Effect of inorganic salts on ferric oxalate-induced decomposition of CI Acid Black 234 under different weather conditions

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Received: 28 August 2007; Accepted: 16 November 2007

In this study, sodium chloride and sodium sulphate were used for investigating their effects on photocatalytic decomposition of a triazo acid dye, CI Acid Black 234, used widely for the coloration of leather and wool products by the Fe^{III}-oxalate complexes/hydrogen peroxide system under different weather conditions, respectively. Moreover, the photocatalytic degradation and mineralisation of CI Acid Black 234 was also examined by ultraviolet-visible spectrum and total organic carbon measurements. The results indicated that photocatalytic decoloration of CI Acid Black 234 was significantly limited in the presence of inorganic salt. Increasing the concentration of inorganic salt led to a lower decoloration percentage and kinetic reaction constant. The effect of inorganic salt on dye decomposition varied with solar light intensity. Sodium chloride exhibits a much stronger reduction effect on photocatalytic decoloration, degradation and mineralisation than sodium sulphate at similar reaction conditions, especially on a cloudy day.

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Introduction

Acid dyes are water-soluble anionic dyes that are applied to fibres such as silk, wool and nylon, using neutral to acid dyebaths at near boiling point. It is difficult to produce a uniform dyeing because acid dyes have a relatively high sensitivity to protein fibres. To overcome this, either sodium sulphate or sodium chloride, serving as a dyeing rate retardant, is usually added to the dyeing liquor to govern the dyeing process by surface diffusion [1] and to help level the dye at the dye bath pH below the isoelectric point (pH 4.2–4.8) of wool. At a high pH, sodium sulphate also behaves as an exhausting agent for acid dyes on wool [2]. Moreover, it is said that either sodium sulphate or sodium chloride is added to maintain or protect the strength of the silk or woollen fibre in the acidic dyeing. In addition, commercial acid dyes are usually mixtures containing dyes, intermediates produced during the dye synthesis and inorganic salts; for example, sodium sulphate, sodium chloride, etc. [3,4]. More importantly, protein fibres are usually dyed with acid dye at a pH of 2–5 and a temperature of 95–100 °C, and the discharged effluent is acidic wastewater. The photo-Fenton process is also likely to be carried out at a pH of 2–5. The similarity in acidity between acidic dyeing and the photo-Fenton process made it possible to easily treat acid dye wastewater using the photo-Fenton process, thus avoiding any adjustment of the pH and resulting in a low-cost treatment. However, the addition of these inorganic salts in the synthesis and application of the acid dye increases the pollution loads on the effluent generated and has an effect on various effluent treatment processes.

Fe(III)-oxalate complexes are photochemically active under sunlight because these species exhibit strong ligand-to-metal charge absorption bands in the near-ultraviolet (UV) and visible region. Fe(III)-oxalate complexes can generate Fe(II) ions when irradiated and the Fe(II) ions can in turn participate in the Fenton reaction and generate additional hydroxyl radicals [5,6]. The net reaction for the production of hydroxyl radicals is shown in Eqns 1 and 2:

The hydroxyl radical is a powerful oxidant and starts a cascade of oxidation reactions that can ultimately lead to the total mineralisation of organic pollutants. In the past, Fe(III)-oxalate complexes were used as the catalysts or promoters in the photodegradation of textile dyes in water [7,8] and are expected to play an important role in the degradation of textile dyes in the future.

