

Degradation of commercial azo dye reactive Black B in photo/ferrioxalate system

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Received 3 May 2006; received in revised form 26 October 2006; accepted 26 October 2006

Available online 1 November 2006

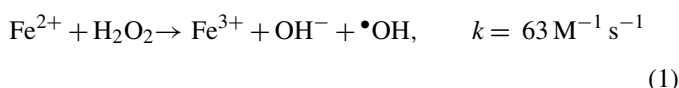
Abstract

The photolysis and photo-catalysis of ferrioxalate in the presence of hydrogen peroxide with UV irradiation (UV/ferrioxalate/H₂O₂ process) for treating the commercial azo dye, reactive Black B (RBB), is examined. An effort is made to decolorize textile effluents at near neutral pH for suitable discharge of waste water. pH value, light source, type of initial catalyst (Fe³⁺ or Fe²⁺) and concentration of oxalic acid (Ox) strongly affected the RBB removal efficiency. The degradation rate of RBB increased as pH or the wavelength of light declined. The optimal molar ratio of oxalic acid to Fe(III) is three, and complete color removal is achieved at pH 5 in 2 h of the reaction. Applying oxalate in such a photo process increases both the RBB removal efficiency and the COD removal from 68% and 21% to 99.8% and 71%, respectively.
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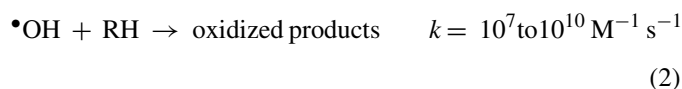
Keywords: Reactive dye; Wastewater; Advanced oxidation processes; Photo-Fenton; Ferrioxalate

1. Introduction

Advanced oxidation processes (AOPs) are the conventional used approaches for treating dye wastewater. Most of them, including heterogeneous photocatalytic oxidation [1–3], treatment with ozone (often combined with H₂O₂, UVA or both) [4–6], and H₂O₂/UV systems [7–10], involve the generation of highly reactive hydroxyl radicals (•OH). Various studies [11–14] have demonstrated that numerous organic pollutants, including phenol, chlorophenols, chlorobenzene, and others can be treated by Fenton's reagents,



because, the •OH radicals produced in the reaction are strongly oxidizing, non-selective and able to decompose numerous organic compounds, including dyes and pesticides. Several researchers have proposed the mechanism of the degradation of organic molecules by •OH radicals:

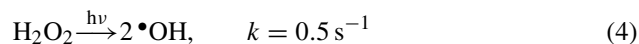


The rate of destruction of organic pollutants and the extent of mineralization can be considerably increased by using an Fe(II,III)/H₂O₂ reagent irradiated with near-UV and/or visible light [15–18], in a reaction that is called the “photo-Fenton reaction”. Photo-enhancement is thought to be described by,

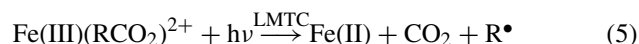
- (1) Photoreduction of ferric ion to ferrous ion [19–21]:



- (2) Photolysis of hydrogen peroxide [22]:



- (3) Photodecarboxylation of ferric carboxylate complexes [19]:

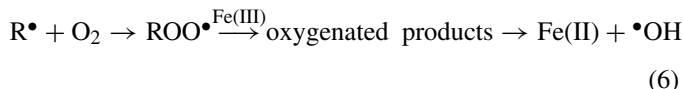


In a photo-Fenton system, most hydroxyl radicals (•OH) are formed by the conventional Fenton reaction (Eq. (1)), and by the photolysis of ferric species (Eq. (3)). Eq. (3) also reveals that the acceleration of degradation by irradiation is caused by

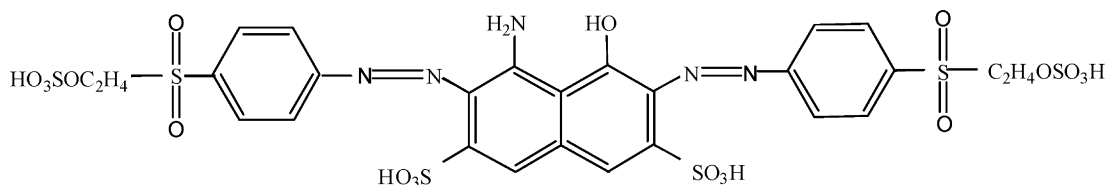
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the photoreduction of Fe(III) to Fe(II) ions, a step that produces new HO• radicals and regenerates Fe(II) ions that can react further with more H₂O₂ molecules. Since the maximum absorption wavelength of Fe(OH)²⁺ species is less than 400 nm, visible irradiation (>470 nm) [23] may not drive the reaction (Eq. (3)); accordingly, UV light is more effective.

