

Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton

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Abstract

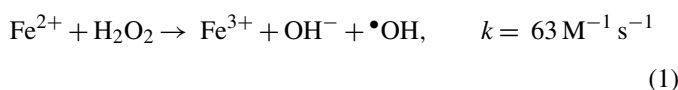
This study makes a comparison between photo-Fenton and a novel electro-Fenton called Fered-Fenton to study the mineralization of 10,000 mg/L of dye-Reactive Black B (RBB) aqueous solution, which was chosen as the model dye contaminant. Results indicate that the traditional Fenton process only yields 70% mineralization. This result can be improved by using Fered-Fenton to yield 93% mineralization resulting from the action of ferrous ion regenerated on the cathode. Furthermore, photo-Fenton allows a fast and more complete destruction of dye solutions and as a result of the action of ferrous ion regenerated by UV irradiation yields more than 98% mineralization. In all treatments, the RBB is rapidly decayed to some carboxylic acid intermediates. The major intermediates found are formic acid and oxalic acid. This study finds that formic acid can be completely mineralized by photo-Fenton, but its destruction is problematic using the Fenton method. Oxalic acid is much more difficult to treat than other organic acids. It could get further mineralization with the use of the Fered-Fenton process.

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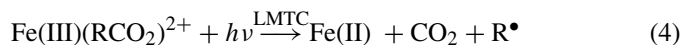
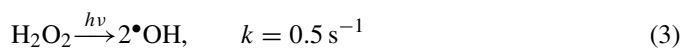
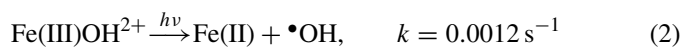
Keywords: Advanced oxidation processes (AOPs); Fenton; Fered-Fenton; Photo-Fenton; Mineralization

1. Introduction

Most azo dye compounds are resistant to bacterial activity, and direct biological treatment is not effective [1,2]. Consequently, alternative technology must be developed to help solve the problem. Advanced oxidation processes (AOPs) have been developed for the destruction of certain pollutants in water. The most frequently used AOPs include: heterogeneous photocatalytic oxidation [3–5], treatment with ozone (often combined with H₂O₂, UVA or both) [6,7], and H₂O₂/UV systems [8–10]. Many studies [6–12] have shown that a variety of organic pollutants, such as phenol, chlorophenols, chlorobenzene, etc., can be treated by Fenton's reagents (reaction (1)):



This catalytic reaction is propagated from Fe²⁺ regeneration, which mainly takes place as a result of the reduction of Fe³⁺ species with H₂O₂. When a H₂O₂/Fe³⁺/UV (photo-Fenton system) process is utilized, UV light can accelerate the mineralization process through the following possible pathways: (i) the enhancement of Fe²⁺ regeneration from the additional photo-reduction of Fe³⁺ species [13–16]; (ii) the photolysis of hydrogen peroxide [17]; and (iii) the photolysis of complexes of Fe³⁺ with some oxidation products, such as oxalic acid [11,13] from the following reactions:



A slow reaction of Eq. (2) will occur only when no complexing ligands are present. As complexing ligands exist in a photo-Fenton system, reaction (4) should be considered. Fe(III) complexes of oligocarboxylic acids that absorb in the UV–vis

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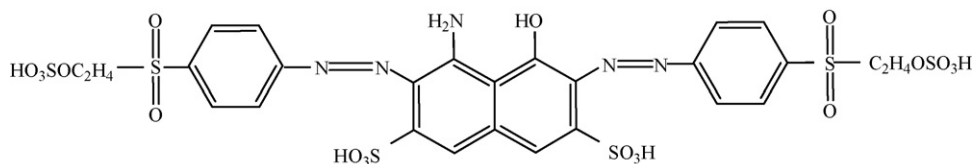
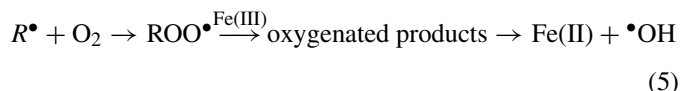


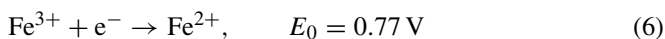
Fig. 1. Chemical structure of dye-Reactive Black B (RBB).

range are photolyzed through a ligand to metal charge transfer (LMCT) reaction (reaction (4)), yielding Fe^{2+} and HO^\bullet with good quantum yields, even in the absence of the H_2O_2 (reaction (5)):

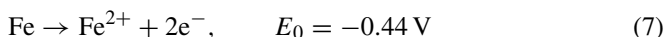


Recently, there has been great interest in the use of electro-Fenton [18–22] for mineralization of toxic organic pollutants in an aqueous medium. These studies applied a kind of electro-Fenton, called Fered–Fenton [23–25] to treat RBB. Its electromotive force of reduction is greater than that of oxidation, meaning it is much easier to obtain ferrous ions using this kind of electrolysis (E_0 is standard reduction potential):

Reduction reaction:



Oxidation reaction:



The aim of this work is to clarify whether RBB can be efficiently mineralized by Fered–Fenton or photo-oxidation methods. To do this, the degradative behavior of concentrated solutions with 10,000 mg/L of RBB was studied. This paper reports a comparative study on the treatment of the RBB by Fered–Fenton and photo-Fenton.