There have been some studies regarding the effect of inorganic salts on the decoloration of textile dyes using advanced oxidation technologies (AOTs). Gahr *et al.* reported that, at higher pH levels, the presence of salt lowers the decomposition of reactive dyes during ozone decoloration [9]. Muthukumar and Selvakumar found that the salt content in the effluent increases the decoloration time of the acid dye effluent [10]. The study of Aye *et al.* indicated that chloride ions could reduce the amount of hydroxyl radicals available for the oxidation reaction [4]. However, Muruganandham and Swaminathan [11]

concluded that the addition of sodium chloride does not affect the dye removal rate significantly during the UV- H_2O_2 process. Sokmen and Ozkan reported that the catalytic activity of titanium dioxide (TiO_2) was significantly retarded in the presence of common inorganic anions [12]. Arslan-Alaton concluded that the efficiency of most Advanced Oxidation Processes is significantly inhibited in the presence of dye-assisting chemicals including chloride and sulphate sodium salts that are used in high amounts in the reactive dyeing process [13]. However, very little research has concentrated on the solar decomposition of azo dyes by the photocatalysis of the Fe(III) -oxalate complexes/ H_2O_2 system in the presence of inorganic salts and the information regarding the role of inorganic salts in the photocatalytic degradation of water-soluble azo dyes, especially acid dyes under solar irradiation, is very limited.

Hence, this study investigated the photocatalytic degradation of a triazo dye, CI Acid Black 234, using Fe(III) -oxalate complexes/ H_2O_2 under different solar light in the presence of inorganic salt. This dye was selected as the model pollutant, mainly because of its relatively high consumption rate in China for the dyeing of leather products and wool textiles. It has been produced by more than 20 chemical companies in China, but has been unable to meet the effluent colour standard of China [40–80 (dilution multiple method) from the National Standard of China GB4287-82: *Discharge standard of water pollutants for dyeing and finishing of textile industry*]. In this current study, the solar-induced degradation behaviour of CI Acid Black 234 mediated by ferrioxalate/ H_2O_2 was examined in the presence of sodium sulphate or chloride sodium under different weather conditions. By comparing results with and without the presence of inorganic salt, this work is helpful in further understanding the role of inorganic salt in the degradation of azo dye, especially under different solar lights. Moreover, some possible ways in which inorganic salt influenced dye degradation are also discussed.

Methods

Reagents and chemicals

An original acid dye, CI Acid Black 234 (**1**) was provided by the Tianjin Sanhuan Chemical Company (China) and used in this experiment without future purification. Ferric sulphate, oxalic acid and hydrogen peroxide (30% w/w) were of analytic grade. Sodium chloride and sodium sulphate were of reagent grade. These chemicals were obtained from the Tianjin Chemical Reagent Company (China). Double-distilled and deionised water was used throughout the study.

Photoreactor

The photoreactor consists of a reaction receiver and a rack at a 30° angle from the horizontal. The rack was made of plastic board and an open Pyrex vessel of 150 ml capacity was used as reaction receiver on the rack. With this rack, the reaction receiver could be put in and removed from sunlight within 5–10 s. The sunlight intensity reaching the solutions in the reaction receiver was recorded using an FZ-A radiometer that responds to light of 400–1000 nm and a UV-A radiometer responding to UV light of 365 nm (BNU Light and Electronic Instrumental Factory, China), respectively.

Procedure

Solar light experiments were performed on the top of the Material Chemical Engineering Building at the campus of Tianjin Polytechnic University (located at Hedong District, Tianjin, about 19 m above sea level, $39^\circ31'\text{N}$, $117^\circ98'\text{E}$) on selected sunny or cloudy days at times ranging from 10.00 to 14.30 hours from April to June 2005. The ambient temperature was usually $25\text{--}30^\circ\text{C}$ during the experiments. A stock dye solution was prepared by dissolving the appropriate weight of the solid dye in double-distilled water. Sodium chloride or sodium sulphate (1.0 M) was prepared by dissolving the calculated weight in double-distilled water. More diluted solutions were prepared by further dilution of the stock. The test solutions contained 0.058 mM dye and varied concentrations of the salts (0.2 mM Fe(III) , 0.6 mM oxalate ions and 1.0 mM hydrogen peroxide) at an initial pH of 3.0 ± 0.1 . With the exception of the salts, these concentrations had been optimised towards the dye decomposition in our previous experiments. The 100 ml samples of test solutions were then placed into reaction vessels on the photoreactor mentioned above and exposed to sunlight irradiation. At different time intervals, the reaction receiver was briefly shaken by hand to stir the test solution and then 1–2 ml of solution was withdrawn from the reaction receiver and diluted appropriately; the absorbance was then measured at the λ_{max} (466 nm) of the different solutions. The concentration of the dye was determined and the ultraviolet-visible (UV-vis) spectrum from 190 to 800 nm was recorded with a UV-2401 Shimadzu spectrophotometer (Japan). The pH of the solution was measured using a DHS-25C digital pH meter (Shanghai Jingmi Instrumental Company, China). The decoloration percentage of the dye was expressed as: $\text{decoloration \%} = (1 - C/C_0) \times 100\%$, where C_0 is the initial concentration of the dye (mM) and C is the residual concentration of the dye (mM). The total organic carbon (TOC) was also measured using a 1020A TOC analyser (OI Instrumental Corp., USA). The TOC analyser was usually calibrated with a standard sucrose solution before use.

