The Degradation of Reactive Brilliant Blue by Fe(III)/H_2O_2 Systems

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Abstract. The degradation of anthraquinone dye reactive brilliant blue (KN-R) by Fe(III)/H_2O_2 system was investigated in details. The results demonstrated that KN-R was degraded efficiently in the Fenton-like reaction system. 94.40 % removal of KN-R in solution (pH=3) was reached after 40 min when the initial concentrations of H_2O_2 and Fe(III) were 7.5 mmol/L and 0.5 mmol/L, respectively. And further experiments verified that the main degradation mechanism of KN-R was attributed to hydroxyl radical (·OH) attack in the Fe(III)/H_2O_2 reaction system.

Introduction

Printing and dyeing industry, as the traditional and preponderant industry of our country, has developed rapidly since 90 years of 20 century. The discharge of dye wastewater has also increased a lot in this industry. According to incomplete statistics, annual emissions of printing and dyeing wastewater are likely to be about 20 million tons, which was nearly the fifth in the total discharge of industrial wastewater in our country.

The printing wastewater is one of the hard-deal industrial wastewater in China because of its large quantity, high organic pollutant content, chromaticity, alkalescence and water quality fluctuation. With the rapid development of dyestuff industry, the dosages of PVA, rayon saponification and a lot of new additives and refractory organic compounds in wastewater are increasing, which makes the wastewater very hard to be treated [1].

Reactive brilliant blue KN-R is classed as the anthraquinone dyes [2], and the chemical formula is $C_{22}H_{16}N_2Na_2O_{11}S_3$. The structure formula of it can be described by Fig. 1.
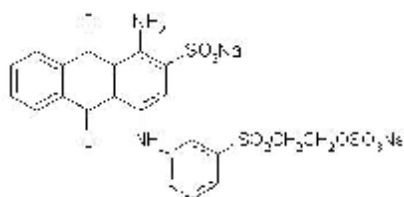

Fig. 1. The structure formula of reactive brilliant blue (KN-R)

At present, KN-R is one of the best dyestuff in exhaust dyeing, mainly used for cotton and ramie dyeing. The number of anthraquinone dyes is ranked second only to azo dyes [3]. Due to the highly toxic and nonbiodegradable, the treatment of anthraquinone dyes wastewater is important in the field of ecological environmental protection.

Materials and methods

Materials. $Fe(NO_3)_3 \cdot 9H_2O$ was purchased from Tianjin Kemio Chemical Reagent Co. Ltd and had a purity of 98.5%. H_2O_2(30%) was obtained from Tianjin Tianli Chemical Co. Ltd. KN-R stock solution ($[KN\text{-}R]_0$=1000 mg/L) was prepared by dissolving the appropriate amount of KN-R in deionized water. A stock solution of Fe(III) ($[Fe(III)]_0$=100 mM) was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in deionized water that was adjusted to pH 3 by adding 0.1M H_2SO_4. Hydrogen peroxide (H_2O_2) concentration was prepared and controlled in 1 M.

The reaction solution was brought to the appropriate pH by adding 0.1M NaOH or H_2SO_4.

Procedures. A certain amount of KN-R, Fe(III) solution and deionized water were filled into the reaction vessel. Degradation experiments were conducted at least twice. Samples were taken out at the given reaction time intervals and the absorbance of KN-R was analyzed by measuring the UV-vis spectra at λ=592 nm using UV-vis spectrophotometer. In general, the formula of degradation rate is shown as following.

$$\text{The degradation rate (\%)} = \left(1 - \frac{A_t}{A_0}\right) * 100\%$$

Where: A_0 - the absorbance before reaction; A_t - the absorbance at t minutes.

The reaction was started by adding the appropriate amount of H_2O_2 (30%, w/w). All experiments were conducted at room temperature (T = 23±2℃) and mixed with magnetic stirring apparatus.

Results and discussion

Variation of the concentration of H_2O_2. The initial reaction conditions were $[KN-R]_0$=150 mg/L, pH=3, $[Fe(III)]_0$=0.5 mM, $[H_2O_2]_0$ /$[Fe(III)]_0$= 1/1，3/1，5/1，10/1 and 15/1 and the reaction time is 40 minutes. There were two ways to add H_2O_2. One way was adding H_2O_2 in a whole at reaction time of 0 min and the result is shown in Fig.2a. The other way was adding H_2O_2 in five equal portions over initial 20 min, and the result is shown in Fig.2b.
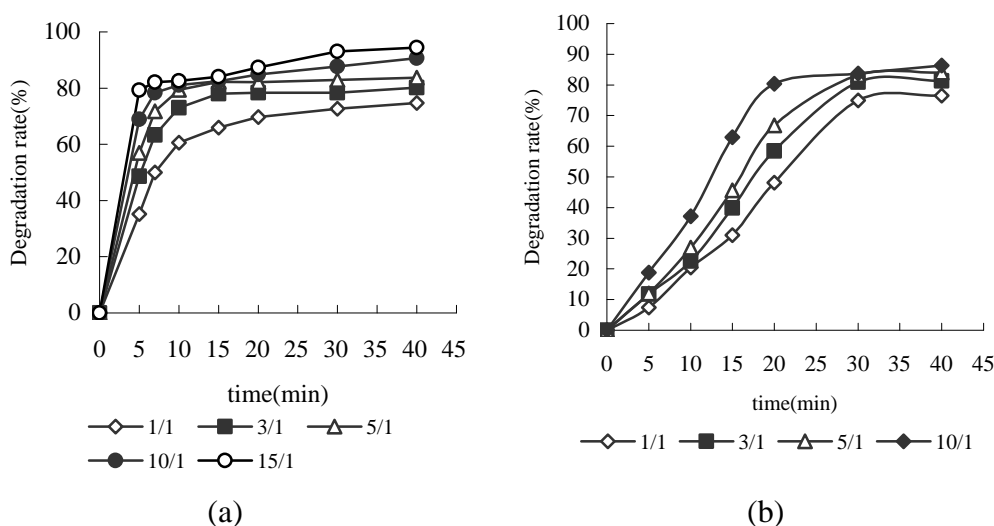