As complexing ligands are present in the photo-Fenton system, Eq. (5) should be considered. Fe(III) complexes of oligocarboxylic acids in the UV–Vis absorbance are photolyzed through a ligand-to-metal charge transfer (LMCT) reaction (Eq. (5)), yielding Fe²⁺ and HO• with high quantum yields, even in the absence of H₂O₂ (Eq. (6)):

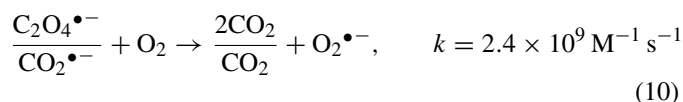
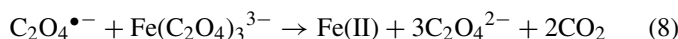
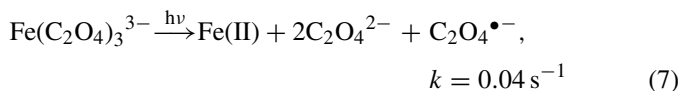


The ferrioxalate complex Fe(C₂O₄)₃³⁻ is the best known and most extensively studied Fe(III)–polycarboxylate complex. It is



Chemical structure of dye-Reactive Black B (RBB)

a popular actinometer and is used extensively to measure light intensity [24]. Irradiation of ferrioxalate has been suggested to proceed as follows in acid solution.



In air-saturated solution at pH 3, the intermediate oxalate radical reacts with molecular oxygen and generates the hydroperoxyl radical (O₂^{•-}) which disproportionates to form H₂O₂ [25–27]. The ferrous ion formed in reactions (7) and (8) can react with the H₂O₂ that is present in solution to generate hydroxyl radicals (Eq. (1)). Hence, the photolysis of ferrioxalate in the presence of H₂O₂ is a continuous source of Fenton's reagent. Furthermore, the irradiation of ferric ions in the presence of carboxylic acids (including oxalic acid, [28]) induces the oxidation of the acid, releasing carbon dioxide [19], greatly favoring the application of oxalic acid in the photo-Fenton system, because, it can be further decarboxylated and completely mineralized.

The use of ferrioxalate in the photo-Fenton reaction to degrade organic pollutants in acidic media at approximately pH 3 has been reported to be highly effective [29,30]. However, the main

goal of this investigation is to maintain a pH of 5, which was selected tentatively to simulate natural bodies of water (pH 5–9) for suitable discharge to be more environmental friendly.

2. Experimental

2.1. Materials

Reactive dye-Black B was purchased from Aldrich. For reference, the structure of the reactive dye-Black B is displayed as the target dye used in all trials. Hydrogen peroxide (50 wt%) solution was obtained from Union Chemical Works (Taiwan). Ferric sulfate and ferrous sulfate were purchased from Hayashi Pure Chemical (Taiwan). Oxalic acid was purchased from J.T. Baker (India). Other chemicals used herein, including perchloric acid and sodium hydroxide, were of reagent grade and used to adjust pH. All sample solutions were prepared using DI water from the Millipore Milli-Q system.

2.2. Experimental procedures and analysis

The photo-enhancement of the RBB degradation reactions in a batch photoreactor (Fig. 1) at room temperature was evaluated using irradiation at an intensity of 5.4 mW cm⁻². The irradiation source was a set of three 15 W UVA lamps (UVP

