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Degradation of Acid Red 18 by Fenton Reagent Combined with UV

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Degradation of acid red 18 (AR18) by mean of Fenton reagent (FR) combinated with UV was investigated for a variety of operating conditions. It is found that the degradation rate of acid red 18 is dependent on the pH value, the Fe^{2+} and H_2O_2 dosage and the initial concentration of the dye. Under the given test conditions, 99.6 % degradation efficiency was achived after 0.5 h reaction by Fenton reagent combined with UV (UV/FR). The results show that the UV/FR can be an effective technology for the treatment of azo dyes in wastewater.

Key Words: Degradation, Acid red 18, Fenton Reagent, UV.

INTRODUCTION

Wastewater from dyes production and application pose a major threat to the surrounding ecosystems and human health. Azo dyes occupy the largest percentage among the total dyes. It is known that azo dyes are poisonous and have potentially carcinogenic nature. Because of their stable chemical property and low biodegradation, dyes in wastewater display largely difficult reduction. A variety of physical[1], chemical[2-4] and biological methods[5,6] are presently available for the treatment of azo dyes. Commonly used chemical methods, such as adsorption on activated carbon[1] and coagulation by a chemical agent, are non-destructive and generally transfer contaminants from one phase to another. Today the chemical degradation study concentrated on catalytic oxidation degradation and further study on the process facilitated by ultraviolet light[4,7] and ultrasonic irradiation[8,9].

Fenton reagent (FR) is one of the most popular advanced oxidation processes (AOPs). Fenton reagent is widely known in its simplified version, which is presented in reaction (1). It can be described as the generation of the hydroxyl radical ($OH^\bullet$) through the catalytic decomposition of hydrogen peroxide (H_2O_2), carried out by a transition metal such as ferrous iron (Fe^{2+})[10].

$$H_2O_2 + Fe^{2+} \rightarrow OH^\bullet + OH^- + Fe^{3+} \qquad (1)$$

$OH^\bullet$ is a highly reative and non-selective chemical species which oxidize organic matter present in wastewater. It is confirmed that ultraviolet (UV) conduct

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to degradation of Fenton process. Over the last few years, the combination of UV and Fenton reagent (UV/FR) as treatment for the degradation of organic pollutants in water has been extensively studied[11-13]. Application of the method stands out due to its high oxidation power, rapid oxidation kinetics, being relatively inexpensive and easy to operate.

The purpose of this work is to investigate degradation of acid red 18 (AR18) (Fig. 1) in aqueous solution using UV/FR process and to investigate the effects of operational parameters such as pH value, Fe^{2+} and H_2O_2 dosage, initial concentration of dye. Also degradation mechanism of the process is the subject of the present research.

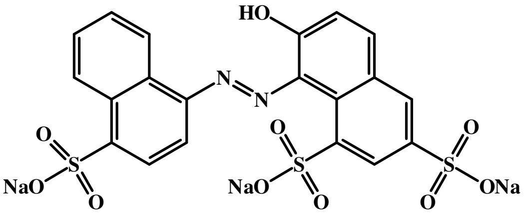

Fig. 1. Molecular structure of acid red 18 (AR18)

EXPERIMENTAL

Azo dye, acid red 18 is an industrial product and was obtained from Mancheng Chemicals Works. Hydrogen peroxide (30 % v/v), ferrous sulfate ($FeSO_4\cdot7H_2O$), nitric acid and sodium hydroxide were all obtained from Tianjin Chemical Reagents Co. (Tianjin, China). All chemicals were of analytical grade and were used without any further purication. The pure water purifed by an apparatus ATC-2-5-U was used throughout this study.

Procedure: All dye oxidation reactions were carried out in a 400 mL Pyrex UV reactor irradiated with a 16 W viltalight lamp (365 nm) and simultaneously stirred with a stirring bar (20 mm) using a magnetic stirrer. In each experimental run, appropriate amount of stock acid red 18 solution were added to a 100 mL volumetric flask, then diluting with pure water. After transferred to the reactor, the solution was adjusted to a desired pH value using nitric acid and sodium hydroxide. The reactions were initiated by adding appropriate amounts of hydrogen peroxide and ferrous ion to the reactor and turning on the viltalight lamp at the same time. At certain reaction intervals, a volume approximate to 5mL of sample was withdrawn using a haustorial tube and the concentration of acid red 18 was determined immediately.

