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Solar degradation of two azo dyes by photocatalysis using Fe(III)-oxalate complexes/H_2O_2 under different weather conditions

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Abstract

C. I. Acid Black 234 and C. I. Mordant Black 9 were decomposed in water using ferrioxlate and H_2O_2 during sunny or cloudy days, respectively. Some effecting factors such as Fe(III) ion, oxalate ion, H_2O_2 and solar irradiation intensity were investigated. The decomposition of the two dyes was evaluated with respect to decoloration percentage or reaction rate constant. Also, their degradation and mineralization under different solar irradiation were examined by UV–vis spectrum and TOC measurements. The results indicate that the effects of concentration of Fe(III), oxalate and H_2O_2 on dye decomposition are dependent significantly upon solar illumination. Increasing irradiation intensity caused the proportional enhancements in decoloration rate constant. We also found it more difficult to decompose C. I. Acid Black 234 under two weather conditions, comparing with C. I. Mordant Black 9. In addition, the degradation and mineralization of the two dyes was reduced by low irradiation.

Keywords: Azo dye; Decomposition; Fe(III)-oxalate complexes; Solar irradiation

1. Introduction

Azo dyes are an abundant class of purely synthetic organic compounds, which are characterized by the presence of one or more azo bonds. Generally, over 15% of the textile dyes are lost in wastewater stream during their synthesis and dyeing processes and often cause environmental problems [1]. In recent years, azo dye pollution of the water environment in China has been of increasing concern with the rapid development of rural printing, dyeing and synthetic dye industries of the country. These azo dyes are known to be largely non-biodegradable in aerobic conditions and strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [2]. For the treatment of these dyes, the adsorption on activated carbon and coagulation by a chemical agent are ineffective since these methods merely transfer dyes from water to solid, hence, further treatment is necessary for the ultimate solution [3]. The solar driven photo-Fenton process based on Fe(III)-oxalate complexes as an important advanced oxidation processes (AOP) technology has been attracting growing interest for the degradation of hazardous and non-biodegradable organic compounds such as dyes commonly found in industrial effluents. Such processes are based on the light-enhanced generation of the highly reactive hydroxyl radicals, which oxidize the organic matter in solution and convert it completely into water, carbon dioxide, and inorganic compounds [4]. In the past years, Fe(III)-oxalate complexes were used as a kind of catalysts or promoters in the photodegradation of textile dyes in water [5,6] and are expected to play an important role in degradation and mineralization of textile dyes in days to come.

Reports in the literature revealed that there are a few studies on the decoloration and degradation of textile dyes by using AOPs under visible light or solar irradiation. Wu et al. examined the photodegradation of malachite green MG under

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visible light irradiation and obtained the evidence for enhancement of hydroxyl radical generation by visible light irradiation [7]. Xie and coworkers found that visible irradiation not only enhances apparently the generation of hydroxyl radicals but also accelerates effectively the degradation of the dyes [8]. Park and Choi reported that the photodegradation of Acid Orange 7 was successfully achieved in the presence of Fe(III) ions only under visible light [1]. Neamtu et al. evaluated the degradation of the two reactive dyes by photo-Fenton and Fenton-like oxidations and proposed that effective system conditions were H_2O_2-to-iron molar ratio of 20:1 and UV or solar irradiation [9]. On the other hand, TiO_2 was used as photocatalysts for the solar photodegradation of the dyes such as acid dyes [10,11] and reactive dyes [12].

It is summarized that most of the researchers have focused their studies on the degradation of these simple azo dyes containing no more than two azo linkages by the photo-Fenton or UV/TiO_2 processes. However, a very limited amount of information is available on the decomposition of the azo dyes bearing more than two azo linkages, especially by using Fe(III)-oxalate complexes/H_2O_2 under sunlight irradiation. In this work, a triazo dye containing three azo linkages, C. I. Acid Black 234 was selected and decomposed in water in the presence of Fe(III)-oxalate complexes and H_2O_2 during sunny and cloudy days. For comparison, a monoazo dye, C. I. Mordant Black 9 was used and also decomposed at the similar conditions. Moreover, the degradation of these dyes under different solar irradiations was examined and compared through UV–vis spectrum and TOC measurements.

2. Experimental

2.1. Reagents and chemicals

The azo dyes used in this study were C. I. Acid Black 234 (CAS:157577-99-6) and C. I. Mordant Black 9 (CAS:2052-25-7). They were the original dye samples provided by Tianjin Sanhuan Chemical Company, China and used in this study without future purification. Analytical grade ferric sulfate and oxalic acid were the sources of Fe(III) ions and oxalate, respectively. Hydrogen peroxide (30% w/w) was of analytic grade. These chemicals were obtained from Tianjin Chemical Reagent Company (Tianjin, China). Double distilled and deionized water was used throughout the study. The chemical structures of the two azo dyes are shown in Fig. 1.

2.2. Photoreaction procedure

Solar light experiments were conducted using the reaction vessels held in a rack at a 30° angle from the horizontal on the top of Material Chemical Engineering Building at the campus of Tianjin Polytechnic University (Hedong District, Tianjin, about 20 m above sea level, 39.31″N, 117.98″E). With this rack, the reaction vessels could be put in and removed from sunlight within 10 s. The ambient temperature was 20–30 °C. The sunlight intensity was recorded using FZ-A radiometer and UV-A radiometer (BNU Light and Electronic Instrumental Factory, China), respectively.