(a)   (b)

Fig. 2. Influence of H_2O_2 dosage on the degradation of KN-R (a) H_2O_2 was added in a whole. (b) H_2O_2 was added in five equal portions over initial 20 min.

From the Fig. 2a, it shows that when the initial concentration of H_2O_2 was in a range of 0.5-7.5mM, the KN-R degradation rate increased with increasing H_2O_2 dosage and reached a plateau at 20 minutes. After 40 min, the degradation rate of KN-R are 74.74 %, 80.18 %, 83.75 %, 90.66 % and 94.40 %, respectively. It's probably because the production of hydroxyl radical(·OH) which works better in the degradation of KN-R. Possible equations are as follows.

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2\bullet + H^+ \qquad (1)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + HO\bullet \qquad (2)$$
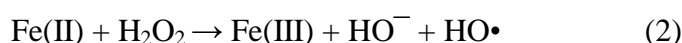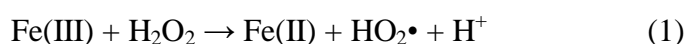
The equations show that the degradation of KN-R has been caused mainly by the Fenton reaction in Fe(III)/H_2O_2 system. It is reported that the rate of reaction 1 is slower significantly compared to the rate of reaction 2 [4, 5]. Accordingly, at the certain initial concentration of Fe(III), the larger the initial concentration of H_2O_2 is, the more [Fe(II)] produces, the greater the degradation rate of KN-R is.

Fig. 2b showed the same general trend that the larger the concentration of H_2O_2 is, the greater degradation rate of KN-R is. However, by comparison with Fig. 2a, the degradation rate of KN-R at the initial stage from 0 to 10 minutes was greatly reduced. This maybe because the initial

concentration of H_2O_2 at 0 min in Fig. 2b is 1/5 comparing with that of Fig. 2a. Then less ·OH can be produced leading to the loss of degradation.

Variation of the concentration of Fe(III). Fig.3 shows the effects of Fe(III) dosage from 0.1 to 1.5 mM on the degradation of KN-R at pH 3, and the corresponding degradation rate of KN-R are 75.96 %, 79.57%, 81.93 %, 83.48 % and 85.05%, respectively.
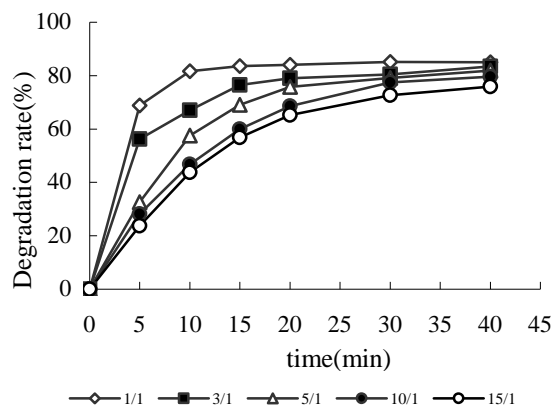

Fig. 3. The effects of initial concentration of Fe(III) on the degradation rate of KN-R. [KN-R]$_0$=150 mg/L, [H$_2$O$_2$]$_0$=1.5mM, pH= 3, reaction time is 40 minutes.

As can be seen from Fig.3, the removal rate of KN-R increased with increasing the initial concentration of Fe(III). With other condition remaining unchanged, the reaction probabilities between Fe(III) and H_2O_2 increased with the increase of the initial concentration of Fe(III). Consequently, it can make more of the Fe(II) to participate in reaction 2 to produce ·OH. As the reaction went on, it's can be seen that the Fe(III) is not consumed, and the catalytic cycle between Fe(II) and Fe(III) is formed. Bring the concentration of Fe(III) from 0.1 mM to 1.5 mM, the KN-R degradation did not change obviously at the reaction time of 40 min, indicating that H_2O_2 has become the limiting factor for reaction. The results of the experiments have shown that the concentration of H_2O_2 had expected to be the rate-limiting step for the production of ·OH in Fe(III)/H_2O_2 systems throughout the whole course of the reaction.