2. Experimental

2.1. Materials

Dye-Reactive Black B (RBB) (55 wt%) was purchased from Aldrich. For reference, the structure of RBB is shown in Fig. 1 as a target dye used in all the 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 in this study include reagent grade perchloric acid and/or sodium hydroxide used for adjusting pH. All sample solutions were prepared with deionized (DI) water from the Millipore Milli-Q system.

2.2. Experimental procedures

The Fenton and Fered–Fenton processes were carried out in an electrolysis reactor system (6 cm × 6 cm cross-section area

and 120 cm height) that was ever used in our previous study [26]. All the reaction solutions were mixed by a circulation pump with a dosage of 500 mg/L or 200 mg/L [Fe^{2+}] and continuous H_2O_2 (~22,000 mg/L as the optimum dosage based on the theoretical chemical oxygen demand (COD) of $[\text{RBB}]_i = 10,000 \text{ mg/L}$) was supplied to the system at room temperature. The anode was a titanium (Ti) rod coated with $\text{IrO}_2/\text{RuO}_2$ (DSA) and the cathode was a stainless steel net (Fig. 2). The working area of the anode and cathode was maintained at a ratio of 1:8 in order to keep a much greater reaction area of the cathode available for Fe^{2+} regeneration rather than for side reactions on the anode. The power supply was turned on for the Fenton reaction. Similarly, UV light (15 W UVA lamp (UVP BL-15 365 nm) fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320 \text{ nm}$ to

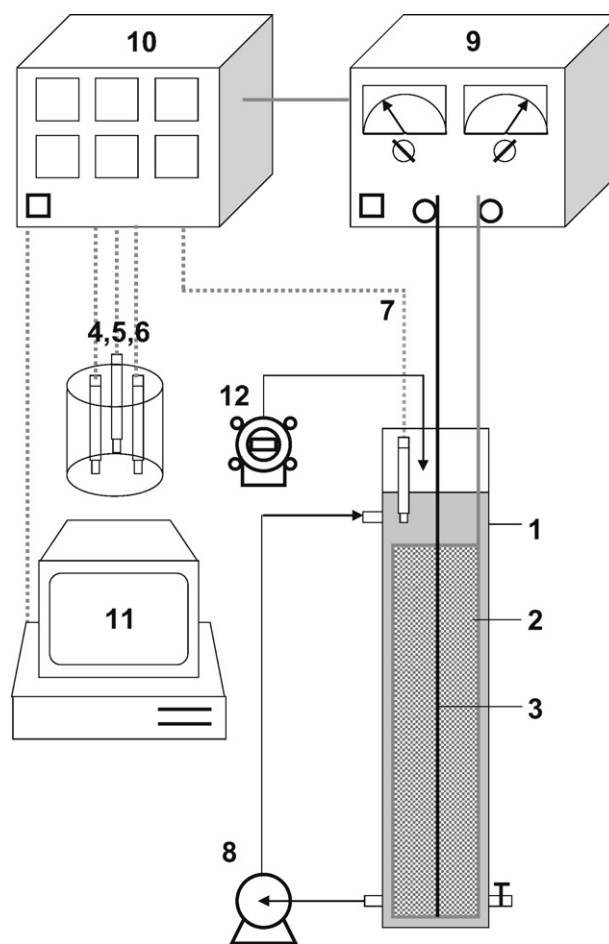


Fig. 2. Experimental equipment (for Fered–Fenton and photo-Fenton processes). (1) Reactor; (2) cathode (stainless steel); (3) anode (DSA rod); (4) pH meter; (5) ORP meter; (6) electric conductivity meter; (7) thermometer; (8) circulating pump; (9) power supply; (10) meter; (11) monitor; (12) H_2O_2 supply.

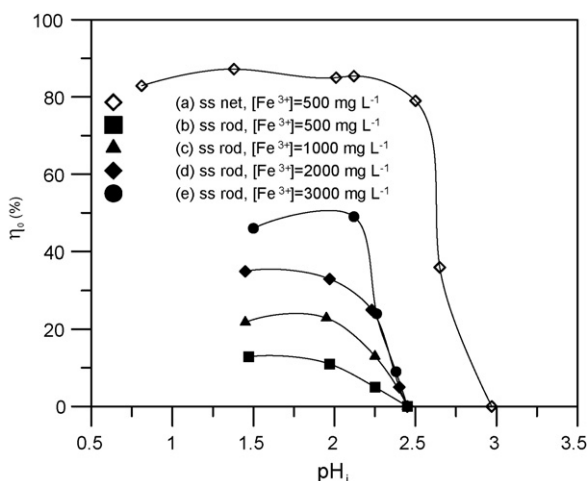


Fig. 3. Effect on current efficiencies using pH_i and Fe^{3+} concentrations at $\text{CDc} = 35.4 \text{ A/m}^2$.