Stock dye solutions were prepared by dissolving 5.0 g of each dye in 1000 mL of boiling deionized water. Test solutions were made by diluting the stock to typical effluent dye concentration of 50 mg $L^{-1}$and followed by addition of ferric sulfate, oxalic acid and H_2O_2. NaOH (0.1 M) and HNO_3 (0.1 M) solutions were used to adjust pH at 3.5 ± 0.1. Test solutions (100 mL) were then placed into reaction vessels and exposed to solar irradiation. At different time intervals, 1–2 mL of the sample was withdrawn and diluted suitably, and the absorbance of which was measured at the λ_{max} of the dye solutions, respectively. Concentration of the dye was determined and UV–vis spectrum from 190 nm 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 decoloration percentage of the dye was expressed as follows:

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

where C_0 is the initial concentration of the dye (mg L^{-1}) and C is the residual concentration of the dye at the reaction time of

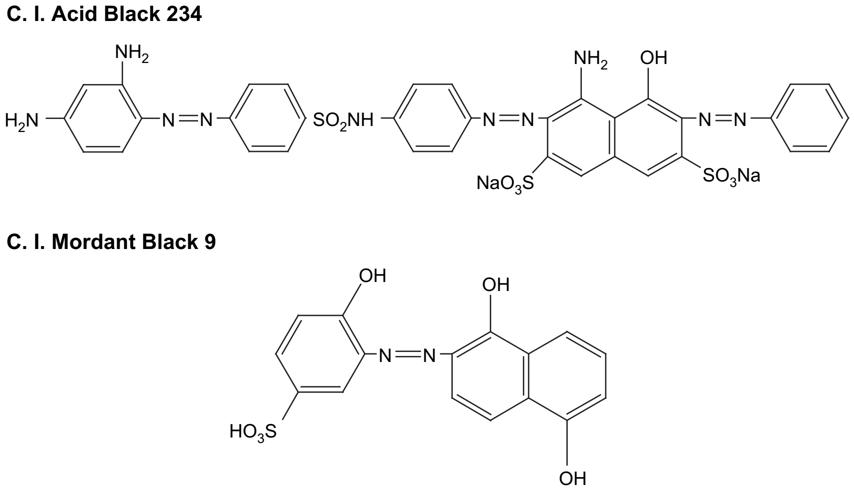

Fig. 1. Chemical structure of the two dyes.

30 min (mg L^{-1}). TOC was measured with a Phoenix 8000 TOC analyzer (Tekmar-Dehrmann Crop., USA) and the TOC removal percentage of the dye was calculated as follows:

$$\text{TOC removal\%} = (1 - \text{TOC}_t/\text{TOC}_0) \times 100\% \qquad (2)$$

where TOC_0 is the initial TOC value of the dye solution (mg L^{-1}) and TOC_t is the residual TOC value of the dye solution (mg L^{-1}).

3. Results and discussion

3.1. Fe(III) ion concentration

The decoloration of the two dyes was carried out by the addition of various amounts of Fe(III) ions to the test solutions containing 0.60 mmol L^{-1} oxalate ions and 1.00 mmol L^{-1} H_2O_2 under two weather conditions and the results are shown in Fig. 2.

Fig. 2 shows that the decoloration percentages of the two dyes gradually increase with increasing amounts of Fe(III) ions in aqueous solution and the increasing tendency becomes level at the concentration of 0.2 mmol L^{-1}. This is due to the more photo-reactive Fe(III)-oxalate complexes produced in the presence of increasing Fe(III) ions. And the photocatalytic decoloration of the dyes may be limited when concentration of Fe(III) ions exceeding 0.20 mmol L^{-1} in aqueous solution, especially during sunny day because of too much Fe(III)-oxalate complexes formed in the reaction. This agreed with the results obtained by Copper and Degraff [13]. Moreover, it is found that the decoloration levels during sunny days are higher than that during cloudy days at the same Fe(III) ions concentration, proposing that the decoloration of the dyes in water is more remarkably accelerated by Fe(III) ions during sunny day than during cloudy day. Comparing two dyes, it can be observed that C. I. Mordant Black 9 has larger decoloration values than C. I. Acid Black 234 at the same Fe(III) ion concentration under two weather conditions, which is mainly

