

Decolorization of Metal-Complex Dye Direct Blue-86 in Wastewater by Potassium Ferrate(VI)

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Study on decolorization of metal-complex dye direct blue-86 in wastewater by potassium ferrate(VI) was carried out. Effects of pH value, oxidant dose, reaction time, initial concentration of dye and temperature on the decolorization were examined. In the absorption spectra during the decolorization process, it is clearly observed that Cu-phthalocyanine macrocycle in direct blue-86 can easily be destroyed by potassium ferrate(VI). Compared with the decolorization, the removal percentage of COD and total organic carbon were only 10.22 and 59.70 % after 1 h, respectively. It indicates that the complete mineralization of direct blue-86 cannot be achieved under oxidation by potassium ferrate(VI).

Key Words: Potassium ferrate(VI), Direct blue-86, Decolorization, Metal-complex.

INTRODUCTION

Dyes are considered as the widespread environmental pollutants associated with many important industries such as textile, food colorants, print and cosmetic manufacturing units. It is estimated that approximate 7×10^5 tons of different dyes are produced annually worldwide¹. Approximate 50 % of the dyes are released in the industrial effluents². Effluents from the dyeing processed in the above mentioned industries usually contain high concentration of organic compounds and are characterized by strong colour, high COD and TOC values as well as low biodegradability³. Dyes from dyeing operations are the major source of colour in textile effluents. Dye pollutants discharged from the above mentioned industries can seriously damage the environment if improperly disposed. Highly coloured components in dye containing wastewater are not only aesthetically displeased but also hinder light penetration and may in consequence upset biological activity of aquatic life⁴. Therefore, the decolourization of dyes from industrial effluents is an area of research attracting increased attention.

Decolourization by oxidation can improve the biodegradability of dyes, which makes conventional biological processes available for further treatment⁵. A wide variety of oxidation technologies have been studied for the decolourization of dye-stuff in wastewater, such as ozone oxidation⁶, H₂O₂-ozone oxidation⁷, H₂O₂-based oxidation^{8,9}, H₂O₂-ultrasound irradiation¹⁰, catalytic ozonation¹¹, photo-catalytic^{12,13} and electrochemical oxidation^{14,15}. However, as far as is known, less study on the decolourization of metal-complex dyes in general by oxidant has been reported.

Ferrate(VI) salts are economically cheap, highly efficient, strong and eco-friendly oxidant, which have been used in the field of water and wastewater treatment¹⁶⁻²². Under both acidic and neutral conditions, the redox potential of ferrate(VI) is greater than that of many other oxidants employed in water and wastewater treatment till now. Moreover, ferrate(VI) is regarded as a dual-function chemical reagent with excellent ability of oxidation, coagulation and disinfection^{14,17-20}. In the process of aqueous oxidation, ferrate(VI) is reduced to a non-toxic byproduct, Fe(OH)₃, which makes ferrate(VI) an environmentally friendly oxidant for water treatment processes^{21,22}. Thus, ferrate(VI) is a promising oxidant to be put into practical application to the decolourization of dye effluent.

In this paper, decolourization of metal-complex dye aqueous by potassium ferrate(VI) was studied. Effects of pH value, quantity of potassium ferrate(VI), reaction time, initial concentration of dye and temperature on the decolourization efficiency were examined. Direct blue-86, a typical soluble metal-complex dye, which is mainly used in the printing of cotton and mucilage glue fabrics as well as, the dyeing silk, wool and vinylon, was chosen as a probe molecule.

EXPERIMENTAL

Potassium ferrate(VI) with high purity (98 %) was prepared *via* the modified chemical wet oxidative method: Fe(NO₃)₃·9H₂O reacted with a concentrated and strong alkaline KClO₃ aqueous under cooling (< 5 °C). After 1 h, higher concentration of ferrate(VI) aqueous was obtained. A certain amount of solid KOH was then added in small portions to the ferrate(VI) aqueous and the mixture was stirred for 20 min.