Variation of the solution pH. The effects of pH on the degradation rate of KN-R in Fe(III)/H_2O_2 system are shown in Fig.4. The initial reaction conditions were [KN-R]$_0$=150 mg/L, [H$_2$O$_2$]$_0$=7.5mM and [Fe(III)]$_0$=0.5mM at reaction time of 40 minutes.

As can be seen from Fig.4, the rate of the reaction decreases with increasing pH in the Fe(III)/H_2O_2 system. It is well known that pH obviously has an effect on the oxidation capacity of Fenton-like system. Higher pH can destabilize H_2O_2 [6,7]. The decomposition of H_2O_2 would occur at higher pH, and H_2O and O_2 were formed (reaction 3). So higher pH can lower the concentration of H_2O_2 as well as the KN-R degradation rate.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (3)$$

Secondly, pH has an important influence on the form of Fe(III) in the water. Therefore, suitable media pH probably favours the progress of reaction. In the proper acidic solution, the Fe(III) exists in the form of ferri ion which is better for reaction between Fe(III) and H_2O_2. However, the Fe(III) exists in the form of Fe(OH)$_2{}^{+}$ at high pH [8]. It can reduce the concentration of Fe(III) ions, resulting in the reaction probabilities between Fe(III) and H_2O_2 reducing.

Experiment of free radical quenching. ·OH, one of reactive oxygen species, had perfect oxidizing ability. It has been ascribed to can react with biomacromolecules because of its advantages such as efficient oxidation and great potential for rapid reaction. We assumed that the degradation mechanism of KN-R was the degraded by ·OH in Fe(III)/H_2O_2 system though the above analysis. With the rest of the conditions unchanged, KI, the quencher of ·OH, is added, and the variation of the degradation rate of KN-R was studied (Fig. 5).

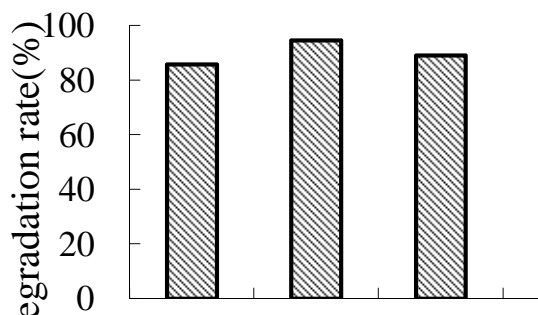Fig.4. The effects of pH on the degradation rate of KN-R in Fe(III)/H_2O_2 system ($[KN-R]_0$=150 mg/L, $[H_2O_2]_0$=7.5mM)
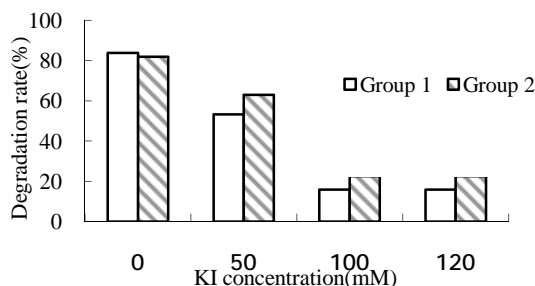
Fig. 5. Effects of the concentration of KI on the degradation rate of KN-R in Fe(III)/H_2O_2 systems

There are two groups experiments in Fig. 5. The conditions of 2.5 mM $[H_2O_2]_0$ and 0.5 mM $[Fe(III)]_0$ were controlled in Group 1, and 1.5 mM $[H_2O_2]_0$ and 0.3 mM $[Fe(III)]_0$ were controlled in Group 2. The concentration gradient of KI for 50 mM, 100 mM and 120 mM were used in each group sets. In Fig. 5, when KI is added, it is found that the degradation rate of KN-R drops rapidly with increasing the concentration of KI. The degradation rate of KN-R has remained unchanged when continue to increase the concentration of KI from 100 to 120 mM. Group 1 reduces by 67.84 %, and Group 2 reduces by 59.44 % with the presence of 100 mM KI. This reflects that ·OH which produced in Fe(III)/H_2O_2 system are quenched by KI, confirming that the degradation mechanism of KN-R was degraded by ·OH in the Fe(III)/H_2O_2 system. However, we can find there are still 20% KN-R degraded by adding 100 or 120 mM KI. This indicated that there are other reactive species produced in Fe(III)/H_2O_2 system to degrade KN-R. This species might relate to HO_2• (reaction 1 and 2).

Conclusions

In Fe(III)/H_2O_2 system, the degradation rate of KN-R increased with increasing concentrations of Fe(III) and H_2O_2. 94.40 % degradation of KN-R was reached after 40 min in solution (pH=3) containing 0.5 mmol/L Fe(III) and 7.5 mmol/L H_2O_2. The way of adding H_2O_2 has the effect on the degradation rate of KN-R, especially for the initial reaction stage. The degradation mechanism of KN-R was mainly degraded by ·OH in the Fe(III)/H_2O_2 system.

Acknowledgements

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