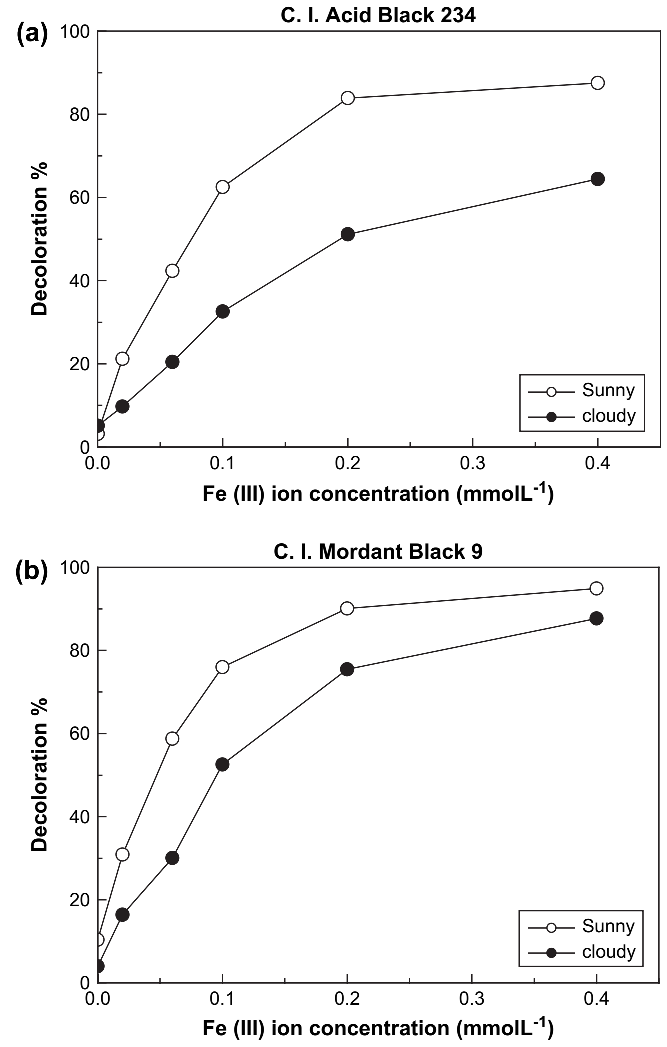

Fig. 2. Effect of Fe(III) ion concentration on decoloration percentage of the two dyes during sunny day, UV-A (365 nm): 0.961 (mW cm^{-2}), visible light (400–1000 nm): 35.0 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.450 (mW cm^{-2}), visible light (400–1000 nm): 19.0 (mW cm^{-2}).

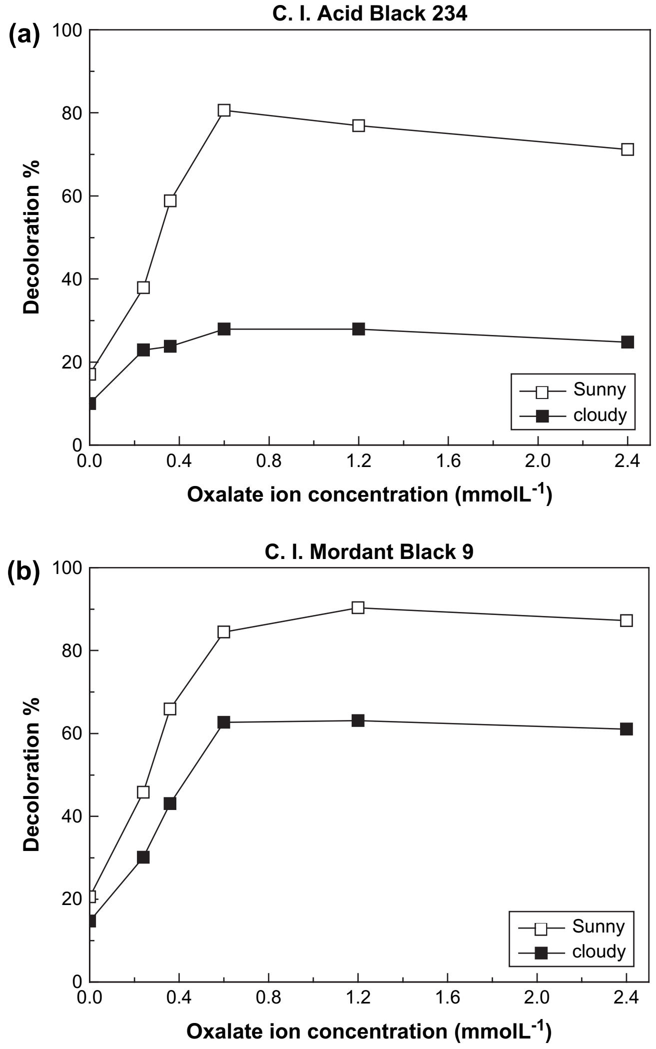

Fig. 3. Effect of oxalate ion concentration on decoloration percentage of the two dyes during sunny day, UV-A (365 nm): 1.26 (mW cm^{-2}), visible light (400–1000 nm): 42.0 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.355 (mW cm^{-2}), visible light (400–1000 nm): 6.10 (mW cm^{-2}).

attributed to the differences in molecule structure, particular in number of azo units between two dyes.

3.2. Oxalate ion concentration

To determine the dependence of decoloration of the dyes exposed to the high or low sunlight on oxalate ions concentration, the Fe(III) ions and H_2O_2 were fixed at 0.20 mmol L^{-1} and 1.00 mmol L^{-1}, respectively. Meanwhile, oxalate ion concentrations were set from 0 mmol L^{-1} to 2.40 mmol L^{-1} and the results are given in Fig. 3.

