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Photocatalytic decoloration of water-soluble azo dyes by reduction based on bisulfite-mediated borohydride

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Abstract

Investigation of the photocatalytic decoloration of nine water-soluble anionic azo dyes widely used for the coloration of textiles was conducted in a photoreactor by a selected reduction based on bisulfite-mediated borohydride. The influence of the irradiation power on their decoloration was discussed in this work. The decoloration processes of two typical azo dyes, Reactive Red MS and C.I. Direct Blue 15 were examined with UV–vis measurement and their decoloration kinetics was also investigated. Moreover, identification of benzidine compounds released from the photoreduction of four direct dyestuffs was undertaken. The results indicated that the reduction of the dyes was significantly enhanced under the increasing irradiation. It was found that the overall degradation followed pseudo-first-order kinetics and two distinct stages were observed in the decoloration processes of Reactive Red MS and C.I. Direct Blue 15. The decay rates at first stage were slightly changed, but the decay rates at second stage were significantly affected by the light intensity. In addition, UV–vis spectra showed that the azo linkages in molecule structure of the dyes were destroyed during the decoloration. Finally, dimethoxyl benzidine or benzidine produced from the photoreduction of four direct dyes was identified as the decoloration products through a rapid spectrophotometric method.

Keywords: Azo dye; Reduction; Irradiation; Bisulfite; Borohydride

1. Introduction

Textile dyeing is a significant consumer of water and producer of contaminated aqueous waste streams. About a half of global production of synthetic textile dyes are classified into azo compounds and over 15% of the textile dyes are lost in wastewater stream during dyeing operation in general. Tighter restrictions on wastewater discharges are forcing textile processors to reuse process water. Azo dyes representing a class of organic pollutants whose associated color in wastewater is quite noticeable to the public, and some azo dyes are proven to be potentially carcinogenic and/or teratogenic on public health [1,2]. Water-soluble azo dyes are generally considered as the most difficult to remove or degrade from the dyeing effluent, due to their high stability and composition ratio of aromatic rings present in their molecule structure. These azo dyes are known to be largely non-biodegradable in aerobic conditions and photochemically active [3], therefore, there have been various approaches to destruct them efficiently in aqueous or dispersion system using ultraviolet light and solar light. Of these technologies, photocatalytic oxidation based on ferric ion or TiO_2 of the dyes has been a major technology in several decade years.

Apart from the photooxidation, the photoreduction of azo dyes is also recognized as an important decolorizing or fading pathway in recent years [4]. Azo dyes can be reduced chemically by dithionite [5]. The mechanism of decolorization of azo dyes based on the extracellular chemical reduction with sulfide was postulated for sulfate reducing environments [6]. In addition, many dyes are noted for their ease of photodecoloration in the absence of oxygen when a suitable electron donor or hydrogen source is present. Chu and Tsui reported that the degradation of hydrophobic and hydrophilic organic dyes has been shown to be effective in aqueous acetone solution under the exposure to UV light. Moreover, they recently investigated the modeling of photodecoloration of a non-biodegradable azo dye, Reactive Red 2, in a cocktail mixture of acetone and triethylamine solution [3]. It was

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found that the cocktail photolysis system was capable of completely decolorizing the azo dye in a very short treating time and the overall dye degradation followed pseudo-first-order decay kinetic.

Borohydride/bisulfite redox couple as a powerful reductant was found to cleave dye azo bonds Reifile and Freeman describes this process as follows [7].

$$BH_4^- + 8HSO_3^- + H^+ \xrightarrow{pH\ 5-8} 4S_2O_4{}^{2-} + B(OH)_3 + 5H_2O \quad (1)$$

$$S_2O_4{}^{2-} \rightarrow 2SO_2{}^{\bullet -} \quad (2)$$

$$BH_4{}^- + 2R_1R_2ArN = NArR_3R_4 + 3\,H_2O \xrightarrow{HSO_3{}^-} B(OH)_3 + 2R_1R_2NH_2 + 2R_3R_4NH_2 \quad (3)$$

$$R_1R_2ArN = NArR_3R_4 + 4\,SO_2{}^{\bullet -} + 4H_2O \xrightarrow{H^+} 4HSO_3{}^- + R_1R_2NH_2 + R_3R_4NH_2 \quad (4)$$