Analytical methods: The spectrogram of acid red 18 solution was scanned from 200 to 800 nm using a UV-2550 spectrophotometer (Shimadzu, Japan) with a 1 cm path length spectrometric quartz cell. The spectrum showed that the maximum absorbance wavelength of acid red 18 was at 506 nm. Therefore the following absorbance of acid red 18 in the experiment can be determined at 506 nm. Before the measurement, a calibration curve was obtained by using the standard acid red

18 solution with a series of known concentrations. After the acid red 18 solution was added in the reactor, the solution pH was measured by using a digital pH meter (Shanghai Precision & Scientific Instrument Co. Ltd., China). Before the measurement, the pH meter was calibrated with standard buffers of 4.0, 6.8 at 25 ºC.

RESULTS AND DISCUSSION

Degradation characteristics of acid red 18 under different processes: The different processes, UV, UV/Fe^{2+}, UV/H_2O_2, Fenton reagent and UV/FR, were carried out as the control experiments for the degradation of acid red 18. The decrease in the acid red 18 concentration was almost not observed by UV irradiation alone. The degradation effect in the processes of UV/Fe^{2+} and UV/H_2O_2 was not significant in comparison with UV alone within reaction time. This low efficiency might be resulting from the lower UV power and little degradation time.

The best degradation result of acid red 18 was received under UV/FR process. Fig. 2 shows the comparison results of the UV-Vis spectra before and after the reaction by UV/FR. As can be seen from the spectra, the UV-Vis absorption of acid red 18 in aqueous solution was characterized by one main band in the visible region, with its maximum absorption at 506 nm and by one band in the ultraviolet region located at 333 nm. After 0.5 h degradation by UV/FR, 99.6 % acid red 18 was degraded. It showed that the oxidation power of low concentration iron of Fenton reagent was enhanced by UV. The degradation efficiency increased 3.6 % under UV/FR process. The results of the low increase may be from the low power of UV lamp, which was only 16W.

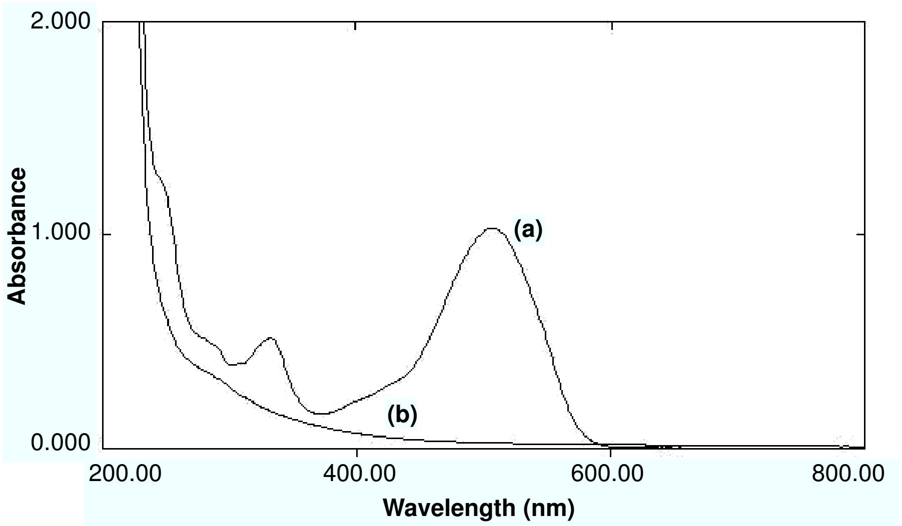

Fig. 2. UV-Vis spectra of acid red 18 before (a) and after (b) UV/FR process. Experimental conditions: $C_0 = 50$ mg L^{-1}; $Fe^{2+} = 0.1$ mM; $H_2O_2 = 5.0$ mM; pH = 3.0; UV lamp power: 16W

Degradation mechanism of acid red 18 by UV/FR : The time trend in the presence of UV/FR is reported in Fig. 3. In this research, the degradation of acid red 18 takes place in two steps. The first is very fast and lasts less than 1 min. In second step, which continues until the end of experiment, the degradation rate is slower and shows a pseudo-first order kinetics.

