Original Research Paper

Effect of H_2O_2/Fe^{2+} Concentration Ratios on Fenton Oxidation of Reactive Red 6B with On-Line Detective Technology

Hang Xu*†, Tianlong Yu*, Jianxu Wang and Mei Li***

*Chemical Engineering and Pharmaceutics School, Henan University of Science and Technology, Luoyang 471023, China
**College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China
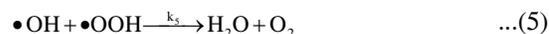†Corresponding Author: Hang Xu

ABSTRACT

The degradation of Reactive Red 6B (RR6B) wastewater was treated by Fenton oxidation using on-line spectrophotometric monitoring technology. The ratio of peroxide hydroxide concentration and ferrous ion dosage (HF) was investigated. Dyeing degradation process followed first order kinetics and Behnajady-Modirshahla-Ghanbery kinetics because of above 0.98 R^2. Fenton process transient reaction rate and instant hydroxyl radical concentration was calculated. The optimum HF was 143 with 98% dye removal, 0.05mol/(L·s) instant transient reaction rate and 2.4×10^{-11} mol/L initial hydroxyl radical concentration.

INTRODUCTION

Modern industry, especially dye-manufactures have brought about tremendous changes in our surrounding life, while a train of man-made colourful contaminations is pouring into environment (Earnhart 2013). In order to improve the stability, dyestuffs are prepared in a complex and stable chemical structure. Therefore, it is difficult for decomposition of dye in environment. The environment is vulnerable to be polluted by dyestuff effluent (Behnajady 2007). Commonly, dye-wastewater treatment methods are biological sludge, chemical precipitation, coagulation, absorption or electrical chemistry, which are not competent for the degradation task and cost highly as well (Tunç 2012).

Fenton's reagent is a classical water treatment technology in chemical oxidation. It is a mixture of Fe^{2+} catalyst and hydrogen peroxide (H_2O_2) to form hydroxyl radicals (OHC) to oxidize contaminants in acid aqueous solutions (Babuponnusami 2014). The OHC serves as very powerful, effective and nonspecific oxidizing agent, second only to fluorine in oxidizing power (Kusic 2006) to destruct chemical structure of dye. Mechanics of Fenton oxidation process could be described some complex redox reactions, as in eqs. (1)-(6). From the mechanics, it is demonstrated clearly that excessive Fe^{2+} and H_2O_2 can consume OHC and decrease degradation efficiency. Therefore, the optimal H_2O_2/Fe^{2+} has to be maintained to achieve the maximal removal efficiency (Siddique et al. 2014). Meanwhile, the ratio of oxidant H_2O_2 and dyeing concentration is another important parameter for Fenton's reagent to treat dyeing wastewater.

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + \bullet OH + OH^- \qquad ...(1)$$

$$D + \bullet OH \xrightarrow{k_2} D_{oxid} \qquad ...(2)$$

$$Fe^{2+} + \bullet OH \xrightarrow{k_3} Fe^{3+} + OH^- \qquad ...(3)$$

$$H_2O_2 + \bullet OH \xrightarrow{k_4} \bullet OOH + H_2O \qquad ...(4)$$

$$\bullet OH + \bullet OOH \xrightarrow{k_5} H_2O + O_2 \qquad ...(5)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_6} Fe^{2+} + H^+ + \bullet OOH \qquad ...(6)$$

In this study, Fenton oxidation was investigated with Reactive Red 6B as the target contamination and the online spectrometric system as monitoring method (Xu 2008). The purpose of this research was to find out the best ratio of peroxide hydroxide concentration and ferrous ion dosage (HF) for maximum colour removal. Fenton process was described by first order kinetics and B-M-G model (Behnajady 2007), and the instant Fenton degradation rate of Reactive Red 6B and transient hydroxyl radical concentration were calculated. This provide more persuasive evidences to comprehend and master the momentary Fenton decomposition of substances.