Fig. 3 shows that increase in concentration of oxalate ions from 0.24 mmol $L^{-1}$to 0.60 mmol L^{-1} is accompanied by increment in decoloration values of the two dyes, especially C. I. Acid Black 234 during sunny or cloudy day. Moreover, it is apparent that the decoloration values are best when oxalate ion concentration varies from 0.60 mmol L^{-1} to 1.20 mmol L^{-1}, and then have decreasing tendency when oxalate ion concentration increased up to 2.40 mmol L^{-1}. This implies that increasing oxalate ion concentration enhanced the photooxidation efficiency, but excessive oxalate ions may not benefit the decomposition of the dyes. Generally, at a given pH level, the Fe(III)/oxalate ratio can determine the species distribution of Fe(III)-oxalate complexes in water. It was found when the Fe(III)/oxalate ratio was less than 1:10, the only significant ferric ion species were the trioxalate complex [14]. These species of Fe(III)-oxalate complex might have a higher photoactivity. Also, excessive oxalate ions can maintain the photochemical redox cycle of Fe(III)/Fe(II) thus continuously produces hydroxyl radicals [15]. But previous studies have also shown that excess oxalate retards the decay of the transient species produced in the primary photoreaction of Fe(III)-oxalate complexes [16], possibly resulting in the low decoloration values of the dyes.

On the other hand, it is also observed from Fig. 3 that increasing concentration of oxalate ions from 0.80 mmol L^{-1}

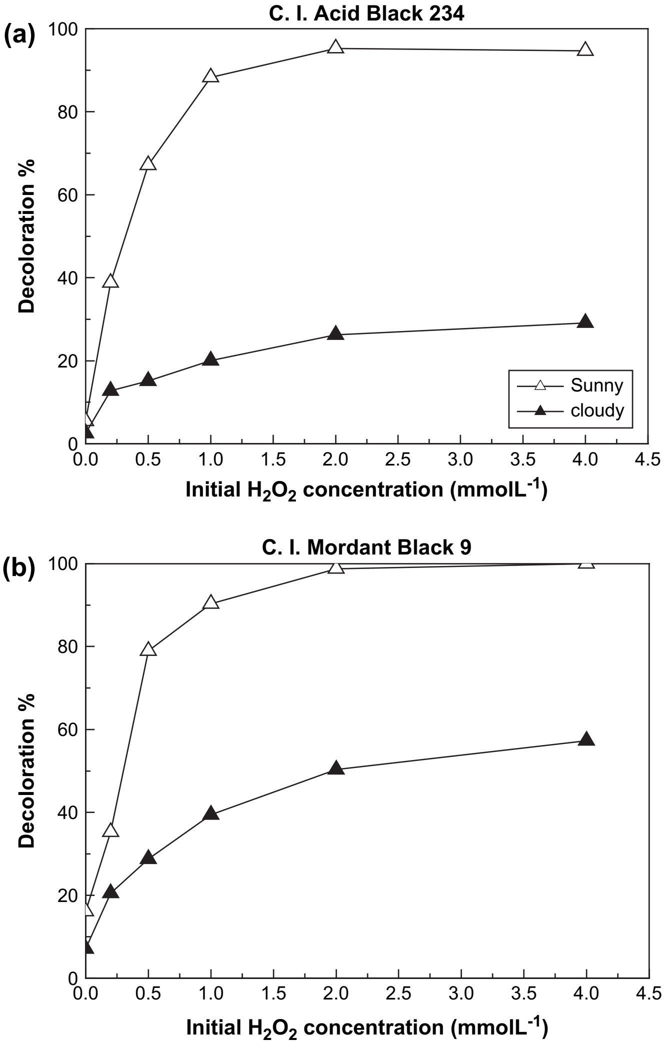

Fig. 4. Effect of initial H_2O_2 concentration on decoloration during sunny day, UV-A (365 nm): 1.55 (mW cm^{-2}), visible light (400–1000 nm): 50.8 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.355 (mW cm^{-2}), visible light (400–1000 nm): 6.10 (mW cm^{-2}).

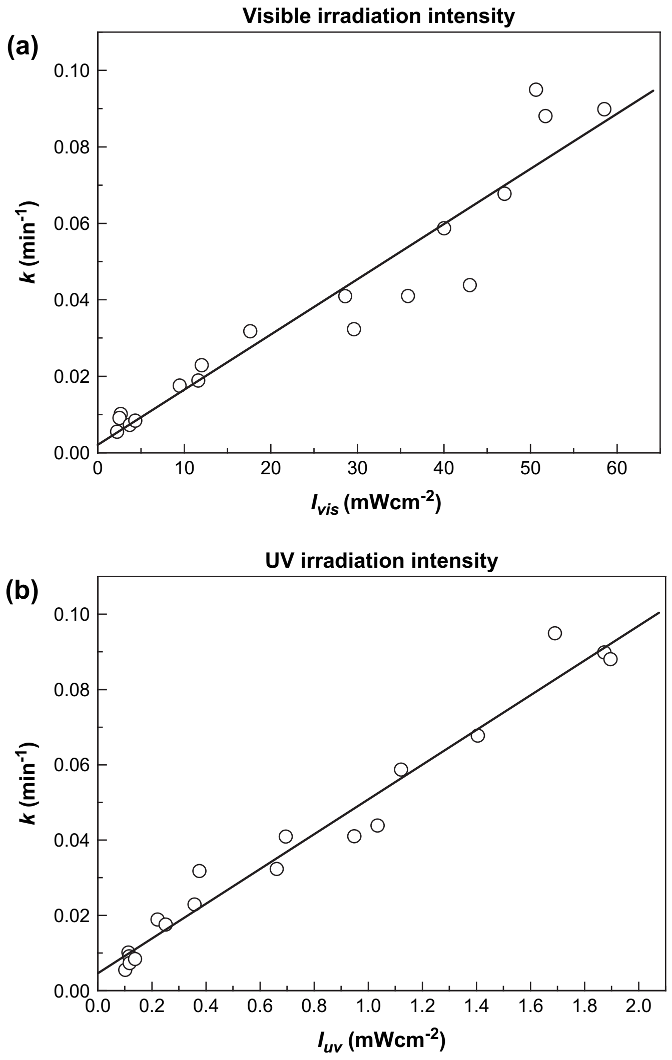

Fig. 5. Effect of irradiation intensity on the pseudo-first order rate constant, *k* of C. I. Acid Black 234, Fe(III): 0.20 mmol L^{-1}, oxalate: 0.60 mmol L^{-1}, H_2O_2: 1.00 mmol L^{-1}.