Moreover, Laszlo reported that some aromatic amines from two monoazo dyes, Orange II and Remazol Red F3B treated with the borohydride/bisulfite redox couple by using UV/Vis and HPLC/MS methods [8]. And the use of bisulfite-mediated borohydride reduction for the decoloration of dyeing effluent containing azo dyes has some commercial success and it is more efficient when treating small volumes of concentrated dyeing effluent. Another advantage of this technology is that borohydride/bisulfite redox couple may decolorize the azo dyes much more quickly than some oxidants based on ferric ion or TiO_2 at the similar condition, especially under no irradiation. However, there has been rare information about the photocatalytic decoloration of water-soluble azo dyes based on this reduction, especially in the effect of irradiation intensity on decoloration of the azo dyes in aqueous solution and their reaction kinetics.

In this work, nine water-soluble azo dyes, especially, Reactive Red MS and C.I. Direct Blue 15 were used to investigate the effect of irradiation intensity on decoloration of the dyes in water by a selected photoreduction based on the borohydride and bisulfite redox couple. And then the photocatalic decoloration processes of the dyes were examined by UV–vis analysis. In addition, the reaction products from the photoreduction of four direct dyes containing benzidine compounds were determined by a simple colormetric method.

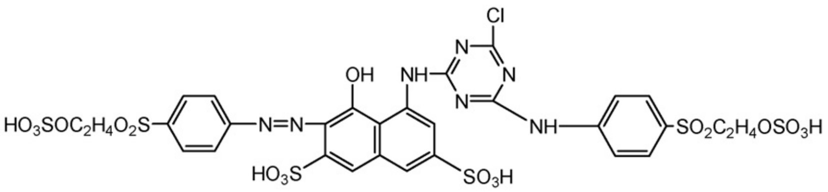
2. Experimental

2.1. Reagents and chemicals

Nine water-soluble anionic azo dyes including Reactive Red MS, C.I. Reactive Red 2, C.I. Acid Black 1, C.I. Acid Orange 156, C.I. C.I. Direct Blue 15, Direct Red 13, C.I. Direct Red 28, C.I. Direct Green 1 and C.I. Direct Brown 1 were commercially available. All dyes used were purified by precipitation from aqueous solution with sodium chloride; desalination using distilled water and finally re-precipitation by addition of alcohol in this experiment. ColorClear^{TM} Solution System (Rohm and Haas China, Inc.) was used as borohydride/bisulfite redox couple, which was a patented, two-component reducing system [9]. A component was a stable aqueous sulution consisted of 12% borohydride and 40% sodium hydroxide and served as inducer. The other was called catalyst containing the aqueous solution of 5% bisulfite. Double distilled and deionized water was used throughout the study. The chemical structure of two typical dyes, Reactive Red MS and C.I. Direct Blue 15 were shown in Fig. 1.

2.2. Photoreactor and light source

The photoreaction system was specially designed in this experiment and consists mainly of chamber, lamps, electromagnetic valve, relay, and water bath. A 400 W high-pressure mercury lamp (Osram Foshan Illuminance Company, China) and a 125 W UV 365 nm lamp obtained from Shanghai Philips-Yaming Company (Shanghai, China) were used for photoreaction. The chamber was made of polished aluminum because it is highly reflective in the UV and visible light range. Ten open Pyrex vessels of 150 ml capacity were used as reaction receivers in water bath. An electromagnetic valve was operated by relay and used to control temperature in water bath. Light intensity inside photoreaction system was adjusted by variation of lamps and measured using FZ-A radiometer that responds to light of 400–1000 nm, UV-A radiometer responding to the



C.I. Direct Blue 15

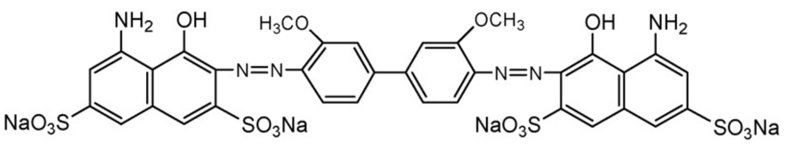


Fig. 1. Chemical structure of two azo dyes.