Figure 1 The effect of concentrations of inorganic salts on the decoloration percentage of CI Acid Black 234 on a sunny day: UV-A (365 nm), 2.28 mWcm⁻²; visible light (400–1000 nm), 53.9 mWcm⁻²; (a) NaCl, (b) Na₂SO₄

Figure 2 The effect of concentrations of inorganic salts on the decoloration percentage of CI Acid Black 234 on a cloudy day: UV-A (365 nm), 0.345 mWcm⁻²; visible light (400–1000 nm), 14.9 mWcm⁻²; (a) NaCl, (b) Na₂SO₄

Results and Discussion

Concentration of inorganic salts

Sodium chloride and sodium sulphate were added at the various concentrations to the test solutions, each containing 0.058 mM dye. The test solutions were then irradiated under different weather conditions and the results are shown in Figures 1 and 2.

These figures show that, in the presence or absence of inorganic salts, the decoloration percentages of CI Acid Black 234 gradually increase with the prolongation of exposure time and increasing concentration of the inorganic salts. It is also shown that the increasing concentration of sodium chloride caused a more significant reduction than sodium sulphate in the decoloration percentage within the exposure time, especially, on a cloudy day. Moreover, the changes in the UV-vis spectra of CI Acid Black 234 in the presence or absence of inorganic salts during photocatalytic degradation are also illustrated in Figures 3 and 4.

Generally, the absorbance at 400–800 nm corresponds with the $n \rightarrow \pi^*$ transition of the azo and hydrazone forms, which is because of the colour of the azo dye and it is used to monitor the decoloration. The absorbance at 200–400 nm is attributed to the $n \rightarrow \pi^*$ transition of the benzene and naphthalene ring, representing the aromatic

content of the azo dyes and its decrease is as a result of the degradation of the aromatic part of the dyes [10]. Figures 3 and 4 shows that both absorbances at 200–400 and 400–800 nm of the dye decrease gradually with prolonged exposure time because of the increase in decoloration and degradation of the CI Acid Black 234 in water.

Compared with the control experiments, the addition of inorganic salts, particularly sodium chloride, to the solution caused a significant enhancement in absorbance levels at the three bands (particular in peaks *a*, *b* and *c*) at the same exposure time under the two irradiation conditions, demonstrating that inorganic salt was simultaneously able to inhibit the breaking of the azo linkages and the decomposition of the aromatic parts such as the benzene and naphthalene ring of the dye molecule. This may be because of the hydroxyl radical scavenging effect of chloride ion. Similar retardation by the addition of sodium chloride has been reported in the ozonation [10], UV-H₂O₂ [11] and UV-TiO₂ processes [12]. It has been confirmed that chloride ions react with hydroxyl radicals at an acidic pH and in turn is converted into chlorine radicals, as described in Eqns 3–5. In addition, chlorine radicals significantly retard the dye oxidation because azo dyes react with chlorine radicals at a rate of $3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; that is,

Figure 3 Changes in UV-vis spectra of CI Acid Black 234 on a sunny day: UV-A (365 nm), 1.00 mWcm^{-2} ; visible light (400–1000 nm), 35.1 mWcm^{-2} ; (a) control, (b) NaCl 25mM, (c) Na_2SO_4 , 25 mM

100–1000 times slower than with hydroxyl radicals ($6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [13,14] as expressed by Eqns 6–9.