pass)) was used in the same reactor mentioned above for the photo-Fenton process. All the volumes of the reactive solutions were about 1.5 L for each trial. After adding the RBB solution with an iron catalyst and adjusting the pH of the solution (pH_i 2.0–2.3) (avoiding $\text{Fe}(\text{OH})_3$ generation), thus achieving the best current efficiency (see Fig. 3), we turned on the power supply or the UV light ($\lambda = 365 \text{ nm}$) to initiate the reaction. Simultaneously, the hydrogen peroxide was estimated and continuously supplied into the system at the beginning of the reaction.

2.3. Analysis

The residual H_2O_2 level was measured using the titanium sulfate method [27] to calculate the remaining amount of H_2O_2 during the reaction or in sampling. After sampling and quenching (i.e. adding NaOH), all the samples were placed overnight to ensure no H_2O_2 remained (checking no color present by UV–vis spectrophotometer using the titanium sulfate method), thus, the COD of the residual dye solution could be measured using the potassium dichromate approach (NIEA W515.53A), published by USEPA [28].

Likewise, the residual dye level was measured after adding NaOH (1 wt%) to each sample to raise the pH (>4) to precipitate ferric ions, and thus terminate the reaction. After sampling following the addition of NaOH and filtrating, all the carboxylic acids (intermediates, i.e. formic acid and oxalic acid) were detected by ion-exclusion chromatography with a 4 mm I.D. \times 150 mm L A SUPP 5-150 column (Metrohm, USA) which did not interfere with the residual H_2O_2 . The constituent of standard eluent was 339 mg/L sodium carbonate solution. The absorption of RBB was maximum at $\lambda_{\text{max}} = 591 \text{ nm}$, and the color removal of RBB was determined using a UV–vis spectrophotometer (Jasco Model 7850) after a suitable dilution (200-folds dilution). The Fe^{2+} ions (re)generated during the degradation of dye in all of the processes were determined using the 1,10-phenanthroline method [29]. The $\text{Fe}(\text{II})$ –phenanthroline complex was evaluated spectrophotometrically at $\lambda_{\text{max}} = 510 \text{ nm}$. RBB and its degraded

intermediates caused no color interference during this determination because their absorptions were almost zero at $\lambda = 510 \text{ nm}$. All samples were analyzed immediately after sampling to prevent further reactions.

3. Results and discussion

3.1. Comparative performance for Fenton, electro-Fenton and photo-Fenton

All methods applied in this study gave a progressive mineralization of 10,000 mg/L RBB solutions with an increasing reaction time. Reproducible values for COD removal were obtained under all experimental conditions tested. No obvious mineralization of RBB solutions was found after direct irradiation with UV light only. It was also found that no further mineralization occurred after adding more than a 16,000 mg/L H_2O_2 dosage, indicating that more potent oxidizing agents are produced in such electrochemical treatments.

As seen in preliminary experiments, it can be found from Fig. 4(a–c) that the result using a Fe^{2+} -coagulation method is much better than that of the Fe^{3+} -coagulation method. It was found that no precipitation occurred during the setting period in the Fe^{2+} -coagulation process. This may be due to the chelation of Fe^{3+} by RBB. Therefore, the small reduction of COD is due to the dilution resulting from the addition of Fe^{3+} . This can be proved by a comparison of Fig. 4(a) with Fig. 4(c). However, there is a large amount of precipitation corresponding to a 28% removal of COD by the use of Fe^{2+} -coagulation. It can also be verified from Fig. 4(b) that the Fe^{2+} -coagulation method supported decolorization, especially with regard to the absorption at $\lambda = 597 \text{ nm}$.

In any case, the Fe^{2+} -coagulation method can effectively decolorize RBB but is not very useful for COD removal. Therefore, the huge amount of $\text{Fe}(\text{II,III})$ ions generated by the use of the $\text{Fe}(\text{II,III})$ -coagulation method will totally work against the purpose of sludge decrement. Based on the reasons described above, the application of the $\text{Fe}(\text{II,III})$ -coagulation method as a preliminary treatment is not suggested due to the cost and benefit concerns.