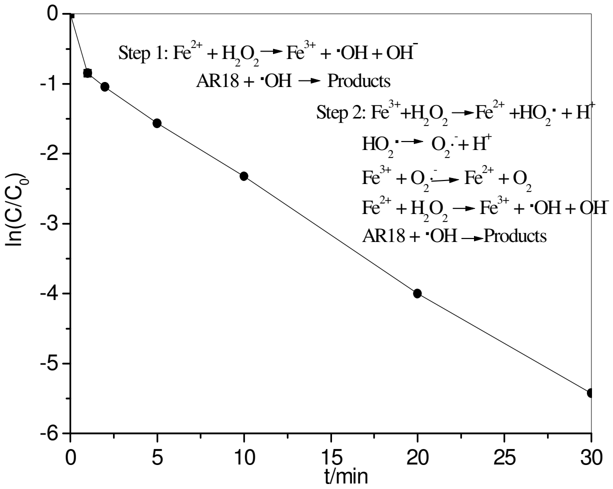

Fig. 3. Degradation characteristics of acid red 18 by UV/FR; Experimental conditions: C_0 = 50 mg L^{-1}; Fe^{2+} = 0.1 mM; H_2O_2 = 5.0 mM; pH = 3.0

The process is initiated by the reaction such as eqn. 1. The measured rate constant (k_1) is 76 M^{-1} s^{-1}, which is the lowest value of k among the possible reactions of the Fenton process[10]. Therefore, the reaction (1) plays a major role at the short beginning of the process when $OH^{\bullet}$ has not been produced. With the generation of $OH^{\bullet}$ the acid red 18 is combined with it rapidly and other reactions start almost simultaneously[14]:

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \qquad k_2 = 3.0 \times 10^8\ M^{-1}\ s^{-1} \qquad (2)$$

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad k_3 = 3.3 \times 10^7\ M^{-1}\ s^{-1} \qquad (3)$$

In succedent process, the degradation rate slows down due to some complex reactions beginning with the generation of the products in eqns. 1-3. The hydroperoxyl radical ($HO_2^{\bullet}$) can transform to superoxide radical($O_2^{\bullet-}$). Fe^{3+} can be reduced back to Fe^{2+} by reaction with H_2O_2, $HO_2^{\bullet}$ and $O_2^{\bullet-}$, respectively, which causes a circle within Fe^{2+} and Fe^{3+}. Because $OH^{\bullet}$ can combine with the other one, the fraction of them is transformed to H_2O_2. So, neither Fe^{2+} nor H_2O_2 were depleted completely in fact and the Fenton reaction was feasible in a duration time.

The experimental result shows that UV irradiation can promote the degradation of the azo dye. As it can be seen in eqns. 1 and 2, Fe^{2+} is transformed to Fe^{3+} rapidly. When pH is about 3.0, which is the optimal acidity in present experiment, Fe^{3+} is partially existed in hydroxyl complex ion $Fe(OH)^{2+}$. The ion produces $OH^{\bullet}$ and Fe^{2+} with UV irradiation and the generation of two productions can accelerate H_2O_2 decomposition, thus promoting the degradation rate[15].

Effect of initial pH values on the degradation of acid red 18 by UV/FR: The effect of the initial pH values on the degradation of acid red 18 by UV/FR was investigated and the results are shown in Fig. 4. It was observed that the degradation of acid red 18 was significantly influenced by the pH value of the solution. The degradation efficiency increases from 93.4 to 99.6 % decreasing the pH value from 6.0 to 3.0 after 0.5 h reaction. However, when the pH value of the solution decreases from 3.0 to 2.0, it will make a decrease of the degradation efficiency from 99.6 to 69 %. Therefore, the degradation of acid red 18 was inefficient in strong acid, because of much $^{\bullet}OH$ being consumed with H^+. In addition, the lower pH value inhibits the transformation between Fe^{2+} and Fe^{3+}, which might be another reason for the decrease of degradtion rate. When pH was higher, the generation of the hydroxyl radical was inhibited as a result of the oxidative decomposition of H_2O_2 and Fe^{2+} and Fe^{3+} might be combined with OH^- which should result in decrease of $^{\bullet}OH$. So, the degradation rate of acid red 18 was slower in a little larger pH. The results have no evident difference after 0.5 h reaction between pH 3.0 and 4.0. Considering that the discolouration efficiency of pH 3.0 was 99.6 %, which had 1.4 % increase than pH 4.0, therefore, pH 3.0 was selected as an optimum condition for acid red 18 degradation.