to 2.40 mmol L^{-1} caused insignificant improvement in decoloration value of the two dyes, especially C. I. Acid Black 234 during cloudy day, implying that influence of oxalate ion concentration on decoloration is also determined by solar irradiation intensity. And this is relative to the characteristics of dye molecules. It is believed that C. I. Acid Black 234 is decomposed by hydroxyl radical generated from Fe(III)-oxalate complex/H_2O_2 in water with more difficulty than C. I. Mordant Black 9 at the same oxalate ion concentration because the former has more azo units and higher molecular weight than the latter which possesses only one azo unit and low molecular weight.

3.3. Initial H_2O_2 concentration

Fe(III) ions and oxalate ions in water were held at 0.20 mmol L^{-1} and 0.60 mmol L^{-1}, respectively, and H_2O_2 concentration varied from 0 mmol L^{-1} to 4.00 mmol L^{-1}. The experimental results are shown in Fig. 4.

Table 1
Relationship between irradiation intensity and k of the two azo dyes

Dyes	Irradiation	Linear equation	R	SD	P
Black 234	Visible	$k = 0.00144\,I_{vis} + 0.00207$	0.9555	0.00914	<0.0001
	UV	$k = 0.0461\,I_{uv} + 0.00207$	0.9843	0.00548	<0.0001
Black 9	Visible	$k = 0.00238\,I_{vis} + 0.0273$	0.9805	0.01266	2.96×10^{-4}
	UV	$k = 0.0872\,I_{uv} + 0.00279$	0.9843	0.01022	1.01×10^{-4}

Fig. 4 indicates that the decomposition of the two dyes increases with the increasing initial concentration of H_2O_2 under sunlight exposure conditions. However, there is an optimum concentration (about 1.00 mmol L^{-1} in this test) of H_2O_2, especially during sunny day. The decoloration percentage began to increase unremarkably when the concentration of H_2O_2 was over the optimum value. This is coincident with the results reported in literatures [9,17]. The main reason is that at low

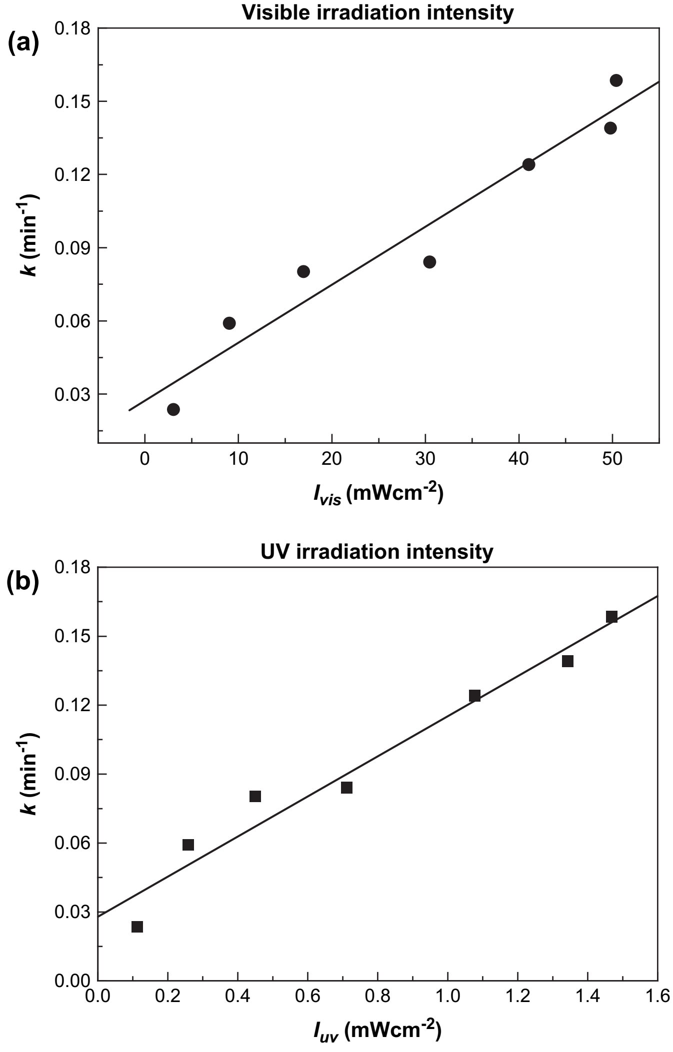

Fig. 6. Effect of irradiation intensity on the pseudo-first order rate constant, k of C. I. Mordant Black 9, Fe(III): 0.20 mmol L^{-1}, oxalate: 0.60 mmol L^{-1}, H_2O_2: 1.00 mmol L^{-1}.