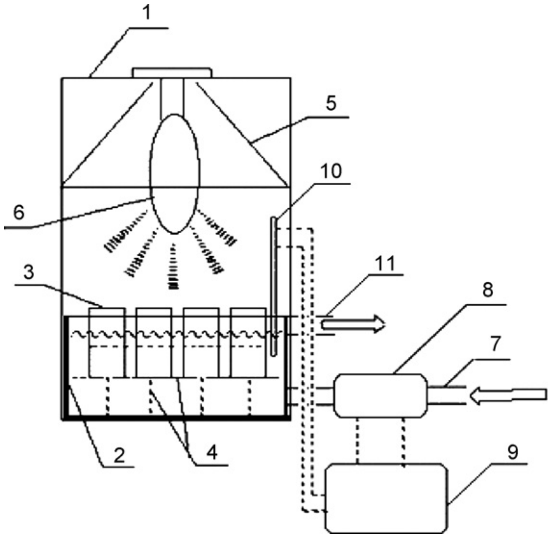


Fig. 2. The schematic diagram of photoreactoion system. (1) Chamber, (2) water bath, (3) glass vessel, (4) support, (5) lamp-chimney, (6) mercury lamp, (7) water in, (8) electromagnetic valve, (9) relay, (10) thermometer and (11) water out.

UV-A region (BNU Light and Electronic Instrumental Factory, China), respectively. The schematic diagram of photoreaction system was presented in Fig. 2.

2.3. Decoloration procedure

One millilitre of inducer was mixed with 100 ml of catalyst solution to establish reduction agent for decoloration of the dyes in water prior to experiment. Stock dye solutions were prepared by dissolving 5.0 g of the dye in 1 l of boiling deionized water. Test solutions were made by diluting the stocks to typical solution of dye concentration (50 mg l^{-1}) and followed by the addition of reduction agent at pH 6.5 ± 0.1. 100 ml of test solutions were then placed into reaction vessels and exposed to irradiation of lamps in photoreaction system. At different time intervals, 1–2 ml of the sample was withdrawn and diluted suitably, and whose absorbance was measured at the λ_{max} of the dye solutions, respectively. Dye concentration was determined and UV–vis spectrum from 190 to 800 nm was recorded with a UV-2401 spectrophotometer (Shimadzu Company, Japan). The pH of the solution was measured by using DHS-25C digital pH meter (Shanghai Jingmi Instrumental Company, China). The temperature in reaction vessel was kept at 25 ± 1 °C. The decoloration percentage of the dyes was expressed as:

$$\text{Decoloration}\ (\%) = \frac{Co - C}{Co} \times 100\%$$

Where C_o is the initial concentration of the dye (mg l^{-1}) and C is the residual concentration of the dye (mg l^{-1}).

2.4. Identification of benzidine compounds [10,11]

One millilitre of reduction agent were added into 100 ml of 50 mg l^{-1} dye solutions in reaction vessels and exposed to the irradiation in photoreaction system at 25 ± 1 °C and pH 6.5 ± 0.1, respectively for the photocatalytic decoloration. After complete decoloration, it was mixed with 1 ml chloramines T and 0.5 ml dilute hydrochloric acid solution to yield a light yellow reaction products by magnetic stirring, then which was extracted by addition of 3 ml chloroform for the determination, and UV–vis spectrum from 200 to 600 nm was recorded with a UV-2401 spectrophotometer.

3. Results and discussion

3.1. Light intensity

The irradiation in a photodecoloration process is a significant factor in increasing the decay rate of the azo dyes. Tests were performed in dye solutions induced by different irradiation levels, as shown in Figs. 3 and 4, a corresponding control dye solution with low irradiation (A) inside room was also examined at the same conditions.

It was observed from the Figs. 3(a) and 4(a) that the decay ratio of the dyes gradually declined with increasing exposure time and decay lines varied with light intensity. Moreover, decay ratio of the dyes in case of strong irradiation were much lower that in the control experiment and decreased with increasing irradiation at the same exposure time. This indicated that the reducing decoloration of two azo dyes was induced by irradiation, and remarkably improved by the increasing