To illustrate the behavior of RBB degradation, Fig. 5(a) shows the comparative COD decay found for a 10,000 mg/L RBB solution. The COD– H_2O_2 dosage plots related to the Fenton treatment show a significantly lower COD removal of RBB and its byproducts, confirming the low oxidative ability of such methods. Comparison of curves in Fig. 5(a) allows the conclusion that mineralization is obviously enhanced in the presence of additional electric current or UV light irradiation, since under these conditions, the solution COD removal is increased to 92.7% by Fered–Fenton and to 98.6% by photo-Fenton at a 22,000 mg/L H_2O_2 dosage, much better than by only 68.5% as seen in the Fenton process. This tendency can be explained by a significant reaction of pollutants with large amounts of $\bullet\text{OH}$ generated from H_2O_2 using the two superior processes. In comparison, the Fered–Fenton treatment with 500 mg/L Fe^{2+} leads to about 92.7% mineralization at a 22,000 mg/L H_2O_2 dosage (see Fig. 5). This faster degradation can then be asso-

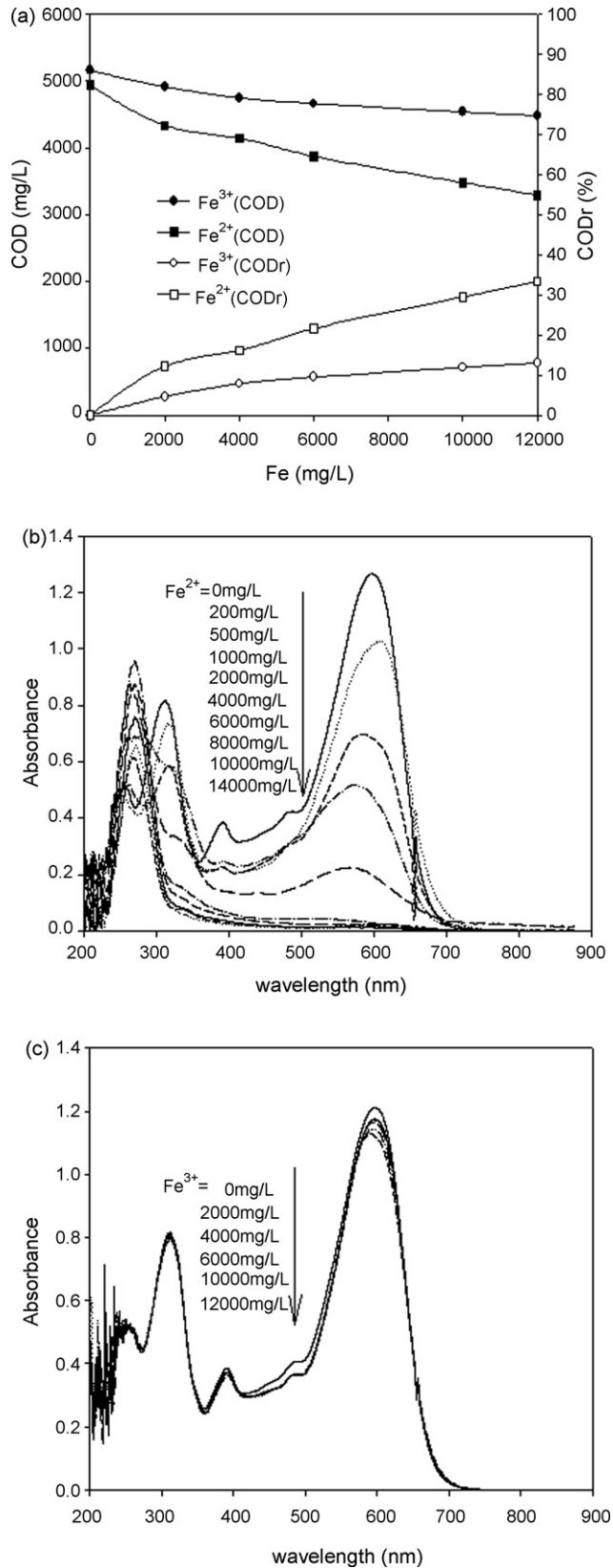


Fig. 4. Effect on COD removal (a) and on decoloration (b and c) of RBB by Fe(II,III) ions (200× dilution for UV–vis spectrophotometer). Fe(II,III) ions were fast-mixed for 5 min with RBB solution at pH 10, and then were re-adjusted to pH 10 for slow-mixing about 15 min. After precipitating, the clear solution was sampled from upper phase for analyzing.