The produced dark purple slurry was filtered with a sand core funnel (G3), after which the precipitate was washed with a certain volume of cold 5 mol/L KOH aqueous solution. The filtrate was added to a chilled saturated KOH aqueous solution and then filtered initially with a sand core funnel (G4). The precipitate was washed with organic solvent. The final product, solid potassium ferrate(VI), was collected and stored in a refrigerator prior to further use.

Direct blue-86 (purity: 97 %; C. I. Direct Fast Turquoise Blue GL; colour index: 74180; CAS NO.: 1330-38-7) was purchased from Third Dyestuff Factory, Wuhan, China and used directly without further purification. The chemical structure of direct blue-86 is shown in Fig. 1. All other chemicals used in this study are analytical grade reagents and used as received. Deionized and double distilled water was used for preparing all of the aqueous and reagents.

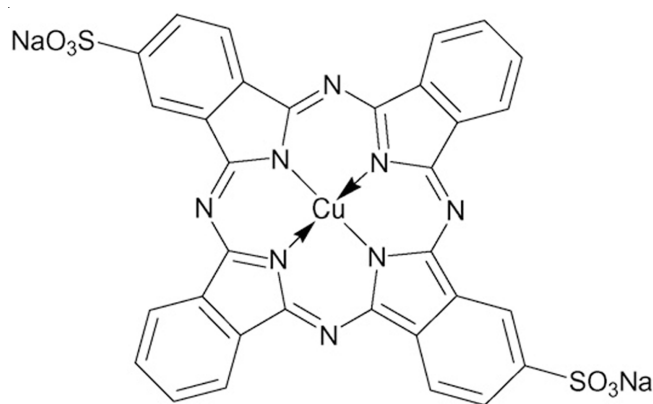


Fig. 1. Chemical structure of direct blue-86. (Chemical formula: $C_{32}H_{14}O_6N_8S_2CuNa_2$; m.w. = 780.16)

Preparation of simulated wastewater: A stock solution of direct blue-86 (1.0 g/L) was prepared by dissolving an appropriate amount of direct blue-86 in 100 mL and diluting to 1000 mL with distilled water. Other aqueous direct blue-86 at different concentrations were prepared from the stock solution and used to obtain a standard curve.

Decolourization experiments: In each experiment, 100 mL aqueous direct blue-86 with a certain specific concentration was used. The decolourization test was carried out by rapid mixing of aqueous direct blue-86 and solid potassium ferrate(VI) and then the pH value was adjusted by 0.1 mol/L HCl or 0.1 mol/L NaOH. The reaction time of the decolourization experiments was 1 h if not specified. At each sampling time, sodium sulfite was added immediately to the sample when it was taken to stop any further reaction (except for COD measurement). The samples were then filtered by a sand core funnel (G3) before analysis.

Analytical measurement: The absorbance of every sample (200-900 nm) was measured using a UV-1700 spectrophotometer (Shimadzu, Japan). The concentration of direct blue-86 was determined by measuring the absorbance at a fixed wavelength (618 nm), which corresponds to a maximum absorption wavelength of direct blue-86 in visible region. The decolourization efficiency was calculated by the following formula:

$$\text{Percentage colour removal} = \frac{A_0 - A_t}{A_0} \times 100 \% \quad (1)$$

here A_0 and A_t are the intensity of the maximum absorption wavelength of the aqueous direct blue-86 before and after decolourization, respectively.

A total organic carbon analyzer (TOC-500, Shimadzu, Japan) was used to measure the concentration of organic carbon in wastewater. The COD concentration of wastewater was measured by a standard $K_2Cr_2O_7$ method²³. The pH value was measured with the Digital Acidimeter (Model pHS-3C, Leici, China). All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than $\pm 5 \%$.