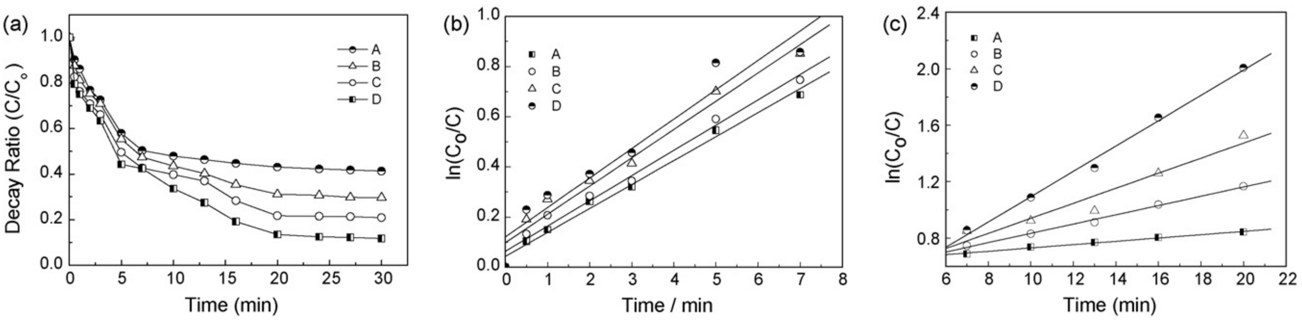


Fig. 3. The photodecoloration of 50 mg l^{-1} Reactive Red MS under different irradiation levels. (a) Decay lines, (b) the first stage and (c) the second stage. Irradiation A, 365 nm: 2.80×10^{-3} mW/cm^2, 400–1000 nm: 0.185 mW/cm^2; Irradiation B, 365 nm: 0.702 mW/cm^2, 400–1000 nm: 2.81 mW/cm^2; Irradiation C, 365 nm: 0.930 mW/cm^2, 400–1000 nm: 10.1 mW/cm^2; Irradiation D, 365 nm: 1.64 mW/cm^2, 400–1000 nm: 13.1 mW/cm^2. Reactive Red MS, 50 mg l^{-1}, reduction agent, 3.0 mg l^{-1}.

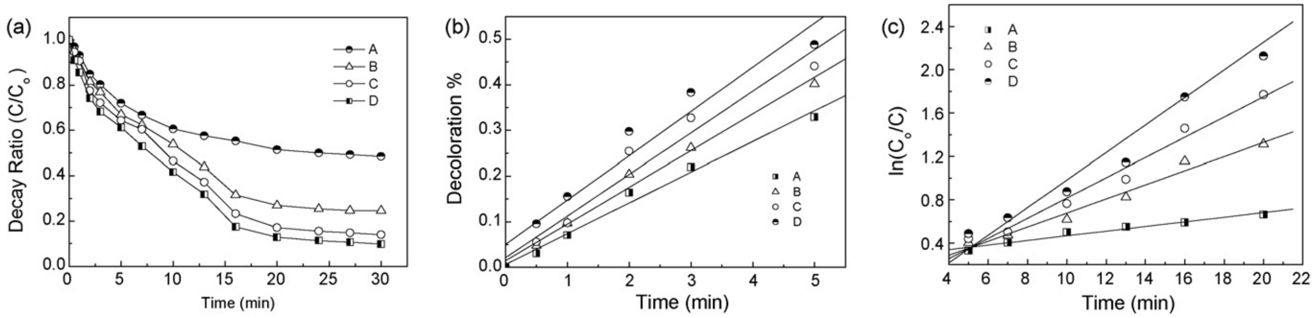


Fig. 4. The photodecoloration of 50 mg l^{-1} Direct Blue 15 under different irradiation levels. (a) Decay lines, (b) the first stage and (c) the second stage. Irradiation A, 365 nm: 2.80×10^{-3} mW/cm^2, 400–1000 nm: 0.185 mW/cm^2; Irradiation B, 365 nm: 0.702 mW/cm^2, 400–1000 nm: 2.81 mW/cm^2; Irradiation C, 365 nm: 0.930 mW/cm^2, 400–1000 nm: 10.1 mW/cm^2; Irradiation D, 365 nm: 1.64 mW/cm^2, 400–1000 nm: 13.1 mW/cm^2. C.I. Direct Blue 15, 50 mg l^{-1}, reduction agent, 3.0 mg l^{-1}.

irradiation in a photoreactor. In addition, the overall photodecay kinetic of the dyes were close to the pseudo-first-order reaction, as shown in Figs. 3(b and c) and 4(b and c). It was noted that the decoloration curves of photocatalysis system could be clearly divided into two distinct stages during reaction time. This is similar to the results obtained from previous study [3]. The first stage was a rapid photochemical reaction, but in which decay rates of dyes were hardly improved by the increasing intensity of illumination; on the other hand, the second stage was a relatively slow decoloration procedure, in which the increasing illumination resulted in the acceleration of dyes photodegradation rates, and the decoloration rate constants at the two stage for the dyes were calculated and summarized in Table 1.

