

Degradation of azo dye C. I. Reactive Black 5 by composite ferrate solution

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Abstract: Composite ferrate solution (CFS) was used directly in oxidation of azo dye wastewater of C. I. Reactive Black 5 (RB5). The optimal oxidation conditions and degradation mechanism were investigated. The results indicated that the optimal pH for the oxidation was $\text{pH} < 10$, and Fe(VI) had higher reactivity in this pH range. For example, with the CFS dosage of $20 \text{ mg} \cdot \text{L}^{-1}$ at $\text{pH} = 8 \sim 9$, about 80% and 95% RB5 had been discolored at 5 min and 20 min, respectively. TOC and COD removal experiments indicated that the organic molecules could be mineralized, but the mineralization rate was much slower than the decolorization rate. UV - Vis and FT - IR results showed that the azo groups could be broken by the oxidation of Fe(VI) , and almost all the characteristic absorption bands of RB5 disappeared which indicates the benzene and naphthalene structure had been destructed. The azo dye wastewater treated by CFS has lower toxicity and improved biodegradability. As a strong oxidant with lower cost, CFS has supplied a feasible choice for the treatment of azo dye in industrial wastewater.

Key words: composite ferrate solution; Reactive Black 5; azo dye; oxidation

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1 Introduction

Azo dyes have been widely used in dyeing industries, and about 10 ~ 15% of dyes were lost during the dyeing process and released as effluents^[1]. These compounds are highly colored and can heavily contaminate water source. With azo group bound to aromatic rings, azo dyes are threat to environment owing to their non - biodegradability, toxicity and potential carcinogenic nature^[2]. Therefore, chemical degradation of azo dyes has attracted much attention in recent years^[3 - 4]. But few have been reported on the degradation of azo dyes in general by potassium ferrate.

Potassium ferrate has been found to be a powerful oxidant, the estimated standard half - cell reduction potential of ferrate ranges from +2.20 V to +0.72 V in acidic and basic solutions, thus its oxidation potential in acidic solution is the strongest of all the oxidants used in water and wastewater treatment, including ozone and hydrogen peroxide. Many studies have considered its role as an oxidant in water and wastewater treatment^[5]. During the aqueous oxidation reaction, Fe(VI) is reduced to a non - toxic by product, Fe(III) , which makes Fe(VI) an environmentally friendly oxidant for water treatment processes^[6]. In this paper, composite ferrate solution (CFS) with improved stability was prepared by modified chemical method with KOH at 65 °C. For eliminating the precipitation

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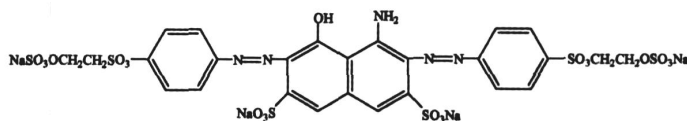
and purification processes needed for solid potassium ferrate synthesis, the preparation process for CFS is simple, time saving and low cost. On this basis, an economically feasible ferrate oxidation technology for degradation of azo dyes in wastewater was proposed. C. I. Reactive Black 5 (RB5), one of the familiar azo dyes, was chosen as a probe molecule in this work.

2 Experimental

2.1 Materials and reagents

Composite ferrate solution (CFS) was prepared by the modified chemical oxidation method: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ reacted with ClO^- in $5.3 \text{ mol} \cdot \text{L}^{-1}$ KOH solution at 65°C , after 60 min, CFS with higher Fe(VI) concentration and improved stability was obtained. The CFS was diluted, then filtered by funnel (G_4) and stored in polyethylene plastic bottle at 4°C . The Fe(VI) concentration in the stored CFS was $1.05 \text{ g} \cdot \text{L}^{-1}$.

The dye of Reactive Black 5 was purchased from the eighth dye chemical factory of Tianjin, China, and used directly without further purification. All other chemicals were of reagent grade, and used as received.



C.I. Reactive Black 5

2.2 Degradation of RB5 by CFS

In each experiment, 100 mL RB5 simulated water with concentration of $50 \text{ mg} \cdot \text{L}^{-1}$ was used. The oxidation tests were carried out by rapid mixing of the two chemical solutions (RB5 and CFS), and then adjusted the pH value by H_2SO_4 quickly. In the oxidation tests, samples were taken periodically up to 60 min. At each sampling time, sodium sulfite solution was added immediately to the sample when it was taken to stop any further reaction. The samples were then filtered by $0.45 \mu\text{m}$ pore size nylon membrane filter before analysis. All the experiments were carried out at room temperature.