RESULTS AND DISCUSSION

Effect of pH on the decolourization of direct blue-86:

The decolourization of direct blue-86 by potassium ferrate(VI) was investigated with different initial pH values using the same initial dye concentration (100 mg/L) at room temperature ($23 \pm 2 \text{ }^\circ\text{C}$). The results are presented in Fig. 2. As shown in Fig. 2, the pH value had a significant effect on the decolourization efficiency of direct blue-86 by potassium ferrate(VI). It was clear that the optimal pH range for the decolourization was pH 4.0-6.0 and the decolourization rate could reach 99 % after 1 h. The decolourization efficiency of direct blue-86 at this pH range may be explained by the higher redox potential of ferrate(VI). The decolourization efficiency of direct blue-86 was obviously lower when pH overpassed 10 owing to the reduced oxidation ability and the improved stability of ferrate(VI). The redox potentials of ferrate(VI) are illustrated as follow:

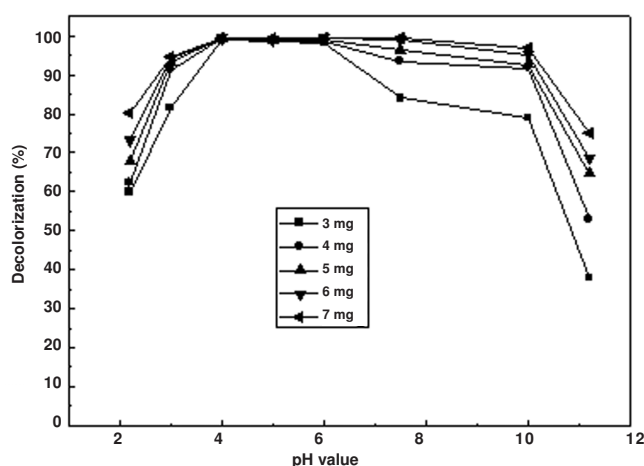
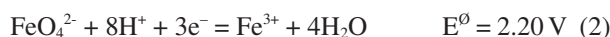


Fig. 2. Effect of pH value on the decolorization of direct blue-86 ($m_{K_2FeO_4}$: 3-7 mg, [direct blue-86]: 100 mg/L, time: 1 h, temperature: $23 \pm 2 \text{ }^\circ\text{C}$)

Under acidic conditions:



Under basic conditions:



When pH value is lower than 4, the decolourization efficiency of direct blue-86 reduced. Although the redox potential of ferrate(VI) is increased with decrease in pH, the decomposition rate of ferrate(VI) is accelerated at the same time. This fact can cause part of ferrate(VI) reduction to Fe(III) compounds before it reacts with direct blue-86 and leads the decolourization of direct blue-86 to decrease. On the other hand, the solubility of direct blue-86 decreases when the pH lower than 4.0, which reduces the opportunity of the reaction between ferrate(VI) and dye molecules and thus reduces the decolourization of direct blue-86.

Effect of K_2FeO_4 dose and reaction time on the decolourization of direct blue-86: The dose of K_2FeO_4 was found to be the most important factor in achieving better decolourization efficiency of direct blue-86. Different K_2FeO_4 doses were employed with the same initial dye concentration (100 mg/L) and pH value (4) at room temperature ($23 \pm 2^\circ C$). The results are shown in Fig. 3. It was evident from Fig. 3 that the decolourization efficiency of direct blue-86 increases with the increasing of potassium ferrate(VI) dose and when an optimal amount of potassium ferrate(VI) (3 mg) is used, more than 99 % direct blue-86 is decolourized. The decolourization efficiency increases with the increasing of potassium ferrate(VI) dose, which can be explained as follows: an increase in amount of potassium ferrate(VI) can promote the collision frequency between the oxidant and direct blue-86, thus enhances the reaction rate.

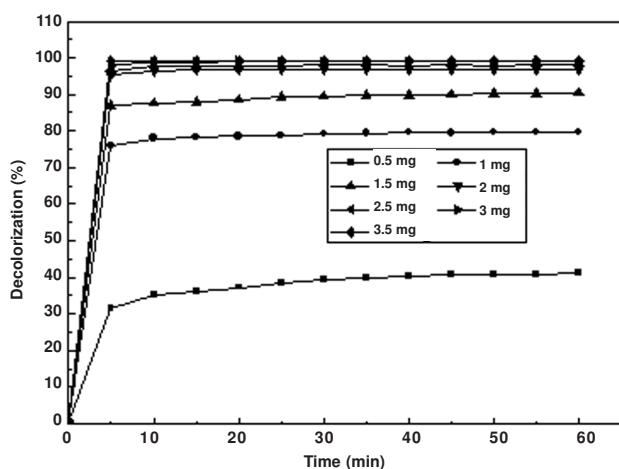


Fig. 3. Effect of K_2FeO_4 dose and reaction time on the decolorization of direct blue-86 ($m_{K_2FeO_4} = 0.5-3.5$ mg, [direct blue-86] = 100 mg/L, pH = 4.0, time: 1 h, temperature: $23 \pm 2^\circ C$)