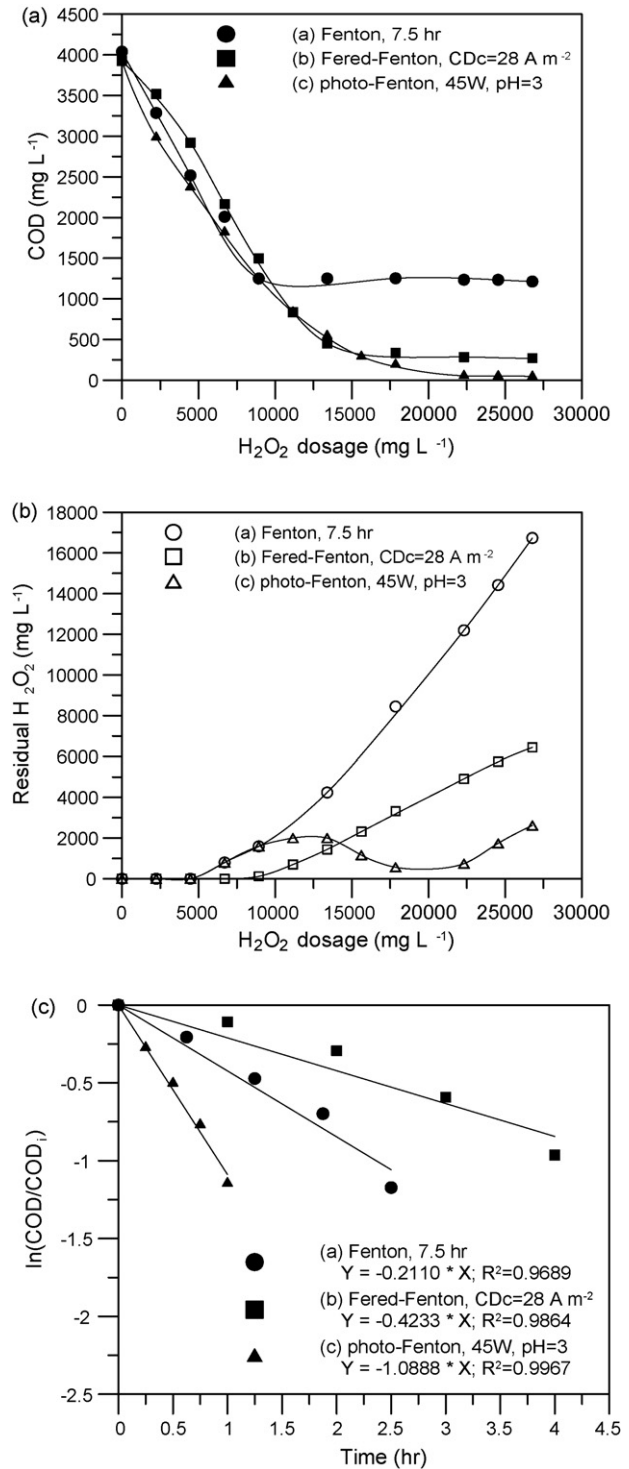


Fig. 5. Comparison of each oxidative technology ([Fe²⁺] = 200 mg/L with a continuous H₂O₂ dosage) including Fenton process at pH 3 for 7.5 h; Fered–Fenton with low CDC = 28 A/m² at pH 2 for 3 h; photo-Fenton with 45 W UV irradiation at pH 3 for 3 h ((a) COD; (b) Residual H₂O₂; (c) removal rate).

ciated with the existence of rapid homogeneous reactions of pollutants with great amounts of $\bullet\text{OH}$ generated in the medium from Fenton's reaction (1). As can be seen in Fig. 5, almost complete mineralization of RBB can be reached by photo-Fenton at 45 W UV light irradiation. The highest COD decay found for this method can be ascribed to the enhancement of the generation rate of $\bullet\text{OH}$ from reaction (3) and additional photolysis of barely oxidizable intermediates under Fered–Fenton conditions.

Correspondingly, the removal rate constants of Fenton, electro-Fenton and photo-Fenton processes are further approached during the same dosage amount of ~ 8925 mg/L H_2O_2 which are 0.4233, 0.2110, and 1.0888, respectively (see Fig. 5(c)).

The degradation in the Fered–Fenton process is not controlled by the diffusion of pollutants towards the DSA anode to react with generated $\bullet\text{OH}$. Its advantages as ascribed previously are due to the higher current utility and the fact that twice the Fe^{2+} amounts as compared to the sacrificed anodic oxidation method are obtained at the anode (see reaction (6)). Like Chou et al. [25], we also proved that a decrease in applied current density causes more COD removal as a result of the higher current efficiency obtained in the operation of lower current density using a stainless steel net cathode of our Fered–Fenton process.

It can be seen from our preliminary experiments (Fig. 6) that the rate control step is conducted by “current density (CDc)”, especially at a higher Fe^{3+} concentration (see below). There are still high current efficiencies ($\eta_0 \sim 90\%$) at $[\text{Fe}^{3+}] = 500$ mg/L and 200 mg/L, but only 40% of the efficiency can be achieved at $[\text{Fe}^{3+}] = 100$ mg/L. Therefore, the “mass transfer resistance” will become the rate control step rather than the original “electrochemical reaction” as compared to decreasing the $[\text{Fe}^{3+}] = 200$ mg/L to 100 mg/L due to the presence of the half current density of $[\text{Fe}^{3+}] = 200$ mg/L.