2.3 Analytical methods

In this study, the RB5 concentration was determined by its absorbance at 600 nm. The COD values were determined at 620 nm after two hours reaction in the COD reactor (HACH, America), TOC was measured by TOC-V_{C_{PN}} total organic carbon analyzer (Shimazu, Japan), UV-vis spectra of the samples were recorded from 200 nm to 900 nm using a UV-2550 spectrophotometer (Shimazu, Japan). Samples for FTIR analyses were prepared as follows: the samples were filtered to remove Fe^{3+} by the method described above, and then the solution was evaporated below 40°C under reduced pressure by N-100 Eylea Rotary Evaporator (Eylea, China). The solids obtained were used to measure FTIR using Spectrum One B type Fourier Transform Infrared Spectrometer (Perkin Elmer Company, USA), in a conventional KBr pellet with a scanning range from 500 to 4000 cm^{-1} and with a resolution of 4 cm^{-1} .

3 Results and discussion

3.1 Effect of pH on the decoloration of RB5 by CFS

The pH had a great effect on the degradation of RB5 by CFS, and the result was shown in Fig. 1. It was clear that the decoloration rate of RB5 increased with the pH decreased, and the optimum pH range was $\text{pH} < 10$. The decoloration rate was 62% after reaction 5 min at $\text{pH} = 10$; while for $\text{pH} = 3$, it was 99% at the same reaction time. Both could reach 99% after reaction for 60 min. This could be explained that Fe(VI)

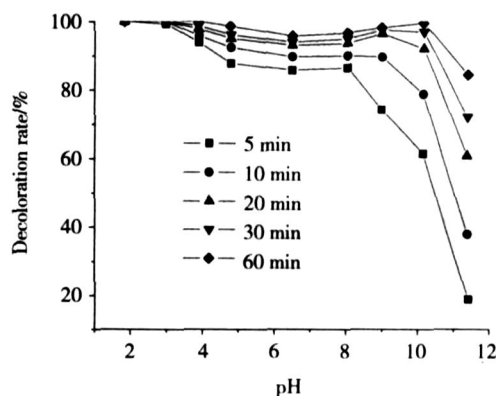


Fig. 1 Effect of pH on the decoloration of RB5 by CFS

has higher oxidation potential at lower pH range, at the same time, the hypochlorite contained in the CFS is also strong oxidant and its oxidation potential also enhanced with pH decreased. The RB5 degradation was gradually lower when pH over passed 10 owing to the relatively low oxidation potential of ferrate and hypochlorite contained in CFS.

Considering the practical application, pH = 8 ~ 9 was selected as the experimental condition. Under this condition, Fe(III) had a minimum solubility, and the RB5 maybe adsorbed on to the insoluble Fe(III) species. However, it was believed that this was not an important effect.

3.2 Effect of CFS dosage on the decoloration of RB5

The dosage of CFS was found to be the most important factor to achieve better decoloration of RB5. Different CFS dosages (as K_2FeO_4) were employed under same conditions, and the results were shown in Fig 2. It was clear that the decoloration rate of RB5 increased with the CFS dosage, and the optimal CFS dosage was $20\text{ mg} \cdot \text{L}^{-1} K_2FeO_4$. Under this condition, about 80% and 95% RB5 were discolored at 5 min and 20 min, respectively; after 20 min, the decoloration rate changed slowly. The experiment results indicated that Fe(VI) with strong oxidant potential had a quickly oxidation rate. It was reported^[7] that there were oxidative intermediates might be generated by decomposition of ferrate ion during the reaction, as Fe(V) and Fe(IV). Both Fe(V) and Fe(IV) have been reported as highly reactive oxidation states. Fe(V) is 3 ~ 5 orders of magnitude more reactive towards compounds than Fe(VI), and the higher reactivity maybe due to the partial free-radical character of Fe(V) ($Fe^V = O \leftrightarrow Fe^V - O$)^[8]. When the Fe(V) dosage was over, the higher Fe(VI) concentration would promote the decomposition of Fe(VI), and most Fe(VI) reduced to Fe(III) by itself to cause a great waste.