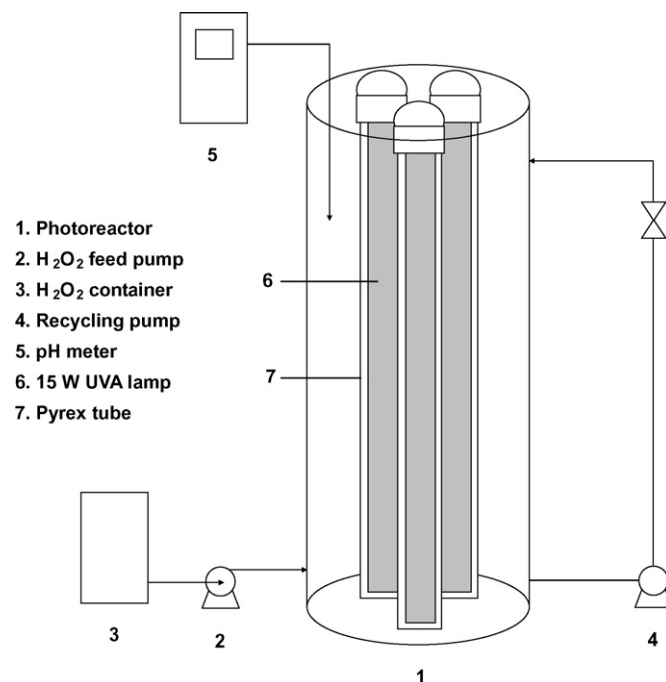


Fig. 1. Experimental photoreactor.

BL-15 365 nm) fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate), and the irradiation sources of the other two long wavelength (440 nm and 550 nm) emitting lamps for compared experiment were both the same set of three 18 W lamps. After oxalic acid and iron catalyst (Fe(II) or Fe(III)) was added to 500 mg/L (0.553 mM) RBB solution (around 1.5 L), the pH of the solution was adjusted and then the UV light turned on to initiate the reaction. The volume of all reactive solutions was 1.5 L in each trial. The optimal amount of 400 mg/L (11.765 mM H_2O_2) hydrogen peroxide (<theoretical demand of 530 mg/L) as oxidant was estimated, and it was supplied to the system at the beginning of the reaction. The residual H_2O_2 level was measured by the titanium sulfate method [31]. The COD was measured by the potassium dichromate approach (NIEA W515.53A), published by USEPA [32].

The residual dye level was measured after NaOH was added to each sample to raise the pH to precipitate ferric ions, and thus, terminate the reaction. The absorption of RBB is maximum at $\lambda_{\text{max}} = 591$ nm and the color removal of RBB was determined using a UV–Vis spectrophotometer (Jasco Model 7850). The Fe^{2+} ions (re)generated during the degradation of dye in all of the processes was determined using the 1,10-phenanthroline method [33]. The Fe(II)-phenanthroline complex was evaluated spectrophotometrically at $\lambda_{\text{max}} = 510$ nm. RBB and its degraded intermediates caused no color interference during this determination, because their absorptions are almost zero at $\lambda = 510$ nm. All samples were analyzed immediately after sampling to prevent further reactions.

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments on 500 mg/L RBB degradation at pH 5 were conducted using 400 mg/L H_2O_2 and 5 mg/L (0.09 mM) iron which was selected below regulation criteria of discharge (10 mg/L) [34] for Fenton, Fenton-like and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ process. As displayed in Fig. 2, the Fenton-like process exhibited the lowest RBB removal efficiency. The removals of RBB by the Fenton-like, Fenton and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ processes are 19%, 65% and 68%, respectively. The residual COD in each process still considerably exceeds 100 mg/L, the maximum allowed criteria of discharge [34]. The degradation rate of RBB by the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ process is initially much lower than that of the Fenton process, but finally greater. Clearly, as indicated in other works, the initial delay time of the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ process can always be found (curve \blacktriangle in Fig. 2), because the photosensitivity of Fe(III) is much lower than that of Fe(II), hence, the initial $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ process conducted Fenton-like reaction. In the latter part of the reaction (after approximately 2 h), the RBB removal efficiency in curve \blacktriangle is maximized since the intermediates of RBB degradation, such as carboxylic acid, promote the reduction of Fe(III) ions to Fe(II) ions, preventing the formation of sludge as the precipitation of $\text{Fe}(\text{OH})_3$.