It was also found in curve (c) ($[\text{Fe}^{3+}] = 500$ mg/L) and curve (b) ($[\text{Fe}^{3+}] = 200$ mg/L) that the more CDc increased the more η_0 decreased. At the CDc = 106 A/m^2 , the rate of the various Fe^{3+}

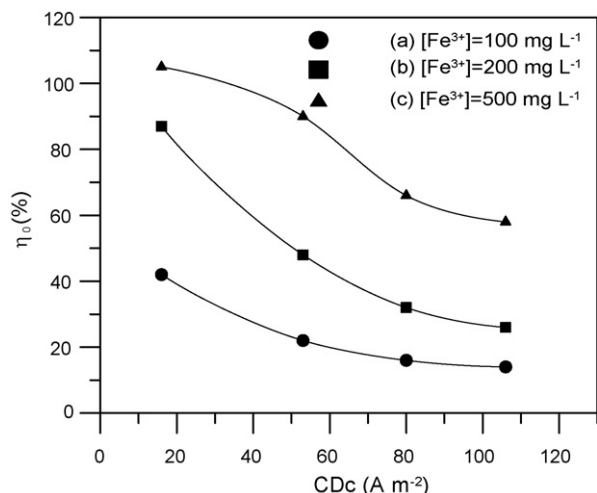


Fig. 6. $[\text{Fe}^{3+}]$ effect on current efficiency with a variation of CDc at pH 2.

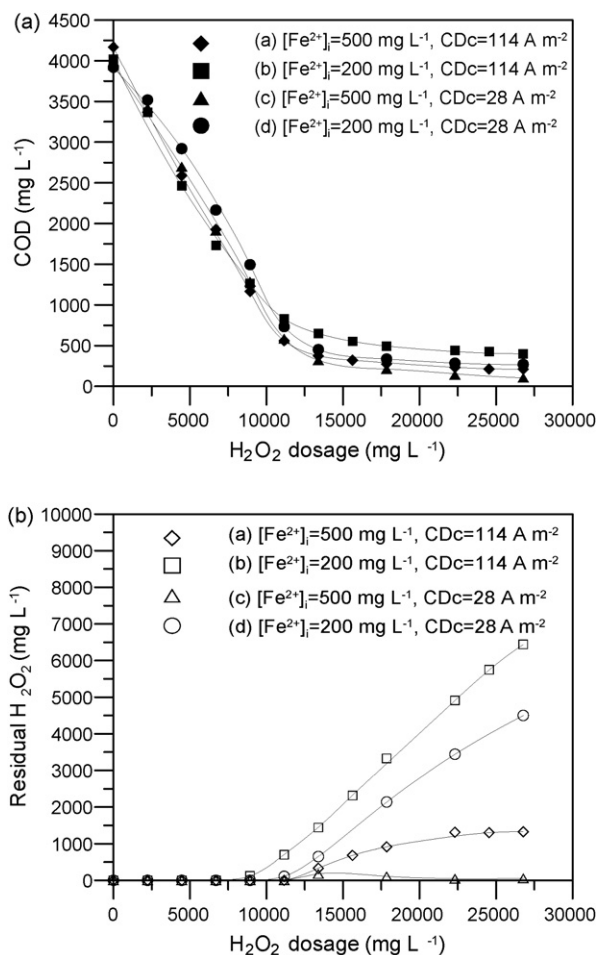


Fig. 7. The COD change with different current densities (high CDc = 114 A/m^2 ; low CDc = 28 A/m^2) and Fe^{2+} concentrations (500 mg/L or 200 mg/L) during treatment of RBB in the Fered–Fenton method ((a) COD; (b) residual H_2O_2).

concentrations is exactly 5:2:1. This refers to that the only one practical way to achieve a high current efficiency at higher CDc is to raise the concentration of Fe^{3+} . But this operational condition will work against the purpose of the ferric sludge decrement, therefore a careful consideration choice should be made between the choice of high current efficiency and the amount of Fe^{3+} as the best experimental condition.

For example, the COD of the RBB solution is decreased to 280 mg/L after a 22,000 mg/L H_2O_2 dosage of anodic oxidation at 114 A/m^2 , whereas under the same H_2O_2 dosages, the COD could be additionally decreased to 169 mg/L at 28 A/m^2 (see Fig. 7). Furthermore, it can also be seen in Fig. 7(a) that a lower COD was reached (curve (c)) as a higher Fe^{2+} concentration ($[\text{Fe}^{2+}] = 500$ mg/L) was present at the same current density (28 A/m^2). This result can be explained by the increase in the collision probability of H_2O_2 with larger Fe^{2+} amounts according to reaction (1), thus favoring its reaction with contaminants and giving better mineralization. Correspondingly, it was proved in Fig. 7(b) that almost no residual H_2O_2 was shown in curve (c) as a result of reaction with sufficient ferrous ions, and the residual H_2O_2 in curve (c) was much less than it was in curve (d).