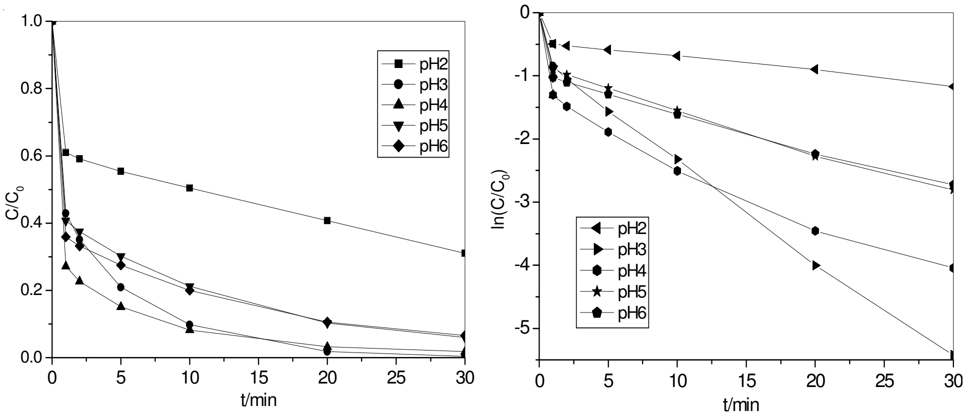

Fig. 4. Effect of pH values on the degradation of AR18 by UV/FR. Experimental conditions: $C_0 = 50$ mg L^{-1}; $Fe^{2+} = 0.1$ mM; $H_2O_2 = 5.0$ mM

Effect of Fe^{2+} dosage on the degradation of acid red 18 by UV/FR: The effect of Fe^{2+} dosage on the degradation of acid red 18 by UV/FR was investigated and the results are shown in Fig. 5. It was observed that the degradation of acid red 18 was significantly influenced by Fe^{2+} dosage, which distinctly increased with the increasing amount of Fe^{2+}. The decolouration efficiency increases from 39.0 to

95.3 % as a consequence of increasing Fe^{2+} dosage from 0.025 to 0.15 mM for 5 min. Degradation rate of step 1 and 2 increases too with increasing Fe^{2+} dosage. It is due to Fe^{2+} initiating the conversion of H_2O_2 to generate the $^{\bullet}OH$ in step 1. $^{\bullet}OH$ as a highly reative chemical species, reacts with acid red 18 to form products. So more $^{\bullet}OH$ was produced with more Fe^{2+}. There was no significant distinction in the degradation efficiency of acid red 18 with Fe^{2+} dosage from 0.1 to 0.15 mM after 0.5 h reaction. Considering that the more chemical substance should be avoided to the water environment, 0.1 mM of Fe^{2+} dosage was selected as an optimum condition for experiments.

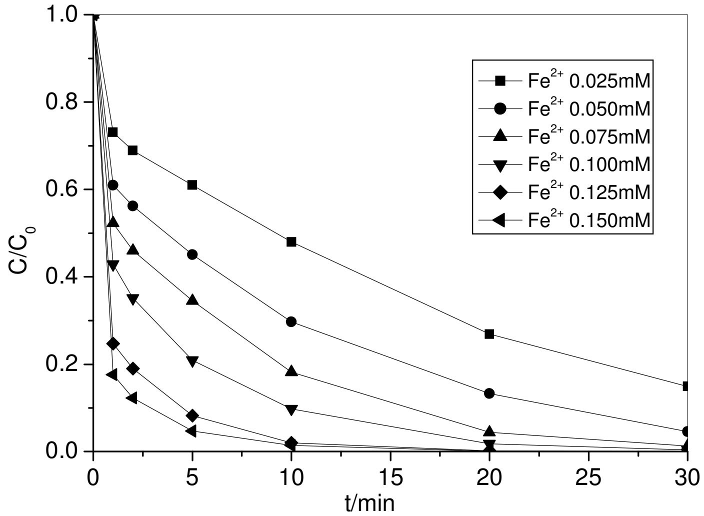

Fig. 5. Effect of Fe^{2+} dosage on the degradation of acid red 18 by UV/FR, Experimental conditions: $C_0 = 50$ mg L^{-1}; $H_2O_2 = 5.0$ mM; pH = 3.0

Effect of H_2O_2 dosage on the degradation of acid red 18 by UV/FR: Fig. 6 shows the effect of H_2O_2 dosage on the degradation of acid red 18 by UV/FR. It was observed that the degradation of acid red 18 was significantly influenced by H_2O_2 dosage. The decolouration efficiency increases from 70.3 to 91.2 % as a consequence of increasing H_2O_2 dosage from 0.5 to 5.0 mM at 10 min. It might be due to the increase of $^{\bullet}OH$ as the addition of H_2O_2. Nevertheless, the degradation rate slows down with H_2O_2 dosage from 5.0 to 10.0 mM. With increasing the H_2O_2 dosage to 10.0 mM, the reduction of the degradation ratio is about 7.2 % after 10 min reaction. It is due to more $^{\bullet}OH$ being consumed with H_2O_2 (eqn. 3), but not combined with acid red 18. In addition, as more Fe^{2+} was transformed to Fe^{3+} with the increasing of H_2O_2 (eqn. 1), which result in the decreasing of the generation of $^{\bullet}OH$.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (3)$$