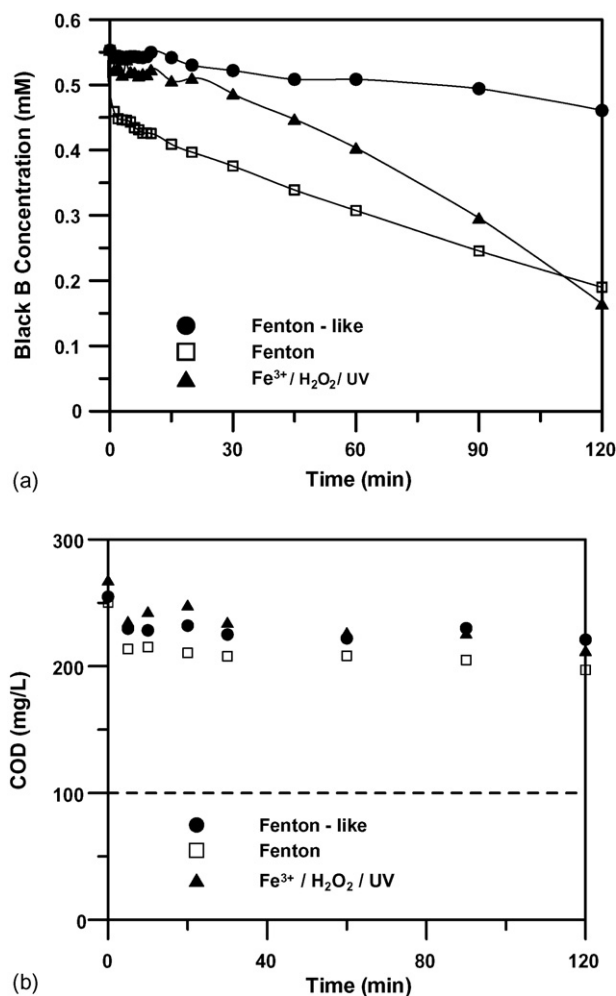


Fig. 2. Preliminary experiments of Black B degradation at pH 5 with different technologies: (●): $[\text{Fe}^{3+}] = 5$ mg/L, $[\text{H}_2\text{O}_2] = 400$ mg/L; (□): $[\text{Fe}^{2+}] = 5$ mg/L, $[\text{H}_2\text{O}_2] = 400$ mg/L; (▲): $[\text{Fe}^{3+}] = 5$ mg/L, $[\text{H}_2\text{O}_2] = 400$ mg/L, UV light (5.4 mW cm^{-2}) ((a) Black B concentration vs. reaction time; (b) COD vs. reaction time).

3.2. Effect of pH and addition of oxalate

The Fenton process is highly efficient at pH 2–4, and the optimal pH value is 2.8, as suggested by Pignatello et al. in 1992 [35]. In this work, the pH of the solution was well controlled in the range 4–6 in all trials. Fig. 3 displays the effect of pH on the degradation of RBB in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ process. The results demonstrate that the degradation of RBB at pH 4 is faster than that at pH 5 or 6, since $\text{Fe}(\text{OH})_3$ is formed at pH 5 and 6. This latter compound has poor catalytic ability and cannot be regenerated to the ferrous ion. Fig. 4 displays similar results of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ process. All three curves at pH 4–6 abruptly drop in 1 min, but the efficiency declines after 1 min, perhaps because of the rapid oxidation of ferrous ions, returning them mostly to the Fenton-like reagent. Although UV irradiation promotes the regeneration of ferrous ions, it was not very effective at such a high pH (>4).

For the reasons described above, the oxalate was added to increase the effectiveness of such photo processes ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{Ox}/\text{UV}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{Ox}/\text{UV}$), as displayed in

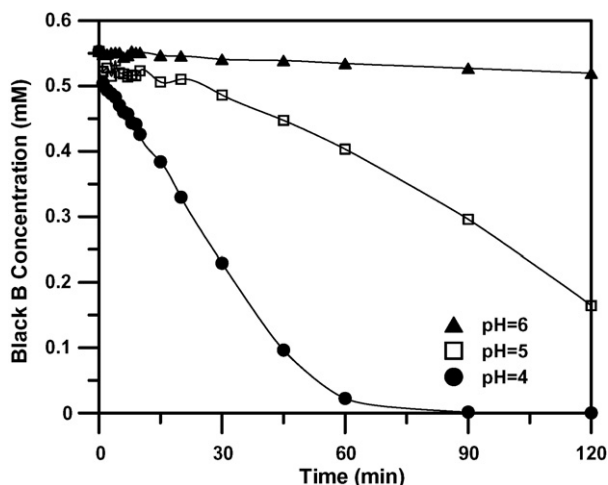


Fig. 3. Black B degradation with $[\text{Fe}^{3+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, UV light (5.4 mW cm^{-2}) at different pH value.

Figs. 5 and 6. Comparing Fig. 5 with Fig. 3 reveals that the removal efficiencies of RBB at pH 4, 5 and 6 increase from 96%, 23% and 3%, to 99%, 88% and 41%, respectively, after 60 min. Accordingly, ferrous ions could be continuously supplied as Fenton's reagent by the photoreduction of the ferrioxalate. Similar results are displayed in Fig. 6, in which Fe^{3+} was converted to Fe^{2+} .

The amount of oxalate (Ox) added is not an arbitrary parameter in these photo processes. Therefore, it should be further examined.

