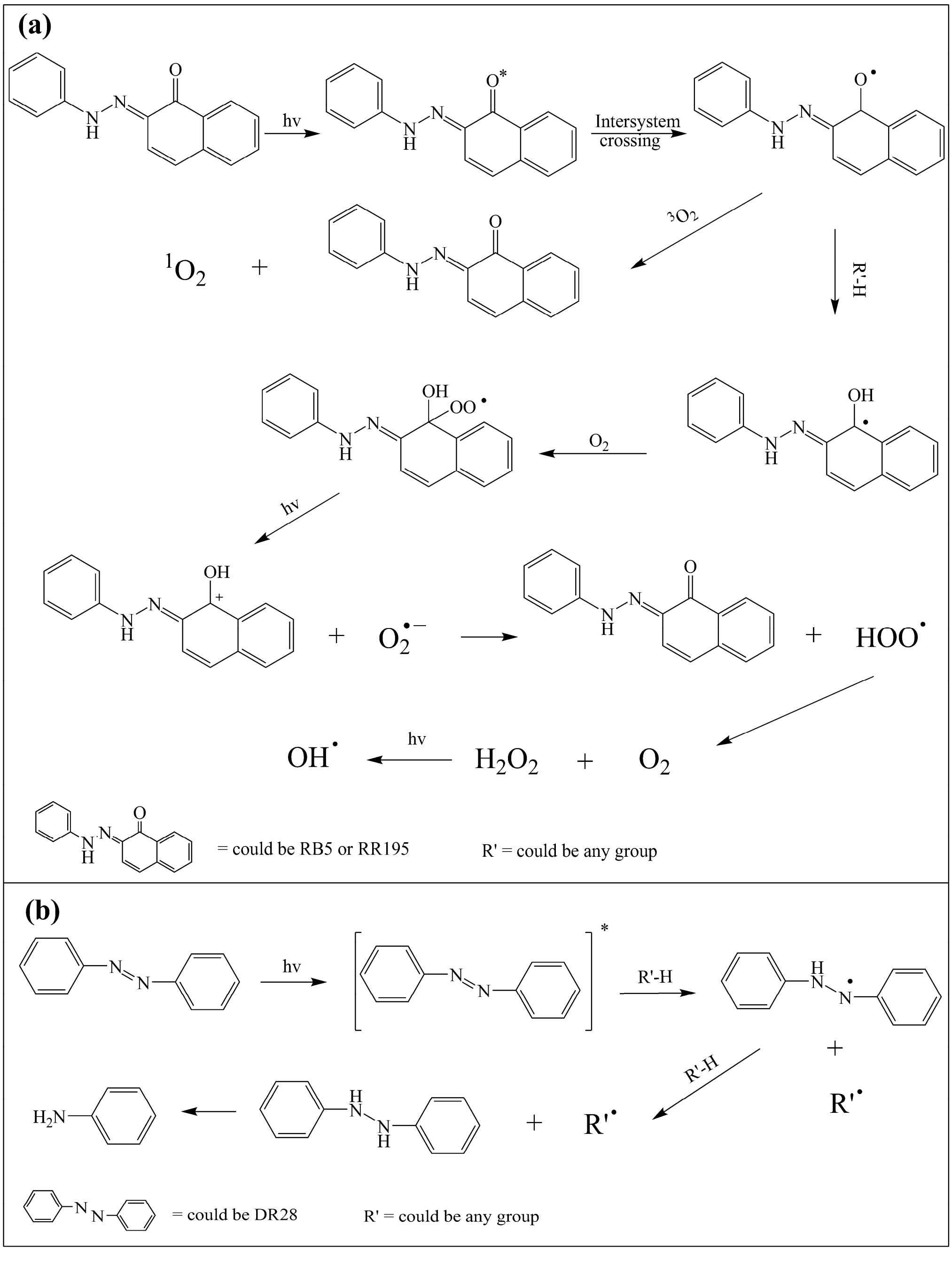


Fig. 4. Decoloration of RB5 solutions purged with different gases

3.5 Proposed mechanisms

According to the above research, several reactive species can be produced when hydrazone dye solution is exposed to UV light. The hydrazone dye has the similar structure feature with phenyl ketone and surprisingly exhibits similar photoinduced activities as anthraquinone compounds [25]. As demonstrated in Scheme 1a, an azo dye in the hydrazone form is excited to singlet state under UV irradiation. In this state, the dye may undergo intersystem crossing to the corresponding triplet state, which is more long-lived. The triple-state dye can collide with triple-state oxygen to produce $^1O_2$. It is also very easy for triple-state dye to abstract a hydrogen atom from the R'H of neighboring molecules (e.g. solvent and polymer substrate) to produce dye radical, which can further react with oxygen (O_2) to form superoxide radical ($O_2^{\bullet -}$) and an intermediate cationic structure under light irradiation. The $O_2^{\bullet -}$ can react with this dye intermediate to form peroxide radical ($HO_2^{\bullet}$). Two peroxide radicals combine together to generate H_2O_2, which can produce $OH^{\bullet}$ under UV-light irradiation. All the reactive oxygen species are able to initiate degradation of azo dye. As the previous discussion, the $OH^{\bullet}$ plays the dominant role in the fading of hydrazone dyes.



Scheme 1. Proposed photochemical reaction mechanisms: (a) for hydrazone dyes; (b) for azo dyes

As reported by van Beek et al [23], an azo dye in the azo form may undergo direct photoreduction under UV irradiation. As shown in Scheme 1b, hydrazyl radical is formed when one electron is added to the triple-state dye accompanied by the simultaneous uptake of a proton from neighboring molecule. The hydrazyl radical is thermally unstable and can further absorb hydrogen to generate hydrazo compounds. The hydrazo compounds are apt to decompose with formation of aromatic amines.

CONCLUSION

In this study, the reactive oxygen species that involved in the azo dye photodegradation were demonstrated. For the hydrazone dyes used here, hydroxyl radical was the most important contributor to the photodegradation, compared with other reactive oxygen species. For the azo dyes in the azo forms, the addition of reactive oxygen quenchers, such as DABCO and benzoic acid, showed no influence in their photodegradation, which meant that reactive oxygen species cannot be involved in their photodegradation processes. Moreover, the decoloration rate of hydrazone dye was dependent on pH value as well as oxygen. The dye photodecoloration rate had a tendency to increase in both extreme pHs. The effect of different atmospheres confirmed the contributions of oxygen in the dye photodegradation.

Acknowledgements

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