MATERIALS AND METHODS

Apparatus: The online monitoring system is shown in Fig. 1. On-line spectrophotometric monitoring system was
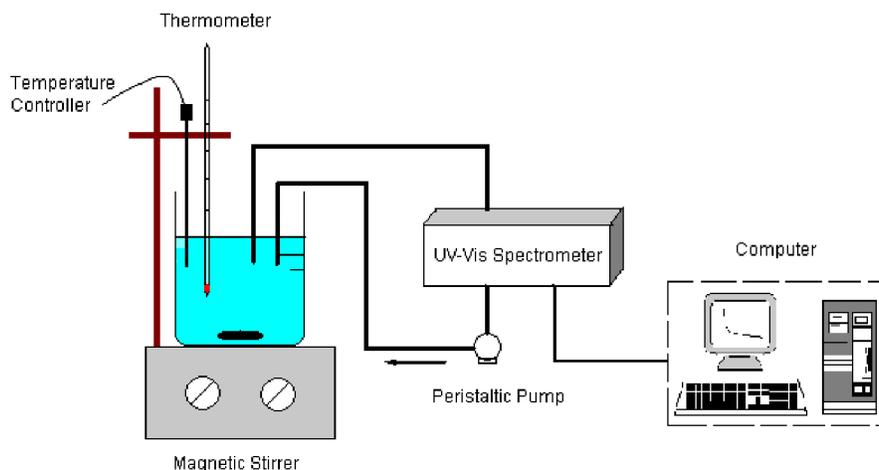
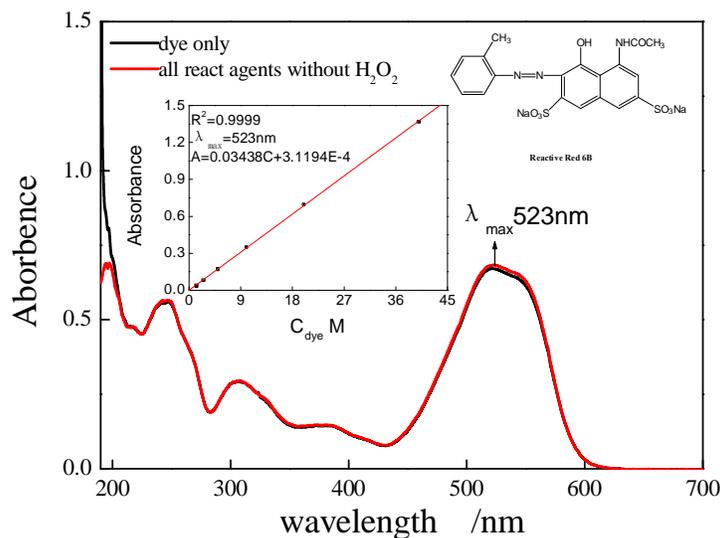Fig. 1: On-line spectrophotometric monitoring system.

Fig. 2: Standard curve of RR6B, reagent influence and chemical structure.

consisted of absorbance recording computer, UV-Vis spectrometer (SP-756PC Shanghai Spectrometric Instrument Ltd. Company), micro-scale flowing cuvette (1 mL) and cycle peristaltic pump (HL-1D Shanghai Instrument Manufactory). The pH of each water sample was adjusted by digital pH meter (PHS-3C-01 experimental pH meter Shanghai Instrument Manufactory).

Fenton process was performed in a beaker containing 200 mL solution, in which the specified concentration of selected dyestuff was taken. At the same time, stir, lamp and pump were applied. The wastewater was pressed into the current colorimetric container in UV-Vis spectrophotometer by peristaltic pump. Absorbance was determined at maximal

absorption peak of dye by UV-Vis spectrophotometer. When H_2O_2 at the calculated concentrations was added into the wastewater, the computer, which was linked with spectrophotometer, began to record experimental absorbance results.

Reagents: The peroxide hydroxide, ferrous sulphate, hydrochloric acid and sodium hydroxide were also analytical grade and purchased from Tianjin Chemical Reagent Company (China). Reactive Red 6B (RR6B) is widely used in reality dyeing and printing industry and it was purchased from Beijing Dye Company. The chemical structure and standard curve of RR 6B of RR6B are shown in Fig. 2. The maximum absorption is at 523 nm and the relationship between absorbance (A) with RR6B concentration (C) is $A = 0.0344C$

and coefficient of association is 0.9999.