Figure 4 Changes in UV-vis spectra of CI Acid Black 234 on a cloudy day: UV-A (365 nm), 0.161 mWcm^{-2} ; visible light (400–1000 nm), 4.64 mWcm^{-2} ; (a) control, (b) NaCl 25mM, (c) Na_2SO_4 , 25 mM

Moreover, the speciation of dissolved Fe(III) in aqueous solution depends on the competition between the formation of Fe(III)-oxalato complexes and Fe(III)-hydroxo complexes. Under the conditions of the acidic solution, where the pH ranges from 3 to 5, Fe(III)-oxalato

complexes could be the predominant dissolved species [15]. However, the presence of chloride ions may cause the decomposition of the Fe(III)-oxalato complexes owing to the formation of Fe(III) Cl_4^- , as shown by Eqn 10.

Another possible explanation is that, once a certain amount of salt such as sodium chloride is dissolved in the aqueous solution, the ionic strength of the aqueous solution dramatically increases, thus enhancing the ionisation and decomposition of the Fe(III)-oxalato complexes in the solution and resulting in a low concentration of Fe(III)-oxalato complexes, in particular $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, as expressed by Eqns 11–13.

$\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ is the best-known and widely used example of the Fe(III)-polycarbonate complexes and is photochemically active under solar light [6]. Consequently, it is obvious that a low concentration of Fe(III)-oxalato complex $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ in solution may limit the photo-Fenton reaction, generating fewer hydroxyl radicals and thus causing the low decoloration level. In contrast, the addition of salts such as sodium chloride is believed to increase the degree of aggregation of ionic dyes in water; this is known as the ‘common ion effect’ [2]. Aggregation of various classes of dyes is a very well-known phenomenon. Generally, the conditions for dissolving dyes in water depend mainly upon their aggregation and ionisation. The aggregation equilibrium of dye molecules in water is particularly affected by the concentration of dye and the ionic strength of the inorganic salts. It has been concluded that, in the presence of salt, the π -electron repulsion between the two ionic dye molecules is small compared with the affinity of the hydrophobic association. Therefore, the addition of sodium chloride can reduce the electrostatic repulsion forces between the dye anions, which will lead to the increase of aggregation tendency of the dye molecules in the solution [16]. Consequently, it is believed that aggregation enhanced by inorganic salts can significantly reduce the solubilisation and ionisation of dye molecules in water, thus lowering the capacity of the dye molecules to react with the hydroxyl radicals.

However, increasing the concentration of sodium sulphate, particularly on a cloudy day, led to a relatively slight decrease in the decoloration percentage of CI Acid Black 234, compared with using sodium chloride. This may be because of the balance on the inhibition and acceleration factors of dye decoloration. It is obvious that changes in the ionic strength of the solution and the ‘common ion effect’ caused by the presence of salt, as mentioned earlier, are able to inhibit the removal of the dye from the water. In contrast, a previous study [10] found that the sulphate ions reacted with the hydroxyl radicals to produce sulphate radicals and peroxydisulphate ions; the reactions are shown in

Eqns 14 and 15. Sulphate radicals and peroxydisulphate ions have relatively high oxidation potential (2.01 V) and, to some degree, can decompose dye molecules in the solution.

Moreover, it has been stated that the sulphate radical has a unique nature by which it attacks the dye molecules at various positions, resulting in rapid fragmentation of the molecules [17], and thus maintaining the high decoloration efficiency of the dye in the aqueous solution.