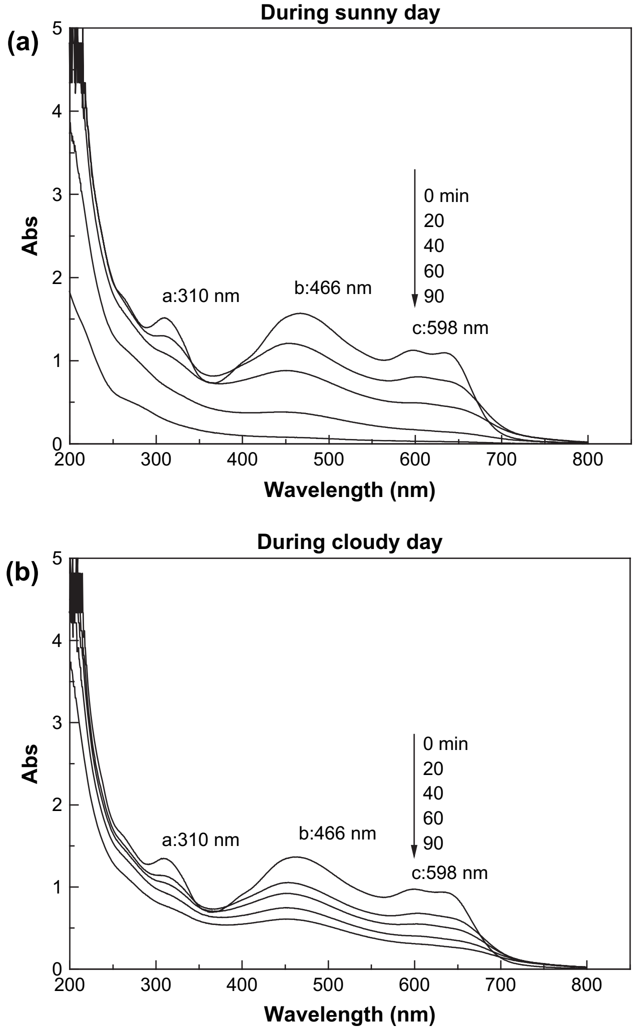

Fig. 7. Changes in UV–vis spectrum of C. I. Acid Black 234 during sunny day, UV-A (365 nm): 1.00 (mW cm^{-2}), visible light (400–1000 nm): 35.1 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.160 (mW cm^{-2}), visible light (400–1000 nm): 4.64 (mW cm^{-2}); Fe(III): 0.20 mmol L^{-1}, oxalate: 0.60 mmol L^{-1}, H_2O_2: 1.00 mmol L^{-1}.

concentration, H_2O_2 molecules cannot generate enough hydroxyl radicals leading to the limited decoloration of the dyes in the solution. Whereas over the optimum concentration, surplus H_2O_2 molecules play the role as a hydroxyl radical quencher, lowering the hydroxyl radical concentration. The quenching of H_2O_2 molecules is described as Eqs. (3) and (4) [17].

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}O_2H + H_2O \tag{3}$$

$$^{\bullet}O_2H + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{4}$$

On the other hand, as seen in Fig. 4, H_2O_2 concentration has much less effect on the decoloration during cloudy day than during sunny day at the same conditions. This means that H_2O_2 concentration effect is significantly relied upon sunlight exposure power.

3.4. Solar irradiation intensity

Photocatalytic decoloration of the azo dyes in water based on Fe(III)-oxalate complexes/H_2O_2 can be well described by using pseudo-first order kinetics with respect to their concentration. In this study, the pseudo-first order rate constants, k of the two dyes decoloration under different solar irradiations within 15 min of reaction time are calculated with all regression coefficients greater than 0.95 and the relationship between k and visible irradiation intensity, I_{vis} or UV irradiation intensity, I_{uv} are presented in Figs. 5 and 6 and Table 1, respectively.

As seen from Figs. 5 and 6, and Table 1, increasing visible irradiation intensity or UV irradiation intensity gives rise to the proportional enhancements in the pseudo-first order rate constants of the dye decomposition. This confirms the opinion that Fe(III)-oxalate complexes are photochemically active under sunlight because they exhibit strong absorption bands in the near-UV and visible regions. Moreover, it is noticed in Table 1 that there is a linear relationship between k and I_{vis} or I_{uv}, and the slope of linear equation obtained under UV light irradiation is much higher than that under visible light irradiation, suggesting that the photocatalytic decomposition of the dyes is more dependent on the UV light irradiation than visible light irradiation in the presence of Fe(III)-oxalate complex/H_2O_2. On the other hand, the slope of linear equation in case of C. I. Acid Black 234 is much lower than that in case of C. I. Mordant Black 9. This indicates that latter is decomposed more easily by photocatalysis of Fe(III)-oxalate complex than the former at the same condition.

3.5. UV–vis spectrum

The obvious changes of photocatalytic decoloration and degradation of the two dyes in the presence of Fe(III)-oxalate complex/H_2O_2 under solar illumination using UV–vis absorbance spectra are shown in Figs. 7 and 8, respectively. The characteristic absorbance of the two dyes is summarized in Table 2.