$$2^{\bullet}OH \rightarrow H_2O_2 \quad (4)$$

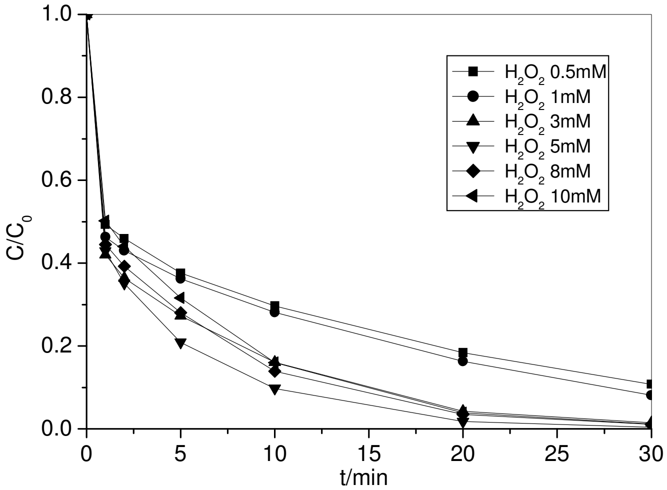

Fig. 6. Effect of H_2O_2 dosage on the degradation of acid red 18 by UV/FR; Experimental conditions: $C_0 = 50$ mg L^{-1}; $Fe^{2+} = 0.1$ mM; pH = 3.0

Effect of initial concentration on the degradation of acid red 18 by UV/FR: The effect of acid red 18 initial concentration on the degradation of acid red 18 by UV/FR was investigated and the results are shown in Fig. 7. It showed that the degradation of acid red 18 slowed down with the increasing of initial concentration of acid red 18. When the initial concentration was 25 mg L^{-1}, the degradation efficiency of acid red 18 was 99.6 % at 20 min and all dye was degraded within 0.5 h. With increasing the initial concentration to 150 mg L^{-1} the degradation ratio at 0.5 h decreased to 95.8 %.

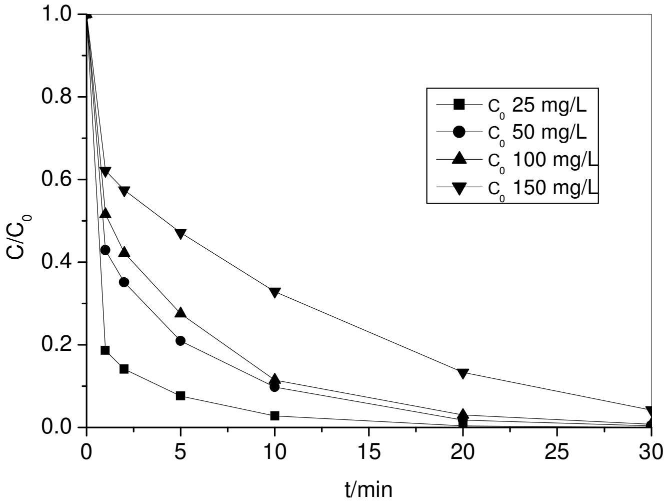

Fig. 7. Effect of initial concentration on the degradation of acid red 18 by UV/FR; Experimental conditions: $Fe^{2+} = 0.1$ mM; $H_2O_2 = 5.0$ mM; pH = 3.0

Conclusion

In this study, the degradation of acid red 18 in aqueous solution by Fenton reagent combined with UV was investigated for a variety of operating conditions. The results showed that the UV irradiation could promote the degradation efficiency of acid red 18. The effects of some parameters on the degradation were discussed and found that the degradation rate of acid red 18 is dependent on the pH value and the initial concentration of the dye. The optimal pH value of solutions was observed at 3.0. The effects of Fe^{2+} and H_2O_2 dosage on the degradation of acid red 18 were also investigated. Increasing the initial concentration of acid red 18 and the dose of Fe^{2+} and H_2O_2 could enhance the degradation efficiency of acid red 18. However, the higher levels of H_2O_2 will inhibit the reaction. The results indicate that the UV/FR can be an effective technology for treating azo dyes like acid red 18.

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