Dependence of decolourization efficiency of direct blue-86 on reaction time is shown in Fig. 3. As illustrated in Fig. 3, the mainly decolourization of direct blue-86 is occurred at the first 5 min and the decolourization rate changes little after 20 min. Maximum decolourization efficiency of direct blue-86 is achieved within 40-50 min, after which the decolourization rate is almost constant. The rapid decolourization at the initial reaction time is due to strong oxidation of potassium ferrate(VI). The later slow rate of direct blue-86 decolourization is probably due to the absorption of the hydrolyzate of Fe(III) compounds, such as $Fe(OH)_{3,aq}$ and $Fe(OH)_3$ colloid,

which is capable of absorbing dye pollutants and removing them from wastewater. The equilibrium is found to be near 50 min when the maximum decolourization of direct blue-86 by potassium ferrate(VI) reaches.

Effect of dye concentration on the decolourization of direct blue-86: The impact of various initial dye concentrations (50, 100, 150, 200 and 250 mg/L) on the decolourization of direct blue-86 was investigated using 3 mg K_2FeO_4 , pH of 4.0 and at room temperature ($23 \pm 2^\circ C$) (Fig. 4). As demonstrated in Fig. 4, the decolourization efficiency decreases from 99.87-88.71 % when the initial concentration of direct blue-86 increases from 50 mg/L to 250 mg/L. Although the decolourization efficiency decreases with increase in initial dye concentration, the actual decoloured amount increases. For example, when the concentration of direct blue-86 increases from 50-250 mg/L, the decoloured amount increases from 49.93-221.77 mg/L. It is indicated that an increase of initial dye concentration can promote the collision frequency between the oxidant and direct blue-86.

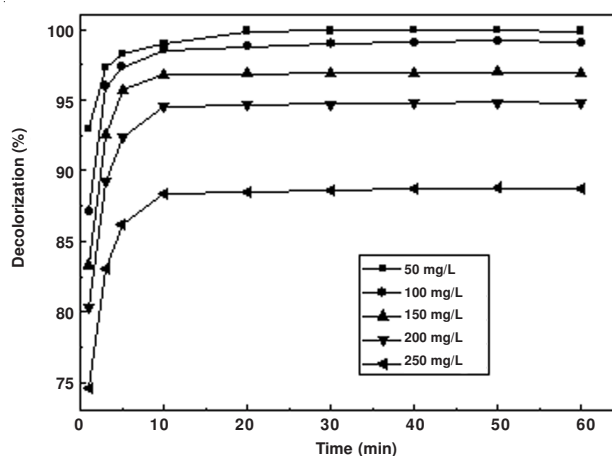


Fig. 4. Effect of initial dye concentration on the decolorization of direct blue-86 ($m_{K_2FeO_4} = 3$ mg, pH = 4.0, time: 1 h, temperature: $23 \pm 2^\circ C$)

Effect of temperature on the decolourization of direct blue-86: The decolourization of aqueous direct blue-86 by K_2FeO_4 was carried out at different temperatures (25, 35, 45 and $55^\circ C$) under the conditions: initial dye concentration of 100 mg/L, K_2FeO_4 dose of 3 mg and pH of 4.0. Fig. 5 shows the effect of reaction temperature on the decolourization efficiency of direct blue-86. It is evident from Fig. 5 that the decolourization efficiency of direct blue-86 increases with the increase of temperature. However, effect of reaction temperature on the decolorization efficiency of direct blue-86 is slight because this sort of dye has already a high decolourization efficiency at $25^\circ C$. Although the increase of the temperature benefits the decolourization efficiency, both investment and operation costs are high for actual treatment of effluent. Thus, decolourization of direct blue-86 by ferrate(VI) can be carried out at ambient temperature with a high decolourization efficiency.