3.3. Effect of ferrioxalate concentration $[\text{Ox}]/[\text{Fe}^{3+}]$ ratio

Some of the intermediates (carboxylic acids) that are formed during the oxidation of organic pollutants can react with and activate Fe(III) ions in solution (via reaction (5)). It was confirmed and discussed above, in the UV/ferrioxalate/ H_2O_2 process at pH 5, RBB was effectively destroyed as oxalic acid was added. A different $[\text{Ox}]/[\text{Fe}^{3+}]$ molar ratio (based on $[\text{Fe}^{3+}] = 5 \text{ mg/L}$) was considered to realize the effect of the oxalate concentration in

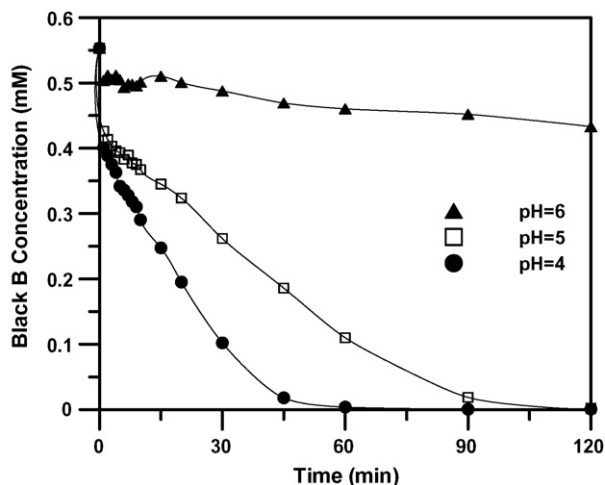


Fig. 4. Black B degradation with $[\text{Fe}^{2+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, UV light (5.4 mW cm^{-2}) at different pH value.

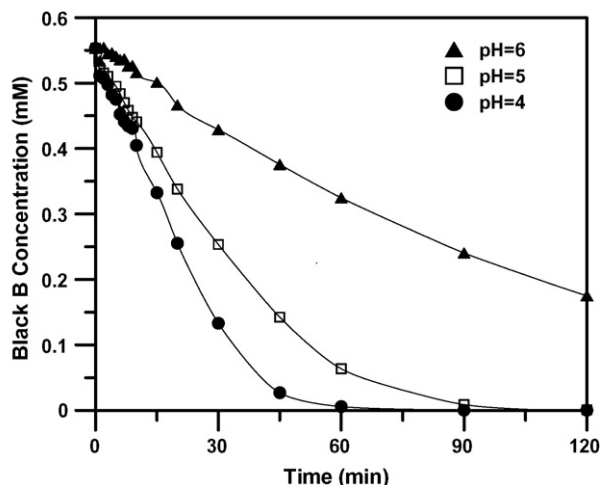


Fig. 5. Black B degradation with $[\text{Fe}^{3+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, UV light (5.4 mW cm^{-2}), and $[\text{Ox}]/[\text{Fe}^{3+}] = 3$ at different pH value.

this system. Fig. 7 displays the effect of the $[\text{Ox}]/[\text{Fe}^{3+}]$ molar ratio on the degradation of RBB by the UV/ferrioxalate/ H_2O_2 process (for $[\text{Ox}]/[\text{Fe}^{3+}]$ molar ratios from 1 to 5). Fig. 7(a) indicates that the rate of destruction of dye-Black B in the presence of ferrioxalate is much higher than that in the presence of Fe(III) alone, because of greater absorption of UV and a higher quantum yield of ferrous ions regenerated from ferrioxalate, promoting the supply of $\bullet\text{OH}$ radical by such a Fenton's reagent (regenerated Fe(II) ions) and of additional H_2O_2 from the hydroperoxyl radicals ($\text{O}_2^{\bullet-}$), by reactions (7)–(10).

The effect of oxalate concentration on the color removal of RBB (Fig. 7(b)) is rather similar to that on degradation of RBB (Fig. 7(a)). Both the color and efficiencies of RBB removal increased with the $[\text{Ox}]/[\text{Fe}^{3+}]$ molar ratio up to three, beyond which they declined, because at an $[\text{Ox}]/[\text{Fe}^{3+}]$ molar ratio of 3, the Fe(III) ions were complexed with the maximum amount of oxalate, in the form of the saturated complex $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ (which is a ferric ion complexed with three oxalate molecules as its limit load). When irradiated by UV, the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ com-