Figures 1 and 2 also show that the decoloration percentages of the dye on sunny days were always higher than on cloudy days, with or without inorganic salt under the same conditions. Using sodium chloride, the decoloration curves were usually lower than with sodium sulphate at the same concentrations, especially on cloudy days; therefore, suggesting that sodium chloride exhibited a much stronger reduction effect on dye decoloration than sodium sulphate at the same concentration with low sun irradiation. In addition, Figures 3 and 4 demonstrate that, on sunny days, absorbance levels at the three bands mentioned earlier (*a*, *b* and *c*), are much less than on cloudy days, with the same exposure time and in the presence or absence of inorganic salts, suggesting that high solar irradiation benefits both the decoloration and degradation of the dye molecules in the solution.

Decoloration kinetics

Photocatalytic decoloration of 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:

$$\frac{-dc}{dt} = kt \quad (16)$$

where *k* is the pseudo-first order rate constant (min^{-1}), *t* is the irradiation time (min), *C* is the dye concentration (mM) at a given time. Eqn 16 can be solved by integration between the limits ($t_0 = 0$, C_0) and (*t*, *C*) [18]. The integrated expression is:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (17)$$

The pseudo-first order rate constants of dye decoloration from Figures 1 and 2 within 20 min of reaction time were calculated from linear regression $\ln(C_0/C)$ vs time plots with all regression coefficients >0.98, and are listed in Tables 1 and 2, respectively.

As shown in Table 1, a remarkable decrease in the decoloration rate constant was observed when the sodium chloride concentration and ionic strength was increased from 0 to 100 mM within the exposure time, on both sunny and cloudy days, indicating that sodium chloride is a substance that tends to inhibit the dye removal rate from aqueous solution. Also, the decoloration rate constants decreased more significantly with an increasing sodium chloride concentration and ionic strength, especially when increasing from 30 to 100 mM on a cloudy day rather than a sunny day. This implies sodium

Table 1 Effect of NaCl concentration and ionic strength on initial decoloration rate constants

NaCl conc. (mM)	Ionic strength (mM)	Sunny day		Cloudy day	
		k (min ⁻¹)	R	k (min ⁻¹)	R
0.0	0.0	0.0320	0.9987	0.0141	0.9934
5.0	5.0	0.0255	0.9975	0.0108	0.9923
10.0	10.0	0.0202	0.9983	0.0079	0.9941
30.0	30.0	0.0177	0.9984	0.0060	0.9930
50.0	50.0	0.0142	0.9942	0.0039	0.9929
100.0	100.0	0.0135	0.9999	0.0012	0.9903

Table 2 Effect of Na₂SO₄ concentration and ionic strength on initial decoloration rate constants

Na ₂ SO ₄ conc. (mM)	Ionic strength (mM)	Sunny day		Cloudy day	
		k_s (min ⁻¹)	R	k_c (min ⁻¹)	R
0.0	0.0	0.0320	0.9987	0.0141	0.9934
5.0	15.0	0.0291	0.9980	0.0129	0.9842
10.0	30.0	0.0277	0.9963	0.0106	0.9809
30.0	90.0	0.0254	0.9960	0.0092	0.9881
50.0	150.0	0.0253	0.9913	0.0083	0.9842
100.0	300.0	0.0200	0.09869	0.0065	0.9902

chloride has a relatively stronger reduction effect on decoloration with a cloudy sky rather than a clear sky. In the case of sodium sulphate, Table 2 shows that the decoloration rate constant decreases slowly when increasing the concentration and ionic strength under the two weather conditions, suggesting that, because of its molecular characteristics, it has a relatively low reduction influence on dye decoloration. The inhibitory effect of sodium chloride or sodium sulphate could also be explained by the fact that an increase in the ionic strength enhanced the free counter ion concentration, thereby decreasing the energy of repulsion between the charged head group of the ionic dyes, which induced an increase in the aggregation number of the dyes.