The removal percentage of RR6B was characterized by such equation as following:

$$R = \frac{C_0 - C_i}{C_0} \times 100\% \qquad \text{...(7)}$$

In the equation 7, R is the removal percentage. C_0 and C_i represent the RR6B concentration at time = 0 and time = i, respectively. Fig. 2 depicts the shift of UV-vis spectra of RR6B when Fe^{2+}, Fe^{3+} and H$_2$SO$_4$ are added to the solutions. But the spectra of dyes solution in 500-700 nm does not display any variation with addition of Fe^{2+}, Fe^{3+} and H$_2$SO$_4$, which mean that UV-vis spectra of dyes solution are influenced by Fe^{2+}, Fe^{3+} and H$_2$SO$_4$ in visible spectral range. Therefore, 523 nm is taken as monitoring wavelength in this research.

RESULTS AND DISCUSSION

Dye degradation: The removal percentages of RR6B at different [H$_2$O$_2$]$_0$/[Fe^{2+}]$_0$(HF ratio) are shown in Fig. 3 clearly. Part A shows the effect of Fe^{2+} concentration, HF value decrease accompany with Fe^{2+} concentration augmentation. Therefore, bigger HF means less amount of Fe^{2+} in the reaction. When HF drop from 500 to 143, the final removal rate can reach almost 95% at the end of experimental period. However, if more Fe^{2+} ions take part, side-reaction would undermine the Fenton process to some extent. In fact, over-dosed Fe^{2+} ions react with born hydroxyl radical completely (Masomboon 2010). Hence, terminal removal is dropping down to 90% on the condition that HF is 125. On the other hand, part B mainly indicates the impact by variable H$_2$O$_2$ dosage. In a whole, excessive or inadequate amount of H$_2$O$_2$ go against best removal. For example, as HF is 0.78 or 15.6, lower removal abstained as HF surpass 125 or even reach 500. Equation 4 takes the predominant place compared to RR6B decomposition (Venny 2012), resulting to barely 60% removal. From the part A and part B, the best HF is 143.

First order kinetics: Fenton degradation of RR6B fits the First order kinetics well which can be evidenced from Fig. 4. Each linear fitting coefficient has above 0.99. Part A shows that Fenton process has fastest velocity nearly 0.003 s^{-1} when HF ratio is 143, in which, Fe^{2+} dosage is 3.5×10^{-5} mol/L. Along with HF increase to 500, meanwhile, Fe^{2+} concentration drops down to 1.0×10^{-5} mol/L, and first order rate appears to be smoothly descend. The biggest rate in part B is 0.002 s^{-1} under the moderate HF value of 125, which indicates optimum state of Fenton process needing an appropriate H$_2$O$_2$ dosage.

B-M-G model kinetics: There is a new, advanced kinetics model proposed to depict Fenton process (Behnajady 2007). Detailed formula is as follows:

$$\frac{[RR6B]_i}{[RR6B]_0} = 1 - \frac{t}{m + bt} \qquad \text{...(8)}$$

Where $[RR6B]_i$ represent the concentration of time i, $[RR6B]_0$ is the initial dye concentration, t is the reaction time and m, b are two character constants. Take derivatives of time to B-M-G model equation both side and reaction rate formula as following:

$$r = -\frac{d[RR6B]_i}{dt} = \frac{m[RR6B]_0}{(m + bt)^2} \qquad \text{...(9)}$$

At the starting stage of degradation, in other words, as t is 0, equation (9) can be simplified as:

$$r_0 = \frac{[RR6B]_0}{m} \qquad \text{...(10)}$$

Which indicates that the relation between m and rate lies with inverse proportion, the bigger the value of m is, the lower will be the rate. On other side, if the reaction time inclines to infinite:

$$\lim_{t \to \infty} = \frac{[RR6B]_i}{[RR6B]_0} = 1 - \frac{1}{b} = \frac{b-1}{b} \qquad \text{...(11)}$$

If certain amount of RR6B is decomposed when the time is long enough, $[RR6B]_i \to 0$, hence, the critical situation of completely degradation of RR6B is b-1/$b \le 0$. Theoretically, RR6B can be decomposed as $0 \le b \le 1$, meanwhile, if $b > 1$, it means, RR6B was partially degraded. So as to quantify the two unascertained constants m and b, it is suggested to transfer the form of equation (8) to:

$$\frac{1}{t}m + b = \frac{[RR6B]_0}{[RR6B]_0 - [RR6B]_i} \qquad \text{...(12)}$$

It's obvious that the relationship between $\frac{[RR6]_0}{[RR6]_0 - [RR6]_i}$ and $\frac{1}{t}$ belongs to linear regression scope where m is the slop coefficient and b is the intercept (Fig. 5).