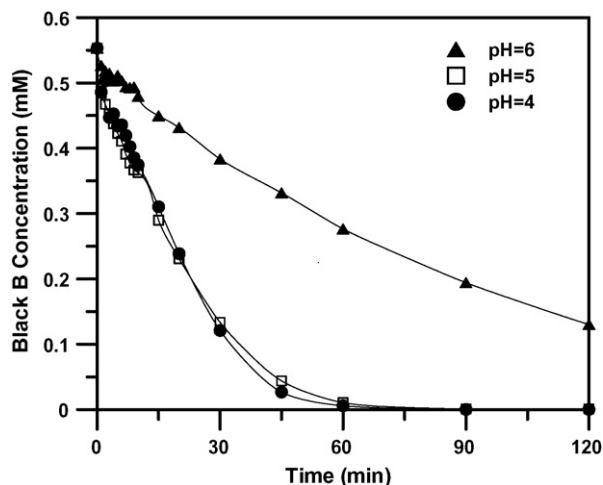
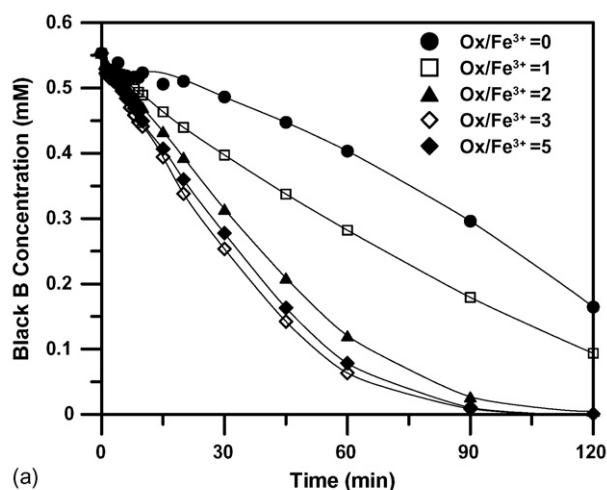
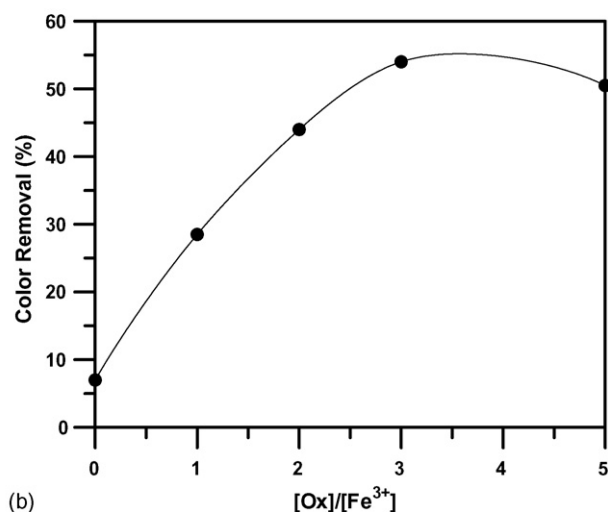


Fig. 6. Black B degradation with $[\text{Fe}^{2+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, UV light (5.4 mW cm^{-2}), and $[\text{Ox}]/[\text{Fe}^{2+}] = 3$ at different pH value.



(a)



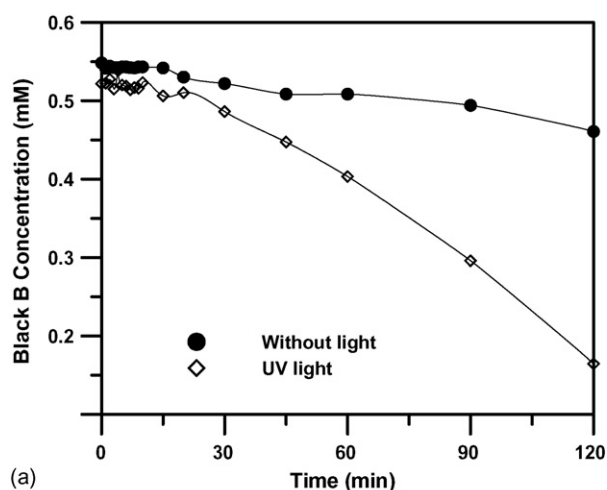
(b)

Fig. 7. Black B degradation at pH 5 with $[\text{Fe}^{3+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, and UV light (5.4 mW cm^{-2}) with different $[\text{Ox}]/[\text{Fe}^{3+}]$ ratio (a) Black B concentration vs. reaction time; (b) color removal vs. $[\text{Ox}]/[\text{Fe}^{3+}]$ ratio at 30 min).