In general, the absorbance at 400–800 nm corresponds to the n → π* transition of the azo and hydrazone forms, which is due to the color of azo dyes and it is used to monitor the decoloration. The absorbance at 200–400 nm is attributed to the n → π* transition of benzene and naphthalene rings, representing the aromatic content of azo dyes and its decrease is due to the degradation of aromatic part of the dye [1,17]. Figs. 7 and 8 show that both the absorbance at 200–400 nm and 400–800 nm of the two dyes decrease gradually with prolonging exposure time due to increase in their decoloration and degradation in water. More importantly, absorbance levels at the three bands (particular in peak a, peak b and peak c) during sunny day are much less than that during cloudy day at the same exposure time, suggesting that powerful solar irradiation benefits not only the breaking of azo linkages in dye molecules but also the decomposition of aromatic parts including benzene and naphthalene rings in the molecular structure.

Moreover, Table 2 demonstrates that the absorption ratios of the two dyes at their characteristic peaks during sunny day are much lower than that during cloudy day at the same exposure

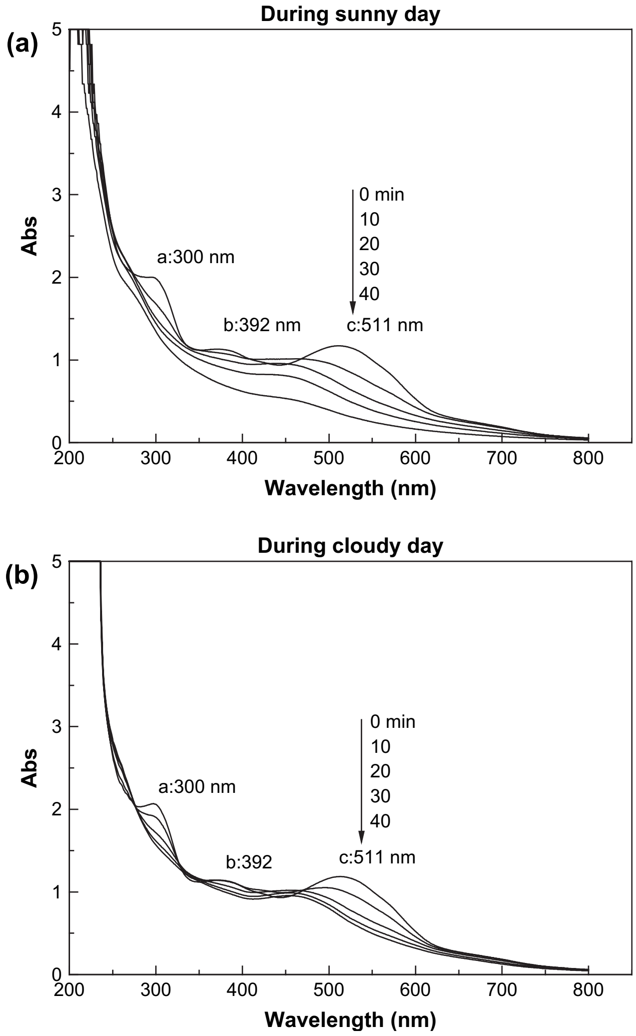

Fig. 8. Changes in UV–vis spectrum of C. I. Mordant Black 9 during sunny day, UV-A (365 nm): 0.676 (mW cm^{-2}), visible light (400–1000 nm): 22.3 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.118 (mW cm^{-2}), visible light (400–1000 nm): 3.69 (mW cm^{-2}); Fe(III): 0.20 mmol L^{-1}, oxalate: 0.60 mmol L^{-1}, H_2O_2: 1.00 mmol L^{-1}.

Table 2
The UV–vis characteristic absorbance of the two dyes under two different weather conditions

C. I. Acid Black 234					C. I. Mordant Black 9				
0 min	Sunny	310 nm	466 nm	598 nm	0 min	Sunny	300 nm	392 nm	511 nm[a]
		1.00	1.00	1.00			1.00	1.00	1.00[b]
	Cloudy	310 nm	466 nm	598 nm		Cloudy	300 nm	392 nm	511 nm
		1.00	1.00	1.00			1.00	1.00	1.00[a]
40 min	Sunny	310 nm	466 nm	598 nm	20 min	Sunny	300 nm	392 nm	440 nm
		0.72	0.55	0.44			0.76	0.89	0.82
	Cloudy	310 nm	466 nm	598 nm		Cloudy	300 nm	392 nm	457 nm
		0.85	0.76	0.70			0.83	0.94	0.86
90 min	Sunny	310 nm	466 nm	598 nm	40 min	Sunny	300 nm	392 nm	440 nm
		0.19	0.049	0.029			0.68	0.59	0.47
	Cloudy	310 nm	466 nm	598 nm		Cloudy	300 nm	392 nm	457 nm
		0.58	0.44	0.32			0.76	0.86	0.81

[a] The characteristic absorption wavelengths of the dyes.

[b] The absorption ratios were calculated by A (residual absorption value at the different exposure times)/A_0 (the initial absorption value of the dyes).