From the Fig. 5, it is clearly seen that Fenton process follows B-M-G model very well. The B-M-G model has advantage in depicting Fenton process with higher fitting coefficients (above 0.997) than First order fitting. Part A presents the effects of ferrous ion dosage on Fenton process, in detail, along with HF increase from 125 to 500, an ascend tendency in ordinate value in general. As HF is 143, there is
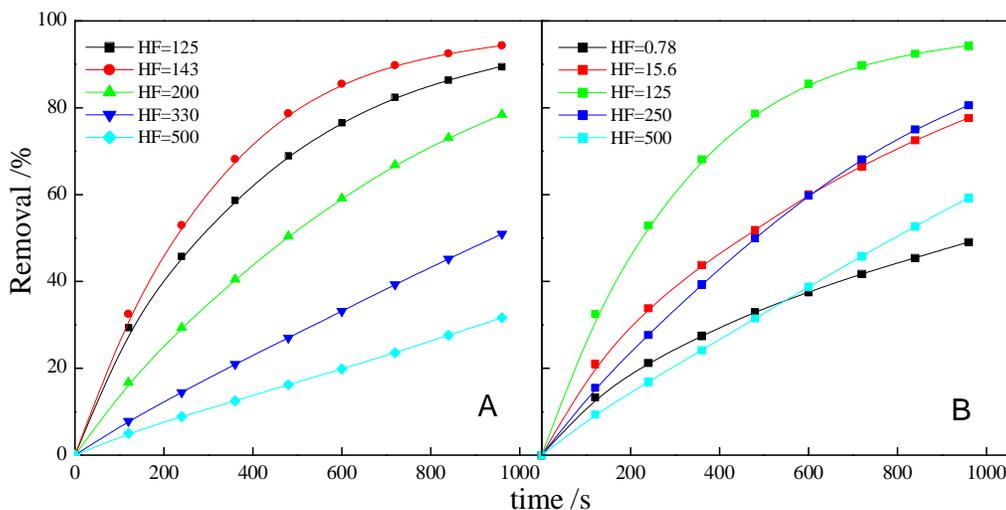
Fig. 3: Removal percentage at different HF ratios ($[RR6B]_0$ = 4.0×10^{-5} mol/L, pH=3.15, T = 15°C).
A. $[H_2O_2]_0$=5.0×10^{-3} mol/L, $[Fe^{2+}]_0$ = 1.0×10^{-5}, 1.5×10^{-5}, 2.5×10^{-5}, 3.5×10^{-5}, 4.0×10^{-5} mol/L
B. $[Fe^{2+}]_0$ = 2.0×10^{-5} mol/L, $[H_2O_2]_0$ = 1.56×10^{-5}, 3.13×10^{4}, 2.5×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2} mol/L
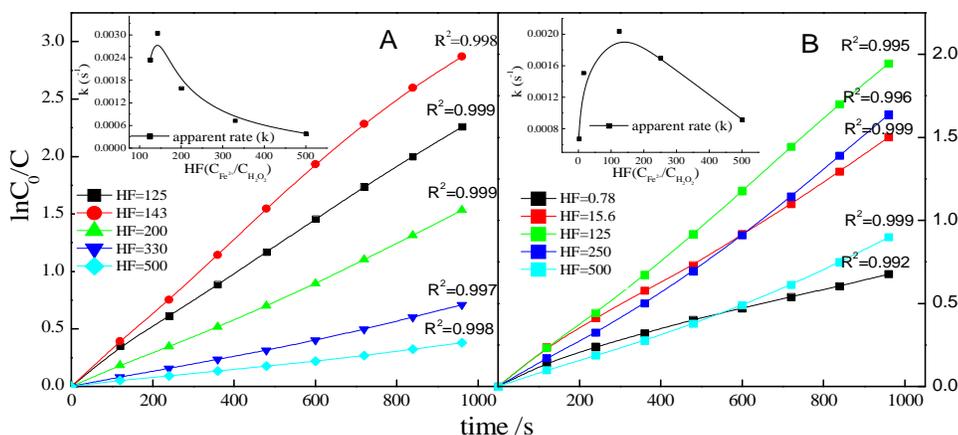