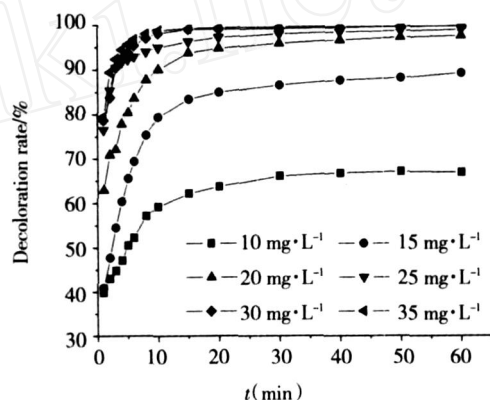


Fig. 2 Effect of CFS dosage (as K_2FeO_4) on the decoloration of RB5

3.3 The removal efficiencies for COD and TOC

The removal efficiencies for COD and TOC by CFS were studied and the results were shown in Fig 3 and Fig 4. Fig 3 showed that the removal rate was quickly in the first 20 min, then it became slowly. The COD removal efficiencies were 18% and 21% for reaction 20 min and 60 min, respectively. And the corresponding decoloration rates, from above, were 95% and 98%. This was due to that during the oxidation by CFS, the RB5 first converted to organic intermediate and then degradation gradually, and after reaction for 20 min and 60 min, there were many organic intermediates had not been degraded. Fig 4 displayed that TOC values decreased with the reaction time, the removal efficiency was 6% after 60 min, and the inorganic carbon (IC) increased with reaction. The results indicated that there existed mineralization reaction for organic molecules during the oxidation to produce CO_2 and CO_3^{2-} etc, but it was much slower than the decolorization rate.

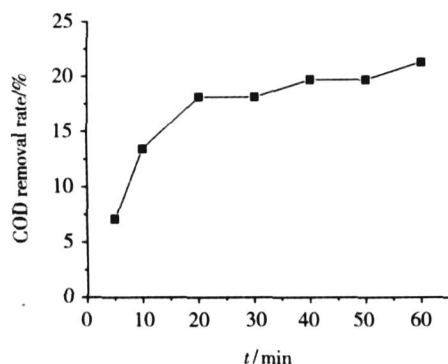


Fig. 3 The removal efficiency of COD by CFS

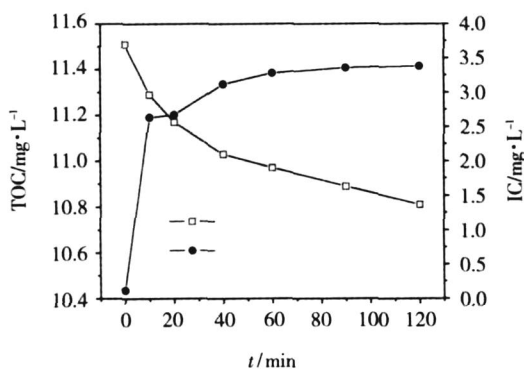


Fig. 4 The removal efficiency of TOC by CFS

3.4 UV - vis and FTIR analysis

UV - vis and FTIR spectrum were measured to study the degradation mechanism, and the results were shown in Fig 5 and Fig 6. Fig 5 displayed that there were two main absorption bands for RB5 in the visible region at 480 nm and 600 nm, and the bands were attributed to the long conjugated π system linked by two azo groups. In the UV region, the absorption bands at 257 nm and 306 nm were attributed to the benzene ring and naphthalene ring^[9]. The absorption peaks weakened sharply in the first 1 min, and then diminished gradually with the reaction, indicating that the azo groups and partial benzene and naphthalene structure were broken.

Fig 6 showed the FTIR spectrum of RB5 and the oxidation products. The vibrations at 3458 cm^{-1} (OH stretching), 2925 cm^{-1} (aromatic C - H stretching), 1628 cm^{-1} (C = N stretching), $1600 \sim 1450\text{ cm}^{-1}$ (aromatic C = C stretching)^[10], 1498 cm^{-1} (N - H bending), 1341 cm^{-1} (C - N special absorption), 1228 cm^{-1} , 1050 cm^{-1} (C = O stretching), 1135 cm^{-1} (SO_3^{2-} stretching), 999 cm^{-1} (benzene ring axially), 844 cm^{-1} (aromatic C - H distortion), 741 cm^{-1} (adjacent hydrogen atomic C - H distortion)^[9,11], respectively represent the characteristic absorption of RB5 in the infrared band. After oxidation for 5 min, the absorption peaks at 1628 cm^{-1} , 1596 cm^{-1} , 1539 cm^{-1} disappeared indicating the benzene ring structure had been broken; the absorption peaks at 1498 cm^{-1} disappeared meaning the azo structure had been destructed; the absorption peaks caused by C - O stretching vibration at 1228 cm^{-1} , 1050 cm^{-1} disappeared; the absorption peaks at 2923 cm^{-1} weakened. At the same time, new vibrations at 1634 cm^{-1} , 1384 cm^{-1} , 1119 cm^{-1} , 620 cm^{-1} appeared. The absorption at 1634 cm^{-1} is coupling of C = C stretching vibration and amino ion distortion vibration; the absorption at 1384 cm^{-1} is the overlapped vibration peaks of C - H distortion and nitro stretching; the absorption at 1119 cm^{-1} is the coupling of C - O stretching vibration and ν_3 stretching vibration of SO_4^{2-} ; the absorption at 620 cm^{-1} is ν_4 stretching vibration of SO_4^{2-} ^[12]. The FTIR spectra for oxidation 30 min was similar to that of 5 min, which indicated that most RB5 had been degraded at the first 5 min, and it was in good agreement with the observation from UV - Vis spectra and decoloration experiments.