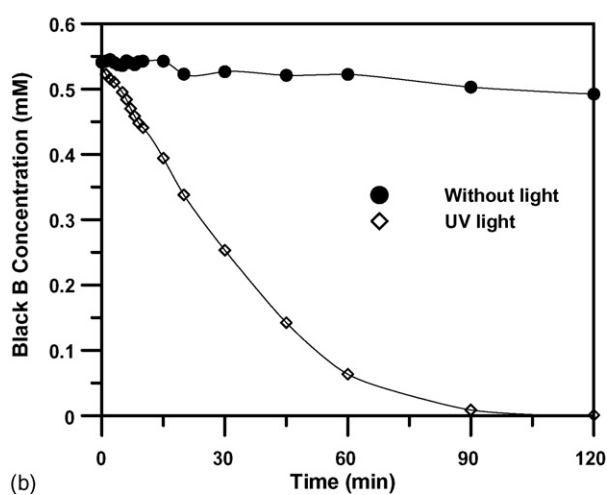
plex ions eventually become CO_2 and are regenerated as ferrous ions in reaction (7)–(10). However, when the molar ratio is under 3, some of the ferric ions precipitate as $\text{Fe}(\text{OH})_3(\text{s})$ because insufficient oxalate is present, reducing the efficiency of Fe^{2+} ion regeneration. In contrast, the efficiency declined as molar ratio increased ($[\text{Ox}]/[\text{Fe}^{3+}] > 3$), perhaps because the excess oxalate could not complex with more ferric ions in solution. Restated, the excess oxalate acts just as an additional organic compounds, such that competing the $\bullet\text{OH}$ radicals with the RBB, reducing the efficiency of RBB degradation.

3.4. Effect of light

As expected, the rate of destruction of organic pollutant by ferrioxalate/ H_2O_2 depends on the intensity and the wavelength of the irradiating UV. A Philips UV light ($\lambda = 365 \text{ nm}$) at pH 5 was adopted to determine whether the oxalate was present, and thus, clarify the effect of UV. Fig. 8(a) reveals that in the absence of oxalate, 2 h of UV irradiation increases the removal of RBB only increased from 16% to 69%. This result verified again



(a)



(b)

Fig. 8. Black B degradation at pH 5 with $[\text{Fe}^{3+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, and with UV light source (5.4 mW cm^{-2}) or not (a) $[\text{Ox}]/[\text{Fe}^{3+}] = 0$; (b) $[\text{Ox}]/[\text{Fe}^{3+}] = 3$.

that although UV light ($\lambda = 365 \text{ nm}$) promotes the reduction of ferric ions (reaction (3)) the fraction reduced at pH 5 is small. However, in the presence of oxalate, as displayed in Fig. 8(b), the efficiency of removal can reach 98% at $[\text{Ox}]/[\text{Fe}^{3+}] = 3$ after irradiation for 90 min.

Wu et al. [36] applied visible light and solar irradiation ($\lambda > 470 \text{ nm}$) to the degradation of dye MG. We adopted various wavelengths of light to confirm that UV light can be applied to such a ferrioxalate/ H_2O_2 process. Fig. 9 displays the different light intensities and wavelengths applied herein. Visible light ($\lambda = 440 \text{ nm}$) and fluorescent light ($\lambda = 550 \text{ nm}$) were compared under the conditions of the aforementioned experiments with UV light ($\lambda = 365 \text{ nm}$), pH 5, $[\text{Fe}^{3+}] = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, and $[\text{Ox}]/[\text{Fe}^{3+}] = 3$. Fig. 10(a) indicates complete removal after 2 h of UV irradiation, but only 88% under irradiation by visible light and 87% using fluorescent light. The COD residuals in Fig. 10(b) obtained using either of the light sources exceeded the water effluent standard even after 210 min.