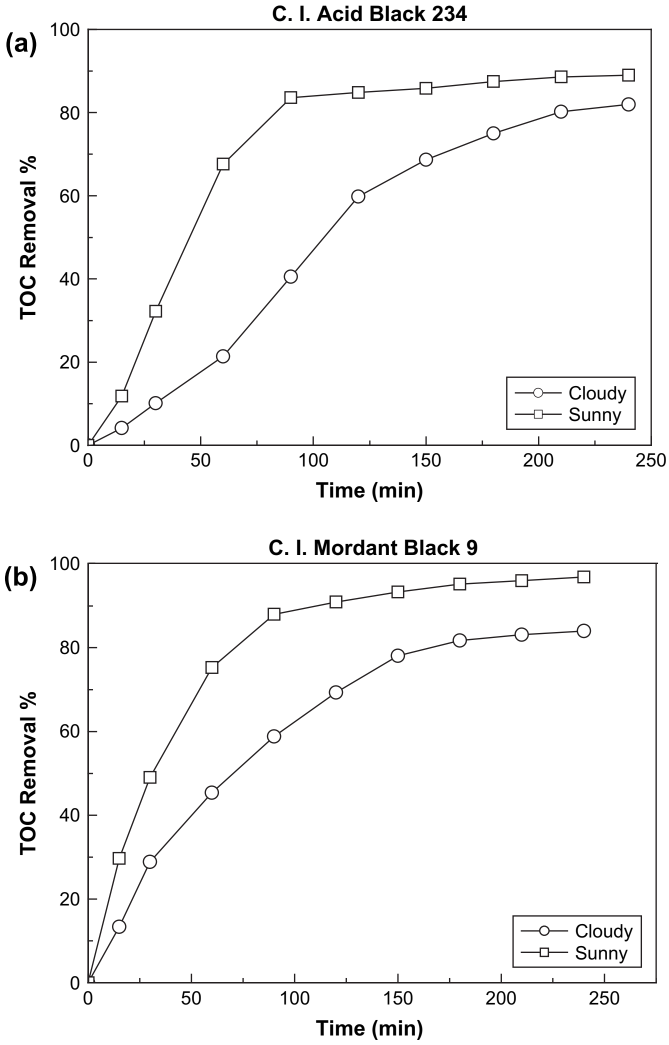

Fig. 9. TOC removal of the two dyes under different solar exposures, UV-A (365 nm): 0.829 (mW cm^{-2}), visible light (400–1000 nm): 32.7 (mW cm^{-2}); during cloudy day, UV-A (365 nm): 0.335 (mW cm^{-2}), visible light (400–1000 nm): 14.7 (mW cm^{-2}); Fe(III): 0.20 mmol L^{-1}, oxalate: 0.60 mmol L^{-1}, H_2O_2: 1.00 mmol L^{-1}.

time. Also, it is observed clearly in Table 2 that the absorption ratios of C. I. Acid Black 234 at 310 nm are generally higher than that at 466 nm and 598 nm at the same conditions. However, C. I. Mordant Black 9 has almost reversed trend, especially during cloudy day compared with C. I. Acid Black 234. This proposes that the aromatic part in the dye molecules, especially those containing more benzene and naphthalene rings such as C. I. Acid Black 234 is decomposed with more difficulty than the azo linkages in their molecules by the photocatalysis of Fe(III)-oxalate complexes/H_2O_2.

3.6. Mineralization

The hydroxyl radical produced from photolysis of Fe(III)-oxalate complexes/H_2O_2 system is a powerful oxidant and can ultimately cause mineralization of textile dyes. In this work, mineralization of the two dyes was conducted under two sunlight exposure conditions and the pseudo-first order rate constants, k_m of mineralization within 100 min of reaction time from linear regression ln(TOC_0/TOC) versus time were calculated and are given in Fig. 9 and Table 3.

Fig. 9 and Table 3 show that the mineralization of the two dyes is carried out and well described by using pseudo-first order kinetics with respect to TOC level under different weather conditions. It is found that TOC removal percentages and mineralization rate constant (k_m) during sunny days were much higher than those during cloudy days. This demonstrates that the TOC removal is mainly determined by solar irradiation intensity, which is well consistent with the impact of solar irradiation intensity on the decoloration and degradation mentioned

Table 3
Mineralization rate constants of the two azo dyes under different weather conditions

Weather condition	Dyes	k_m (min^{-1})	R	N	SD	P
Sunny day	Black 234	20.3×10^{-3}	0.9925	5	0.107	7.84×10^{-4}
	Black 9	23.5×10^{-3}	0.9998	5	0.0169	<0.0001
Cloudy day	Black 234	5.66×10^{-3}	0.9767	5	0.0519	4.27×10^{-3}
	Black 9	9.86×10^{-3}	0.9984	5	0.0234	<0.0001

above. In addition, Table 3 indicates that C. I. Acid Black 234 is lower than C. I. Mordant Black 9 in terms of mineralization rate constants under two weather conditions, which implies that the latter is mineralized more easily than the former at the same photocatalytic circumference.

4. Conclusions

Although the photocatalytic decoloration of the two dyes was improved dramatically by increasing the concentration of Fe(III), oxalate and hydrogen peroxide, very high concentrations of the reagents did not benefit dye decomposition; generally, their effects on dye decomposition depend on weather conditions. The photocatalytic decomposition of the two dyes was characterized using the pseudo-first order kinetics and increasing visible or UV irradiation intensity enhanced the decoloration rate constants. In addition C. I. Acid Black 234 was difficult to degrade and mineralize; the degradation of the aromatic components of the two dyes was reduced by low irradiation. Mineralization of the two dyes, especially that of C. I. Acid Black 234, depended upon the level of solar exposure.

Acknowledgements

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