It was found from Table 1 that the decoloration rate constants of the dyes at the first stage under different irradiations showed a slight improvement, suggesting that decoloration rates were less dependent upon the irradiation power. On the contrary, decoloration rate constants at second stage were dramatically enhanced when irradiation values were increased, particularly, of C.I. Direct Blue 15, implying that high irradiation can promote the photoreduction of the azo dyes in aqueous solution. This is because the photoreduction rates of organic dyes were further improved in the presence of amine as a hydrogen source during photolysis [3]. In general, it is the fact that aromatic amines can be generated by cleavage of azo dyes in the reduction process [12,13]. Therefore, it is believed that the aromatic amines generated from the decoloration of dyes with the mixture of borohydride and bisulfite may promote their decoloration in water by the introduction of hydrogen source. And there were a little aromatic amine generated at the first stage, and which just exhibited a slight influence on the decoloration of dyes in the aqueous solution under the irradiation. The prolong of reaction time got rise to more aromatic amine generated, which was able to improve the reduction of the dyes as a hydrogen source and high decoloration rate constants at second stage were obtained under the increasing irradiation. In addition, Table 1 also showed that k_2, the decoloration rate constants at second stage of C.I. Direct Blue 15 was more significantly increased with irradiation becoming enhanced, and higher than that of Reactive Red MS under the same conditions. This is attributed to more aromatic amines produced in decoloration of C.I. Direct Blue 15 containing two azo groups (–N=N–). Another possible explanation was that the irradiation facilitated the breaking dye aggregation units in water and which caused the easy releasing of dye molecules from aggregation units. Generally, the dissolving situation of dyes in water depends mainly upon their aggregation and ionization. Aggregation and ionization equilibrium of dye molecules in water are described as Fig. 5.

It was found that the aggregation equilibrium of dye molecules in water is affected particularly by concentration of dyes and inorganic salts [14,15]. On the other hand, aggregation of the dyes in water is more dependent on their molecule structure, especially, the dyes bearing large hydrophobic content such as direct dyes, owing to easy and unstable combination among dye molecules. Consequently it is possible that UV and visible irradiation power also changed this aggregation equilibrium and reduced the formation of dye aggregation units due to their weak stability in aqueous solution. The decoloration values of nine soluble azo dyes at different irradiation levels were listed in Table 2.

The data in Table 2 demonstrates that the decoloration values of nine azo dyes were increased with the enhanced irradiation level, particular in the dyes with more azo groups and high

Table 1
The decoloration rate constants at the two stages for Reactive Red MS and Direct Blue 15

Reactive Red MS					C.I. Direct Blue 15				
Irradiation	The first stage		The second stage		Irradiation	The first stage		The second stage	
Level	k_1 (min$^{-1)}$	R	k_2 (min$^{-1)}$	R	Level	k_1 (min$^{-1)}$	R	k_2 (min$^{-1)}$	R
A	0.0955	0.9941	0.0118	0.9943	A	0.0673	0.9937	0.0214	0.9809
B	0.101	0.9901	0.0329	0.9969	B	0.0804	0.9939	0.0650	0.9880
C	0.113	0.9822	0.0533	0.9682	C	0.0911	0.9804	0.0934	0.9891
D	0.117	0.9662	0.0897	0.9962	D	0.0969	0.9721	0.127	0.9809

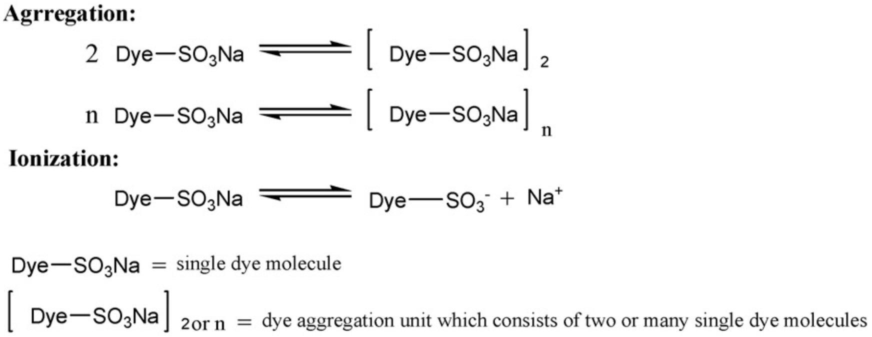


Fig. 5. Schematic model of aggregation and ionization equilibrium of dye molecules in water.