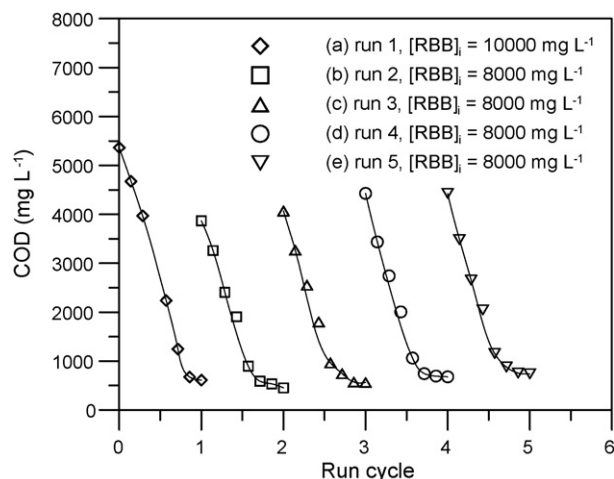


Fig. 8. Reusing efficiencies of Fe^{2+} in treating RBB (recycling efficiencies), regenerated from Fered-Fenton at high current density ($\text{CDc}=144 \text{ A/m}^2$, $[\text{Fe}^{2+}]_0=500 \text{ mg/L}$).

It is worth noting that on the basis of the results for the efficiencies of the ferric sludge reused in the Fered-Fenton presented in Fig. 8, the reusability of regenerated Fe^{2+} (reduced Fe^{3+} by electrolyzing) was examined using the repetition of the cyclic process of Fered-Fenton at the adjusted pH value of 2. Fig. 8 shows four successive cyclic processes in response to the re-treatment in the refilled RBB solution ($[\text{RBB}]_{\text{refilled}}=8000 \text{ mg/L}$). Results showed that all repetitions yielded almost 90% COD removals. Finally, the goal of sludge reduction was reached by this Fered-Fenton method without further disposal and thus led to better economic benefits.

In the photo-Fenton process, a significant reduction of the time required for complete mineralization took place. As can also be seen in Fig. 5, this method allowed nearly total decomposition of the 10,000 mg/L RBB solution after 22,000 mg/L H_2O_2 dosages of photo-catalysis at 45 W UV light irradiation.

In conclusion, the photo-Fenton process is more powerful than the Fered-Fenton process, where very stable products are formed and are then slowly removed as time goes by. A significant increase in COD removal from 83.2% to 98.6% was found after using 22,000 mg/L H_2O_2 dosages when UV irradiation was increased from 15 W to 45 W. This can be explained by the acceleration of the oxidation byproducts (i.e. intermediates) which complexes with Fe^{3+} for photo-catalysis as seen from reaction (4) and the enhancement of Fe^{2+} regeneration according to reaction (5).

3.2. Study of the intermediates

Here, intermediates (formic and oxalic acids) have been detected in the decomposed solutions by ion-exclusion chromatography in order to get a further understanding of the oxidative ability for both Fered-Fenton and photo-Fenton treatments. It can be seen in ion-exclusion chromatograms that two main peaks associated with the carboxylic acids such as formic ($t_r=6.0 \text{ min}$) and oxalic ($t_r=22.5 \text{ min}$) were obtained during

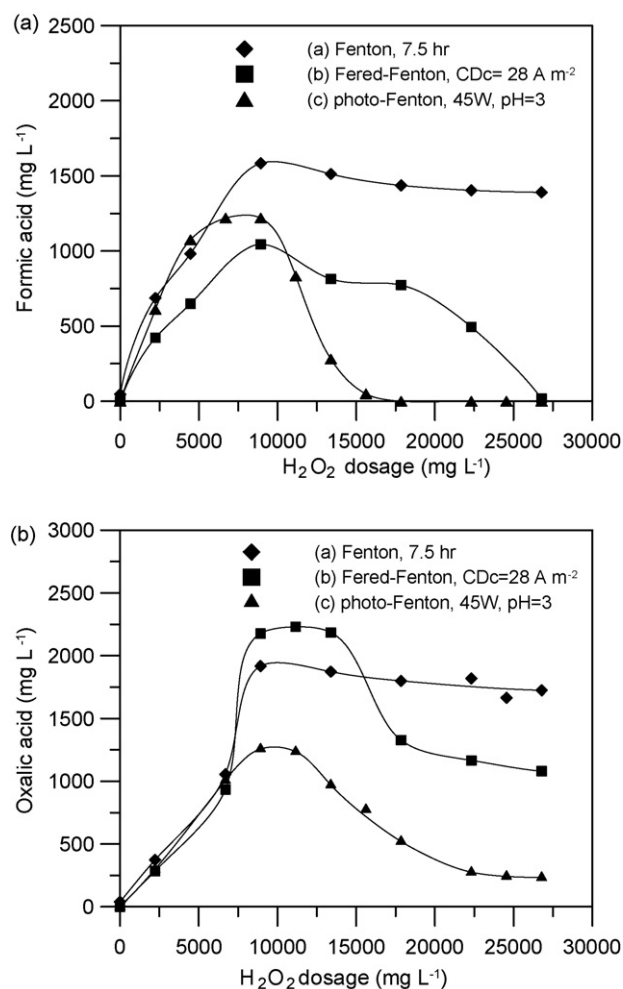


Fig. 9. The variations of formic acid (a) and oxalic acid (b) in each oxidative technology ($[\text{Fe}^{2+}]=200 \text{ mg/L}$) including the Fenton process at pH 3 for 7.5 h; Fered-Fenton with low $\text{CDc}=28 \text{ A/m}^2$ at pH 2 for 3 h; photo-Fenton with 45 W UV irradiation at pH 3 for 3 h.

the electrolysis and/or photo-catalysis of the 10,000 mg/L RBB solution. For each treatment, the concentration of these products (i.e. intermediates) was determined as a function of H_2O_2 dosages (see Fig. 9(a and b)).