Comparing the data in Tables 1 and 2, it can be seen that, although sodium sulphate is higher than sodium chloride in terms of ionic strength of solution at the same concentration, it has a relatively lower reduction influence on dye decoloration than has sodium chloride. This indicates that, in the case of sodium sulphate, high ionic strength is able to reduce significantly the dye decoloration by increasing the 'common ion effect' mentioned above; but this may be partially counteracted by the acceleration factors of dye decoloration. More importantly, it should be noted that sodium chloride and sodium sulphate have a more inhibitory effect on the rate of dye decoloration on a cloudy day. This is because the decoloration rate of the azo dye mediated by ferrioxalate/H₂O₂ is mainly dependent on solar irradiation intensity when other factors are constant, and the decoloration rate is faster under a sunny sky compared with a cloudy sky [6], thus indicating that higher solar irradiation can significantly accelerate the

Figure 5 Relationship between irradiation intensity and k in the presence of inorganic salts: (a) UV-A; (b) visible light

dye decoloration in water. Therefore, it is believed that the inhibitory effect of inorganic salts may be balanced by the higher solar irradiation-induced promotion of decoloration of the dye on a sunny day, thus becoming less significant on a sunny day than on a cloudy day.

Irradiation intensity

Solar irradiation is a significant factor in increasing the photocatalytic decomposition of the azo dyes. In order to investigate the effect of inorganic salts varied with solar irradiation intensity, in this study, the decolorations of CI Acid Black 234 were conducted in the presence or absence of inorganic salts (30 mM) on selected days between April and June. The pseudo-first order rate constants (k) of CI Acid Black 234 decoloration within 20 min of reaction time were then calculated with all regression coefficients >0.95, and the relationship between k and visible (400–100 nm) irradiation intensity (I_{Vis}) or UV-A (365 nm) irradiation intensity (I_{UV}) are presented in Figure 5 and Table 3, respectively.

The data are clearly seen to increase visible irradiation intensity or UV irradiation intensity, causing the proportional enhancement decoloration rate constants of the dye decomposition. This confirms the view that Fe(III)-oxalate complexes are photochemically active under sunlight because they exhibit strong absorption

Table 3 Relationship between irradiation intensity and k in the presence of inorganic salts

Salts	Irradiation	Linear equation	R	SD	P -value
NaCl, 30 mM	Visible	$k = 0.00087 I_{\text{Vis}} + 0.00003$	0.9864	0.0312	<0.0001
	UV-A	$k = 0.0240 I_{\text{UV}} + 0.00343$	0.9786	0.00380	<0.0001
Na ₂ SO ₄ , 30 mM	Visible	$k = 0.00150 I_{\text{Vis}} + 0.00088$	0.9753	0.00728	<0.0001
	UV-A	$k = 0.0444 I_{\text{UV}} + 0.00401$	0.9903	0.00468	<0.0001
Control	Visible	$k = 0.00155 I_{\text{Vis}} + 0.0025$	0.9887	0.00505	<0.0001
	UV-A	$k = 0.0431 I_{\text{UV}} + 0.00703$	0.9805	0.00651	<0.0001

Visible (400–1000 nm), UV-A (365 nm)

bands in the near-UV and visible region, thus generating additional hydroxyl radicals, especially in the presence of H₂O₂. Moreover, the data in Table 3 show 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 CI Acid Black 234 is more dependent on the UV light irradiation than visible light irradiation in the presence of Fe(III)-oxalate complex/H₂O₂. This is because the observed quantum yield of Fe(II) formation during the ferrioxalate-induced photo-Fenton process is about 1.0–2.0 under the irradiation wavelength, range 250–450 nm, and decreases with a further increase of the irradiation wavelength [6], thus indicating that the Fe(III)-oxalate complex can generate more hydroxyl radicals by Fenton reaction under UV irradiation than under visible light irradiation in the presence of H₂O₂. It should also be noted from Figure 5 and Table 3 that the slope of the linear equation in the control experiment is nearly the same as that in the case of sodium sulphate, but much higher than that in sodium chloride, suggesting that, under all weather conditions, sodium chloride shows a stronger reduction effect on dye decoloration than does sodium sulphate. This is similar to the results obtained in terms of decoloration percentage and UV-vis analysis mentioned above.