Decolorization process of Direct blue-86: In order to clear understanding of the oxidation process, the absorption spectra of 100 mg/L aqueous direct blue-86 at pH 4 were

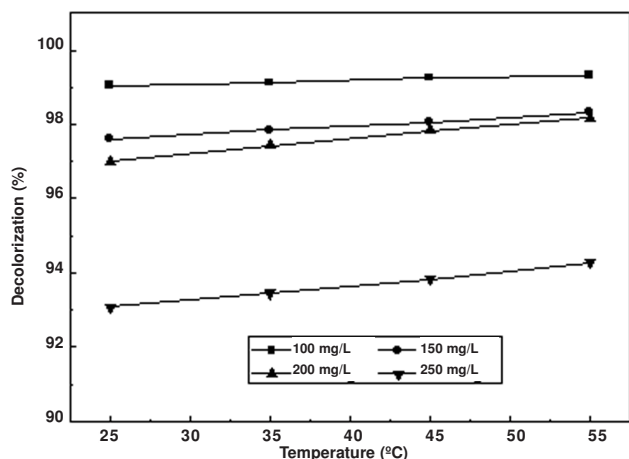


Fig. 5. Effect of temperature on the decolorization of direct blue-86 ($m_{\text{K}_2\text{FeO}_4} = 3 \text{ mg}$, [direct blue-86] = 100-250 mg/L, pH = 4.0, reaction time = 1 h)

recorded during decolourization of direct blue-86 by 3 mg of K_2FeO_4 . As presented in Fig. 6a, direct blue-86 has five absorbance bands. Two bands are in visible region and three in ultraviolet region. The major absorbance band at 618 nm and a shoulder band at 658 nm are attributed to the π - π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Cu-phthalocyanine macrocycle. The bands in the ultraviolet region at 265 and 333 nm are observed due to the transitions from the deeper π levels to the LUMO. Besides, one additional band at 215 nm can be seen (Fig. 6a), which is ascribed to benzene. It is obvious that the residual absorption at visible light region declined dramatically, indicating that Cu-phthalocyanine macrocycle is destroyed. Meanwhile, the absorption at 265 and 333 nm reflects the weak destruction of the aromatic compound in direct blue-86, as demonstrated in Fig. 6b. This is because the aromatic rings are the most difficult to be degraded in dye. By contrast, the absorbance at 215 nm firstly climbs to a peak value at about 5 min and then declines moderately. It is revealed that aromatic intermediates, such as benzene or quinone are generated and destroyed.

Carbon mineralization: The reduction of total organic carbon was monitored to evaluate the mineralization of the direct blue-86. As shown in Fig. 7, the initial total organic carbon is 46.7 mg/L, COD is 48 mg/L. Fig. 7 also shows that the removal percentage of total organic carbon and COD are 4.65 and 31.34 % after 10 min and 10.22 and 59.70 % after 1 h, respectively. However, the decolourization efficiency is 99.09 % after 10 min and 99.16 % after 1 h (Fig. 3). It is indicated that colour decay is considerably faster than the reduction of total organic carbon and COD, which attributed the ease of chromophore destruction. The data suggest that the mineralization percentage of direct blue-86 by potassium ferrate(VI) is low and the mineralization is slow. Much longer time is needed for the conversion of total organic carbon to CO_2 .

Conclusion

Decolourization of aqueous direct blue-86, a typical metal-complex dye, by potassium ferrate(VI) was studied. A series of experiments was performed to study the effects of pH value,