Fig. 4: First order kinetics at different HF ratios ($[RR6B]_0$ = 4.0×10^{-5} mol/L, pH=3.15, T = 15°C).
A. $[H_2O_2]_0$=5.0×10^{-3} mol/L, $[Fe^{2+}]_0$ = 1.0×10^{-5}, 1.5×10^{-5}, 2.5×10^{-5}, 3.5×10^{-5}, 4.0×10^{-5} mol/L
B. $[Fe^{2+}]_0$ = 2.0×10^{-5} mol/L, $[H_2O_2]_0$ = 1.56×10^{-5}, 3.13×10^{4}, 2.5×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2} mol/L

the smallest *m* value which represents the best initial reaction rate. All *b* values of different HF expect 500 are less than 1 which means inadequate Fe^{2+} amount leading to lower degradation efficiency. Here, part B shows the various HF determined by H_2O_2 concentration. It can be clearly figured that Fenton process behaves well at 125 HF with 2.5×10^{-3} mol/L H_2O_2. When HF is 500, it means that H_2O_2 is excessive to the Fenton process, the *m* value is as high as 1200, and at the same time, *b* value is 1.4. On such condition, RR6B cannot be degraded thoroughly.

Transient reaction rate: Fig. 6 shows transient reaction rate at various HF values affected by Fe^{2+} and H_2O_2 concentra-

tions. In part A, transient reaction rates are 0.04, 0.05, 0.02, 0.01 and 0.007 mol/(L·s) at different HF of 125, 143, 200, 330 and 500, respectively. While, the reaction rate in part B seems to be firstly ascend to 0.03 mol/L and then descend down to 0.01 mol/L along with HF increase from 0.78 to 500. Overall, Fenton process rate has a smooth decrease during experimental time because the lack of both hydroxyl radical and total amount of RR6B molecules.