Mineralisation

The hydroxyl radical produced from photolysis of the Fe(III)-oxalate complex/H₂O₂ system is a powerful oxidant which can ultimately cause mineralisation of textile dyes in water. In this study, mineralisation of CI Acid Black 234 was conducted under different sun irradiation levels in the presence of sodium chloride or sodium sulphate, respectively. Within 90 min of reaction time, the pseudo-first order rate constants (k_m) were calculated with all regression coefficients >0.95; for comparison, a control experiment in which these salts were absent in the solution was carried out. These experimental results are given in Figure 6 and Table 4.

The results show that TOC values gradually decreased with the prolongation of reaction time in the aqueous solution by photocatalytic oxidation with or without salts. Generally, in the presence or absence of inorganic salts, TOC curves on a sunny day were lower than the corresponding curves on a cloudy day, but initial mineralisation rate constants exerted a reverse trend, suggesting that dye mineralisation is determined by

Figure 6 Influence of inorganic salts on the TOC values of CI Acid Black 234 (a) on a sunny day: UV-A (365 nm), 0.714 mWcm⁻²; visible light (400–1000 nm), 26.5 mWcm⁻²; and (b) on a cloudy day: UV-A (365 nm), 0.534 mWcm⁻²; visible light (400–1000 nm), 15.5 mWcm⁻²

Table 4 Relationship between inorganic salts and initial mineralisation rate constants

Inorganic salts	Sunny day		Cloudy day	
	k_m (min ⁻¹)	R	k_m (min ⁻¹)	R
Control	0.0209	0.9925	0.0055	0.9590
NaCl 30 mM	0.0121	0.9892	0.0021	0.9728
Na ₂ SO ₄ 30 mM	0.0185	0.9794	0.0049	0.9892

irradiation power. Moreover, the addition of sodium chloride significantly increased the TOC values and decreased the initial mineralisation rate constants, which is consistent with the decoloration and degradation reduced by sodium chloride as mentioned earlier. TOC removal is affected significantly by the kind of salt used: sodium sulphate presented much weaker reduction in mineralisation of the dye than did sodium chloride under the same conditions during sunny or cloudy days. This agrees with the decoloration and degradation retarded by sodium sulphate mentioned above.

Conclusions

Decoloration of CI Acid Black 234 in water by the photocatalysis of Fe(III)-oxalate complexes/H₂O₂ was undertaken under different weather conditions in the presence of inorganic salts. We found that photocatalytic decoloration of the dye was affected dramatically by sodium chloride under low solar irradiation. Increasing the concentration of sodium chloride caused low dye removal from solution. Compared with sodium chloride, sodium sulphate played an unimportant role in dye decomposition under the same conditions. Moreover, photocatalytic decoloration and mineralisation of CI Acid Black 234 in the early stages followed the pseudo-first order kinetics, but initial reaction rate constants decreased in the case of inorganic salts, especially sodium chloride. Additionally, the UV-vis spectrum and the TOC measurements indicate that degradation and mineralisation of the aromatic part of the dye were also remarkably limited in the presence of inorganic salts, especially sodium chloride on a cloudy day. In summary, sodium chloride plays a significant retarding role in all the decomposing processes including decoloration, degradation and mineralisation of CI Acid Black 234, particularly under cloudy weather conditions.

Acknowledgements

The authors thank the Tianjin Municipal Education Committee and the Tianjin Municipal Science and

Technology Committee for a Research Development Grant for Tianjin Municipal Universities (2003-1007) and the Tianjin Municipal Science Programme Foundation (043605911) for their support. This research was also supported in part by an Open-Lab Grant (2005-01) from the State Key Laboratory of Environmental Aquatic Chemistry, Research Center of Eco-Environmental Sciences Chinese Academy of Sciences.

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