Table 2
Effect of irradiation on the decoloration of nine soluble azo dyes

Dyes	Number of –N=N–	MW/S	Concentration of reduction agent (mg l^{-1})	Decoloration %	
				Irradiation A[a]	Irradiation C[b]
Reactive Red MS	1	251	3.0	56.9	78.3
C.I. Reactive Red 2	1	308	2.0	65.7	77.9
C.I. Acid Black 1	1	308	1.5	77.8	94.5
C.I. Acid Orange 156	2	462	3.0	71.7	99.5
C.I. Direct Blue 15	2	248	6.0	48.5	96.2
C.I. Direct Red 13	2	323	5.0	45.6	73.2
C.I. Direct Red 28	2	390	3.0	43.0	51.6
C.I. Direct Green 1	3	390	7.0	30.2	44.3
C.I. Direct Brown 1	3	681	7.0	43.5	74.8

MW/S, molecule weight/number of sulphonate groups.

[a] Irradiation A, 365 nm: 2.80×10^{-3} mW/cm^2, 400–1000 nm: 0.185 mW/cm^2.

[b] Irradiation C, 365 nm: 0.930 mW/cm^2, 400–1000 nm: 10.1 mW/cm^2.

MW/S values, such as C.I. Direct Red 13 and C.I. Direct Brown 1. This is mainly associated with the aggregation of the dyes, which may form the aggregation units in water more easily than other dyes.

3.2. UV–vis spectrum

The obvious changes of photocatalytic decoloration and degradation of Reactive Red MS and C.I. Direct Blue 15 at the different light intensities in photoreactor using UV–vis absorbance spectra were shown in Figs. 6 and 7, respectively.

In general, the absorbance at 400–800 nm corresponds to the $n \rightarrow \pi^*$ transition of the azo and hydrazone form, which is due to the color of azo dyes and it is used to monitor the decoloration. The absorbance at 200–400 nm was attributed to the $n \rightarrow \pi^*$ transition of benzene and naphthalene ring, represents the aromatic content of azo dyes and its decrement is due to the degradation of aromatic part of the dye [16,17]. Figs. 6 and 7 showed that the both absorbance (peak *b*) at 200–400 nm and absorbance (peak *a*) at 400–800 nm of the dyes decrease gradually with prolonging exposure time due to increasing decoloration and degradation of the dyes in water. Moreover, higher light intensity led to significant decline in

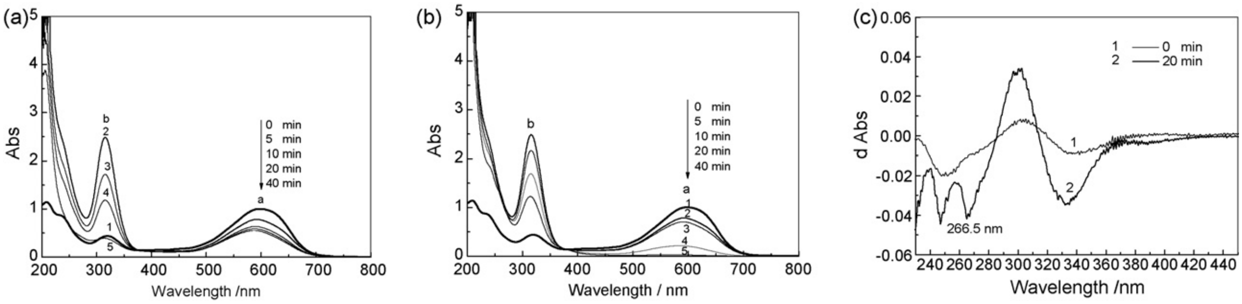


Fig. 6. Changes in UV–vis spectra of C.I. Direct Blue 15 under different irradiation. (a) 365 nm: 0.702 mW/cm^2, 400–1000 nm: 2.81 mW/cm^2; (b) 365 nm: 1.64mW/cm^2, 400–1000 nm: 13.1 mW/cm^2; (c) 365 nm: 1.64 mW/cm^2, 400–1000 nm: 13.1 mW/cm^2. C.I. Direct Blue 15, 50 mg l^{-1}, reduction agent, 3.0 mg l^{-1}