Formic acid is rapidly produced and destroyed with a similar tendency by photo-Fenton or Fered-Fenton with higher Fe^{2+} concentration ($[\text{Fe}^{2+}]_0=200 \text{ mg/L}$), then disappears after ca. 100 min (i.e. ca. 16,000 mg/L H_2O_2 dosages). Differing from the behavior of formic acid, oxalic acid is not actually destroyed by UV light, and it can be inferred that they are only slightly photodecomposed. The comparison shown in Fig. 9(a and b) indicates that the Fenton process displayed worse oxidative ability in destruction of the carboxylic acids, and it is obvious that photo-Fenton showed the best performance. The Fered-Fenton method resulted in an accumulation of oxalic acid, almost reaching a constant concentration of 1165 mg/L after 22,000 mg/L H_2O_2 dosages of electrolysis (Fig. 9(b)). A more complete disappearance of oxalic acid by photo-Fenton was observed after 22,000 mg/L H_2O_2 dosages using even a lower Fe^{2+} concentration ($[\text{Fe}^{2+}]_0=200 \text{ mg/L}$) in the beginning.

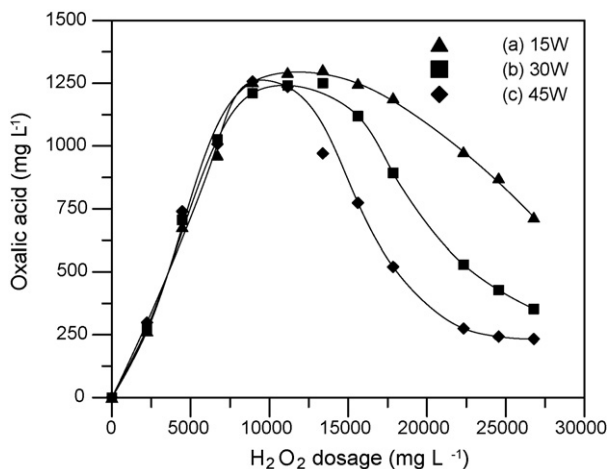


Fig. 10. The UV intensity effects (15 W, 30 W, and 45 W, respectively) in oxalic acids during the photo-Fenton process.

Formic acid is directly mineralized to CO₂, while the oxalic acid is actually not easily decomposable. The high stability of oxalic acid in such Fered–Fenton processes is probably due to the formation of [Fe(C₂O₄)₃]³⁻. However, such Fe³⁺-oxalato complexes are very potential to be photo-catalyzed, indicating treatment by photo-Fenton is much more superior, therefore, confirming its fast disappearance and more complete mineralization in the degraded RBB solution (see Fig. 9(b)).

It should be noted that formic acid could be formed when the RBB carboxylic group is released, while the oxalic acid is probably generated from the further oxidation of certain intermediates formed during the breaking of its aromatic ring. Not only are the aromatic pollutants rapidly transformed into short carboxylic acids by •OH resulting from Fenton's reaction (1), but also further mineralization of such acids occurs while formic acid is completely mineralized, and all other intermediates are finally converted into oxalic acids as seen in Fig. 9(a and b). However, oxidative ability was limited due to the stability of Fe³⁺-oxalato complexes formed in the Fered–Fenton process, so it is difficult for the Fe²⁺ to be regenerated from the complexes. Thus the efficient photo-catalysis of such complexes by UV light can lead to a more complete mineralization of RBB in photo-Fenton. It is shown in Fig. 10 that better oxidative ability and an improvement in the removal efficiency of RBB obtained with greater light intensity indicate the superiority of this method.

4. Conclusion

This study has confirmed that the performances of photo-Fenton and Fered–Fenton methods are significantly superior to the oxidative ability of a Fenton process in the degradation of dye-Reactive Black B solution. The Fered–Fenton process yielded 93% mineralization of the RBB. However, a more complete mineralization (98% COD removal) was obtained in the photo-Fenton process. It was also shown that •OH generated mainly from the Fenton's reaction further destroyed the intermediates such as formic and oxalic acids. Findings presented here

for destruction of oxalic acids in Fered–Fenton are limited but could be enhanced by further experiments such as those decreasing the current density or increasing the initial Fe²⁺ amounts. Similarly, a more complete mineralization by increasing the intensity of UV irradiation can be achieved not only for the goal of dye decoloration but also for obtaining a clean aquatic environment.

Acknowledgement

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