Since the maximum absorption wavelength of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ species is less than 440 nm, visible irradiation ($> 470 \text{ nm}$) may not drive the reaction of Eq. (7) [37], leading to a large quantum

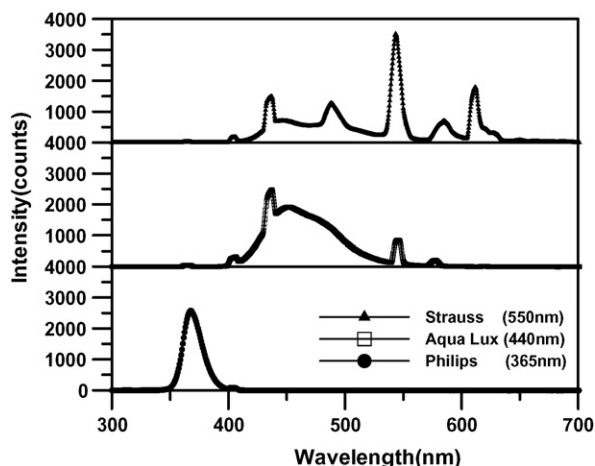
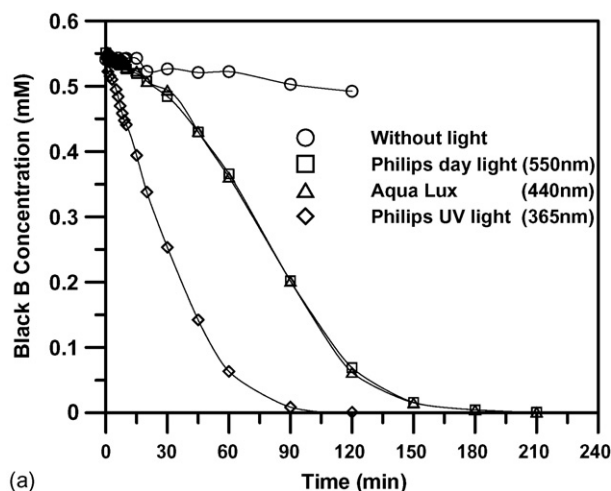
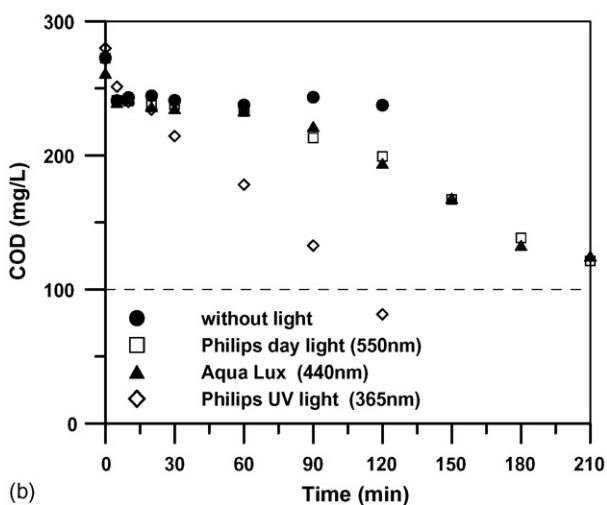


Fig. 9. Properties of different light intensities and wavelengths (●): Philips (UV light, $\lambda = 365$ nm); (□): Aqua Lux (visible light, $\lambda = 440$ nm); (▲): Strauss (fluorescent light, $\lambda = 550$ nm).



(a)



(b)

Fig. 10. Black B degradation at pH 5 with $[\text{Fe}^{3+}] = 5$ mg/L, $[\text{H}_2\text{O}_2] = 400$ mg/L, $[\text{Ox}]/[\text{Fe}^{3+}] = 3$, and UV light (5.4 mW cm^{-2}) with different wavelength of light source ((a) Black B concentration vs. reaction time; (b) COD vs. reaction time).

yield. The higher energy of UV may also reduce ferricoxalate more efficiently.

4. Conclusion

This study compares various AOP processes in treating the commercial azo dye, reactive Black B. The processes of interest are the Fenton reaction, the Fenton-like reaction, the UV/ferrous oxalate/ H_2O_2 process and the UV/ferrioxalate/ H_2O_2 process. In the presence of oxalate, the removal efficiency of RBB by Fe^{2+} complex catalyst (UV/ferrous oxalate/ H_2O_2) exceeded that obtained using the Fe^{3+} complex catalyst (UV/ferrioxalate/ H_2O_2). Dye RBB is degraded very effectively by such a ferrioxalate/ H_2O_2 process under UV irradiation for aqueous solutions at near neutral pH. These results are very helpful in elucidating the mechanism of the photodegradation of dyes in natural bodies of water (pH 5–9). In the presence of oxalate, completely decoloration and low residual COD (under the water effluent standard) were achieved, The RBB removal efficiency was substantially increased to 99%, considerably exceeding that obtained without oxalate at neutral pH (classic photo-Fenton process). Therefore, the proposed procedure has great potential and can be practically implemented in industry.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC94-2211-E-006-032.

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