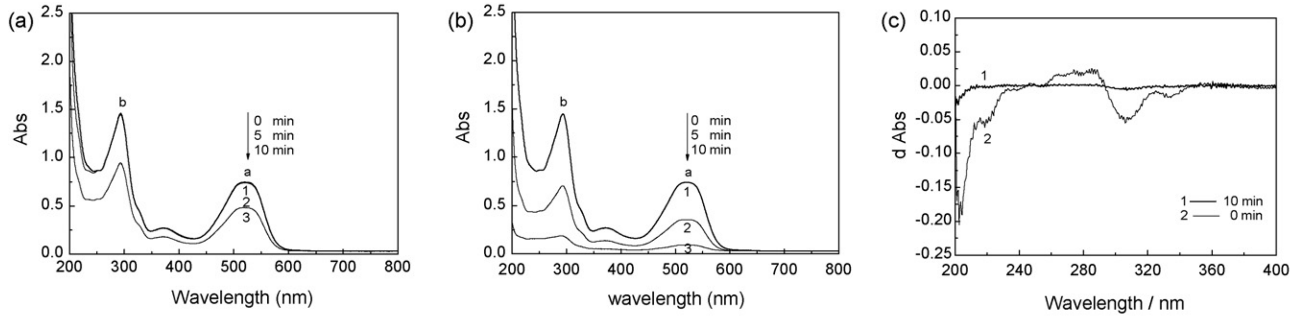


Fig. 7. Changes in UV–vis spectra of Reactive Red MS under different irradiation. (a) 365 nm: 2.80×10^{-3} mW/cm^2, 400–1000 nm: 0.185 mW/cm^2; (b) 365 nm: 1.42 mW/cm^2, 400–1000 nm: 14.6 mW/cm^2; (c) 365 nm: 1.42 mW/cm^2, 400–1000 nm: 14.6 mW/cm^2. Reactive Red MS, 50 mg l^{-1}, reduction agent, 3.0 mg l^{-1}

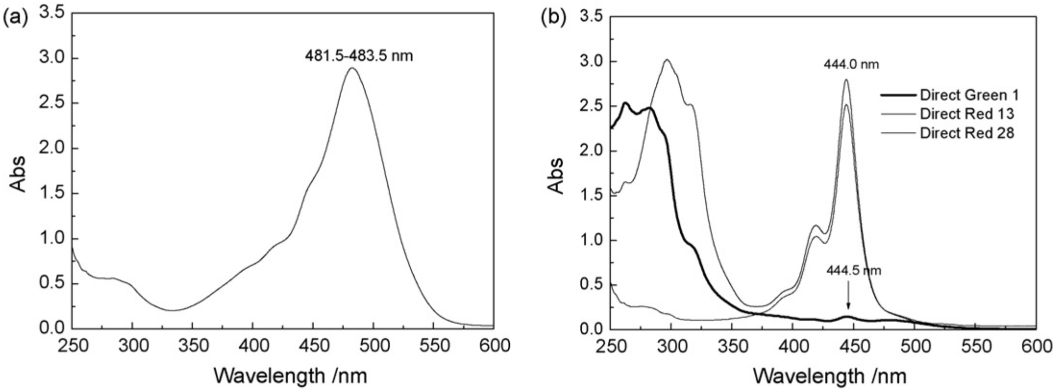


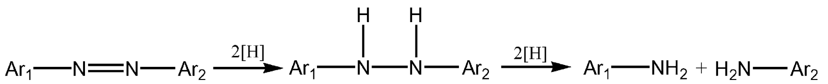
Fig. 8. UV–vis spectra for the reaction products oxidized with chloramines T. (a) C.I. Direct Blue 15 and (b) Other direct dyes.