Instant concentration of hydroxyl radical: Fenton and simulated Fenton processes are based on hydroxyl radical, which is a significant factor needed to be studied. RR6B react with hydroxyl radicals and can be simplified as an equation:
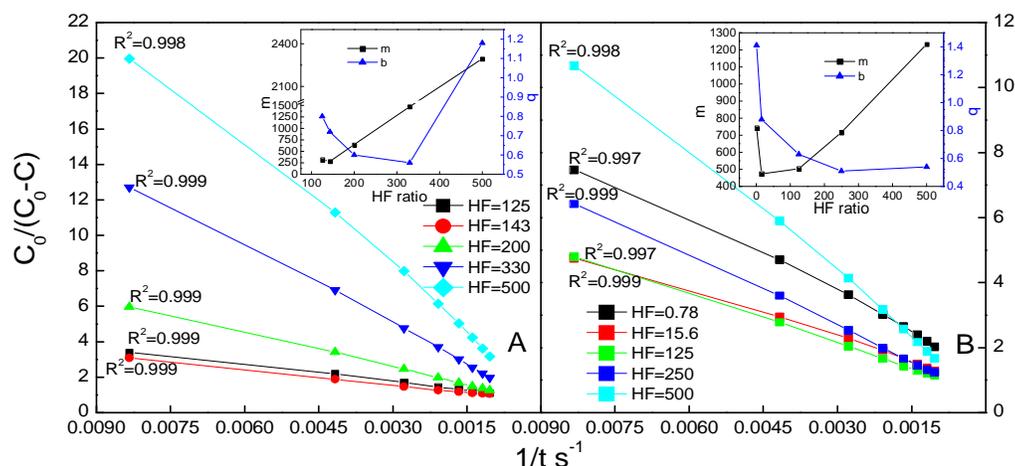
Fig. 5: B-M-G model at different HF ratios ([RR6B]$_0$ = 4.0×10^{-5}mol/L, pH=3.15,T = 15°C)
A. [H$_2$O$_2$]$_0$ = 5.0×10^{-3}mol/L,[Fe^{2+}]$_0$ = 1.0×10^{-5},1.5×10^{-5},2.5×10^{-5},3.5×10^{-5},4.0×10^{-5} mol/L
B. [Fe^{2+}]$_0$ = 2.0×10^{-5}mol/L, [H$_2$O$_2$]$_0$= 1.56×10^{-5}, 3.13×10^{-4},2.5×10^{-3},5.0×10^{-3},1.0×10^{-2} mol/L
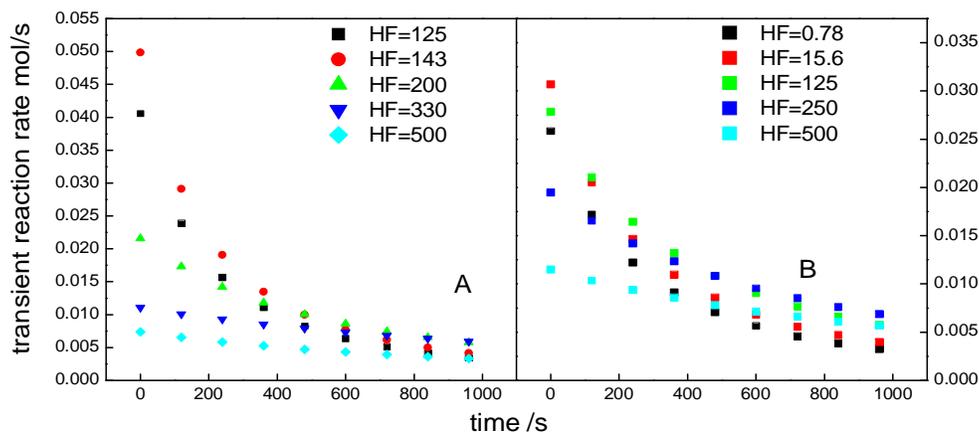
Fig. 6: Transient reaction rate at different HF ratios, ([RR6B]$_0$ =4.0×10^{-5}mol/L, pH = 3.15,T = 15°C)
A.[H$_2$O$_2$]$_0$ = 5.0×10^{-3}mol/L,[Fe^{2+}]$_0$=1.0×10^{-5},1.5×10^{-5},2.5×10^{-5},3.5×10^{-5},4.0×10^{-5} mol/L
B.[Fe^{2+}]$_0$ = 2.0×10^{-5}mol/L, [H$_2$O$_2$]$_0$= 1.56×10^{-5}, 3.13×10^{-4},2.5×10^{-3},5.0×10^{-3},1.0×10^{-2} mol/L

$$RR6B + \bullet OH \longrightarrow P \quad \quad ...(13)$$

The rate of equation (13) can be calculated through steady-state assumption to initial dye concentration First order kinetics; consequently, the value of k is about 1.6×10^8. The apparent rate can be written as:

$$r = -\frac{d[RR6B]}{dt} = k[RR6B][\bullet OH] \quad \quad ...(14)$$

Combine the equation 14 and equation 9:

$$r = -\frac{d[RR6B]}{dt} = k[RR6B][\bullet OH] = \frac{m[RR6B]_0}{(m+bt)^2} \quad ...(15)$$

So, the formula of hydroxyl radical can be characterized as:

$$[\bullet OH] = \frac{m[RR6B]_0}{(m+bt)^2 k[RR6B]} \quad \quad ...(16)$$

Fig. 7 indicates the calculated hydroxyl radical concentration at different HF ratios. It can be seen from part A that radical concentration has a increase at the latter stage when HF is 125, 143 and 200. The available hydroxyl radical is relatively adequate to degradable RR6B molecules. Especially, as HF is 143, the original concentration is highest 2.3×10^{-11} mol/L and the final radical concentration can even reach 3.3×10^{-11} mol/L. Furthermore, curve of radical concentration keeps steady along the experimental time at HF of 330 and 500, which can be explained as producing rate equal to consuming rate.