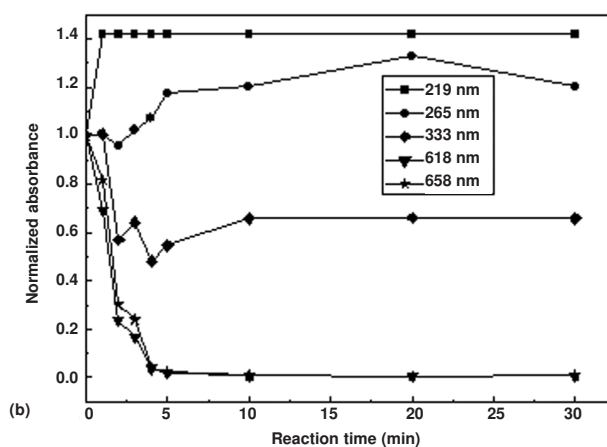
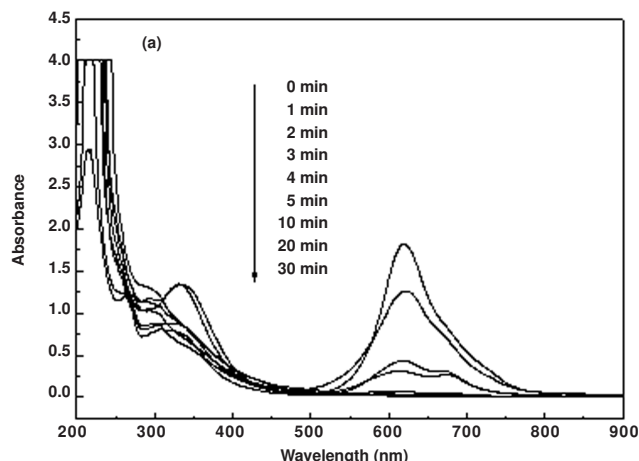


Fig. 6. (a) UV/VIS spectra of aqueous direct blue-86 during oxidation by potassium ferrate(VI) at different reaction times. ($m_{\text{K}_2\text{FeO}_4} = 3 \text{ mg}$, [direct blue-86] = 50 mg/L, pH = 7.5). (b) normalized absorbance at wavelength of 215, 265, 333, 618 and 658 nm

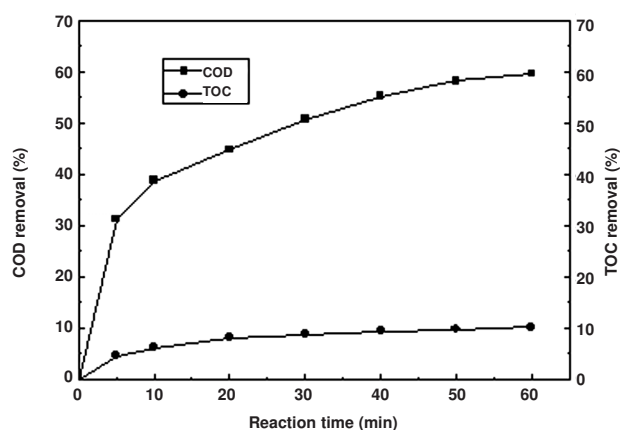


Fig. 7. COD and TOC removal percentage with time. (pH = 4.0, $m_{\text{K}_2\text{FeO}_4} = 3 \text{ mg}$, [direct blue-86] = 100 mg/L)

oxidant dose, reaction time, initial concentration of dye and temperature on the decolourization efficiency. The results show that the optimal pH range for the decolourization was 4-6, because the ferrate(VI) has higher redox potential under the acidic condition. When pH value lowers to 4, the decomposition of ferrate(VI) is accelerated, which cause reduction of ferrate(VI) to Fe(III) compounds before it reacts with direct blue-86, thus

leads decrease of the decolourization efficiency. The decolourization efficiency is increased with the increasing the amount of potassium ferrate(VI), which is due to the elevation of the collision frequency between oxidants and direct blue-86. The oxidation of potassium ferrate(VI) is very strong so that the decolourization efficiency is fast in the initial time of reaction and the decolourization efficiency can reach more than 99 %. Although the decolourization efficiency decreases with the increase of initial dye concentration, the actual decoloured amount of the dye increases. The decolourization efficiency is also increases with the increase in temperature, but the effect is very little. From the absorption spectra during the decolourization process, it is found that the residual absorption at visible light region declines dramatically, while the absorption at near ultraviolet region is increased. It is indicated that Cu-phthalocyanine macrocycle of direct blue-86 is easily destroyed by potassium ferrate(VI) and the aromatic intermediates are generated at the same time. In the decolourization process, it can also be found that the decolourization of the dyes undergoes a fast reaction than the mineralization and the complete mineralization of Direct blue-86 can not be achieved under the oxidation by potassium ferrate(VI).

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