both peaks, especially, peak *a* in spectra of the dyes at the same conditions, which illustrated that the cleavage of azo units (–N=N–) occurred and it was possible that the aromatic content of azo dyes was partially destroyed. It should be noted that a strong peak appeared at 266.5 nm after decoloration reaction was carried out for 20 min in derivative spectrum of C.I. Direct Blue 15 presented in Fig. 6(c), suggesting that a new substance, perhaps hydrided azo dye (Ar_1–NH–NH–Ar_2) may be produced from the partial reduction [18]. Reductive cleavage of the dye chromophore is performed by the photodegradation of dye molecules. The cleavage often takes place on the azo linkage (–N=N–) of the aromatic azo compound, because these p-bond electrons are comparatively more diffusive than the other parts within the molecule [3]. In this research, the chromophore of C.I. Direct Blue 15 was reduced and converted to its corresponding amines involving the hydrogen atom abstraction from the hydrogen source. Also, the reduction of aromatic azo dye is a four-electrons transferring process as eq. (5), and hydrided azo dye was formed as an intermediate during the reaction process.

3.3. Identification of benzidine compounds

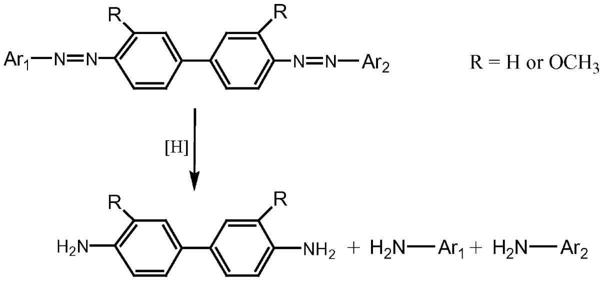
In order to examine benzidine compounds produced by the decoloration of the dyes, four direct dyes based on benzidine compounds including C.I. Direct Blue 15, C.I. Direct Green 1, C.I. Direct Red 13 and C.I. Direct Red 28 were firstly decolorized using the reduction agent mentioned above in a photoreactor, and then the reaction products were determined by the oxidation with chloramines T in the presence of diluted hydrochloric acid, results of which were given in Fig. 8.

It was observed clearly from Fig. 8(a and b) that there were three strong absorption peaks at about 482 nm for C.I. Direct Blue 15 and 444 nm for C.I. Direct Red 13 and C.I. Direct Red 28, respectively. A relatively weak absorbance at 444.5 nm was found in the UV–vis spectrum of C.I. Direct Green 1. Previous studies [10] have reported that these absorption peaks at about 482 and 444 nm in general are attributed to dimethoxyl benzidine and benzidine, respectively in this method. This indicates that four direct dyes could be reduced by borohydride/bisulfite redox couple and released dimethoxyl benzidine or



$$\mathrm{Ar_1{-}N{=}N{-}Ar_2} \xrightarrow{2[H]} \mathrm{Ar_1{-}\overset{H}{N}{-}\overset{H}{N}{-}Ar_2} \xrightarrow{2[H]} \mathrm{Ar_1{-}NH_2 + H_2N{-}Ar_2} \tag{5}$$

benzidine during their decoloration. In addition, Direct Green 1 was reduced with difficulty at the same conditions and led to a relatively weak absorbance at 444.5 nm in the UV–vis spectrum because there are three azo groups in its molecule structure. Therefore, it is believed that the photocatalytic reduction of C.I. Direct Blue 15 resulted in the formation of dimethoxyl benzidine, while other three direct dyes reacted with reduction agent were able to generate benzidines as the reaction products. As a result, their decoloration can be expressed using a general eq. (6).



(6)

4. Conclusions

The reduction of the water-soluble azo dyes with the mixture of borohydride and bisulfite in a photoreactor was remarkably enhanced under the irradiation. The decoloration values of nine azo dyes in water were significantly improved with the increasing irradiation levels. The photoreduction kinetics of the dyes were divided into two stages and described by using pseudo-first-order reaction model, respectively. Moreover, strong irradiation resulted in the high decoloration rate constants at the second stage. UV–vis spectra indicated that the irradiation was able to promote the cleavage of azo linkage and cause partial damage of aromatic rings in the dye molecules. Finally, dimethoxyl benzidine or benzidine generated from the photoreduction of four direct dyes based on benzidine compounds were identified as a reaction products.

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