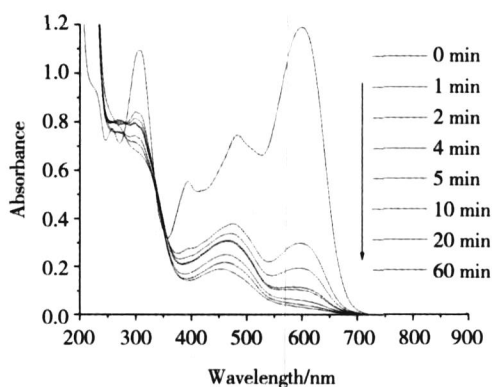


Fig. 5 UV-vis spectra changes of RB5 with reaction time degraded by CFS

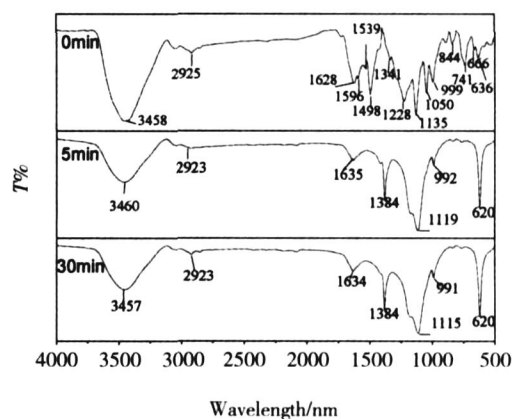


Fig. 6 FTIR spectra of RB5 and the oxidation products

4 Conclusion

Composite ferrate solution with simple preparation process and low cost was prepared in this study, and it has been successfully used in oxidation of azo dye RB5. However, the oxidation was highly affected by pH values, the optimal pH range was $\text{pH} < 10$. At $\text{pH} = 8 \sim 9$, the optimal Fe(VI) dosage was $20\text{ mg} \cdot \text{L}^{-1}$ for $50\text{ mg} \cdot \text{L}^{-1}$ RB5 simulated water, and about 80% RB5 was discolored at first 5 min. It means the Fe(VI) and its oxidative intermediates, Fe(V) and Fe(IV) , have higher reactivity. There existed mineralization reaction for organic molecules during the oxidation for the TOC values decreased with the reaction and IC increased. But the mineralization rate was much slower than the decolorization rate. And about 21% COD was removed by Fe(VI) at 60 min. UV - Vis and FTIR spectrum showed that Fe(VI) could broken the azo groups, benzene ring and naphthalene ring structure,

and to reduce the toxicity and improve the biodegradability of azo dyes. So CFS as a strong oxidant with lower cost is promising for the treatment of azo dye wastewater.

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CFS氧化降解偶氮染料活性黑 RB5

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摘 要:研究了复合高铁酸盐溶液 (CFS) 氧化降解活性黑 (RB5) 染料废水的反应条件和降解机理。结果表明: CFS 氧化降解 RB5 的最佳 pH 范围为 $\text{pH} < 10$, 并且在该范围内 Fe(VI) 的反应速率较快。当 $\text{pH} = 8 \sim 9$, CFS 投加量为 $20 \text{ mg} \cdot \text{L}^{-1}$ 时, 氧化反应 5 min 和 20 min 时, RB5 的脱色率分别为 80% 和 95%。对 TOC 和 COD 的去除实验表明, 在氧化反应过程中存在有机分子的矿化反应, 但矿化速率远低于脱色反应速率。UV - Vis 和 FTIR 结果表明, 染料分子中的偶氮基团能被 Fe(VI) 氧化破坏, 并且处理后样品中 RB5 的特征红外吸收峰消失, 说明了染料分子中部分苯环和萘环被破坏, 从而使得染料废水的毒性降低、可生化性提高。因此, CFS 作为一种高效、低廉的强氧化剂, 为染料工业废水的处理提供了一个可行的方法。

关键词:复合高铁酸盐溶液; 活性黑; 偶氮染料; 氧化

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The exact solution of a class of delay parabolic partial differential equation

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Abstract: It is discussed on how to solve the initial boundary problem of a class of delay parabolic partial differential equation in reproducing kernel spaces. Firstly, by linking two reproducing kernel spaces together, the delay item is turned into a bounded linear operator. Subsequently, using the technique of reproducing kernel, the exact solution of the considered equation, denoted by series, is given. Truncating the series, the approximate solution is obtained. When increasing the number of the nodes, the error of the approximate solution is decrease monotone in the sense of the norm. The final example shows the efficiency of the proposed method.

Key words: delay parabolic; reproducing kernel; exact solution