In general, hydroxyl radical concentration in part B is

Fig. 7: Instant hydroxyl radical concentrations at different HF ratios, ($[RR6B]_0$ = 4.0×10^{-5}mol/L, pH=3.15,T = 15°C)
A. $[H_2O_2]_0$ = 5.0×10^{-3}mol/L,$[Fe^{2+}]_0$ = 1.0×10^{-5},1.5×10^{-5},2.5×10^{-5},3.5×10^{-5},4.0×10^{-5} mol/L
B. $[Fe^{2+}]_0$ = 2.0×10^{-5}mol/L, $[H_2O_2]_0$ = 1.56×10^{-5}, 3.13×10^{-4},2.5×10^{-3},5.0×10^{-3},1.0×10^{-2} mol/L
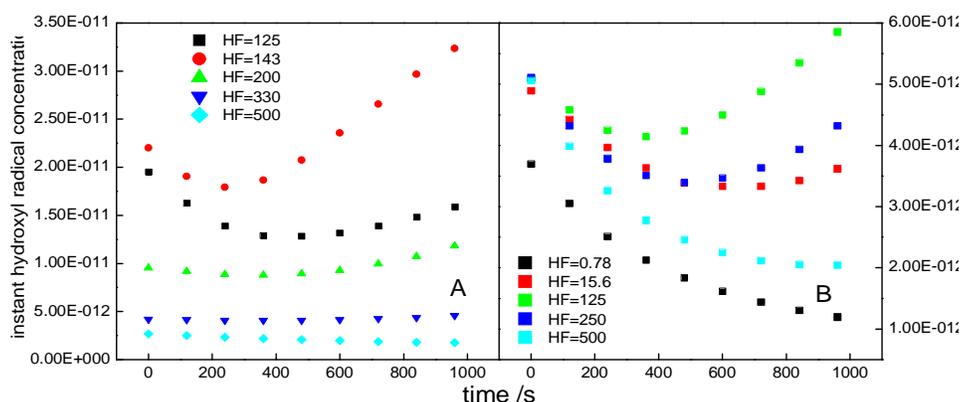
less than former one. With the range of HF form 15.6 to 500, the concentration just almost stays near 5.0×10^{-12}mol/L. When HF is 125, there is highest ending concentration about 6.0×10^{-12}mol/L. Two HF extreme situations such as 0.78 and 500 behave distinguished descend tendency all along compared to other HF value. In these situation, insufficient hydroxyl radicals were brought and continue to be consumed along with process carrying out.

CONCLUSION

Fenton regent was successfully used to treat Reactive Red 6B in aqueous. On-line spectrophotometric monitoring technology was a accurate, convenient and speed method to apply for Fenton oxidation. Based on first order kinetics and B-M-G model, Fenton process was described very well and correlation coefficient was above 0.98. B-M-G model was superior to first order. The optimum HF was 143 with 100% dye removal, 0.05mol/(L·s) instant transient reaction rate and 2.4×10^{-11}mol/L initial hydroxyl radical concentration.

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REFERENCES

Babuponnusami, A. and Muthukumar, K. 2014. A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Engg., 2(1): 557-572.

Behnajady, M.A., Modirshahla, N. and Ghanbary, F. 2007. A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process. J. Hazard. Mater., 148(1): 98-102.

Earnhart, D. 2013. Water pollution from industrial sources. In: Encyclopedia of Energy, Natural Resource and Environmental Economics, Waltham Publishers Inc., pp.114-120.

Kusic, H. 2006. Photo-assisted Fenton type processes for the degradation of phenol: A kinetic study. J. Hazard. Mater., 136(3): 632-644.

Masomboon, N., Ratanatamskul, C. and Lu, M.C. 2010. Mineralization of 2,6-dimethylaniline by photoelectro-Fenton process. App. Catal. A: Gen., 384(1-2): 128-135.

Siddique, M., Farooq, R. and Price, G.J. 2014. Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19. Ultrasonics Sonochemistry, 21(3): 1206-1212.

Tunç, S., Gürkan, T. and Duman, O. 2012. On-line spectrophotometric method for the determination of optimum operation parameters on the decolorization of Acid Red 66 and Direct Blue 71 from aqueous solution by Fenton process. Chem. Engg. J., 181(1): 431-442.

Venny, S.G., and Ng, H.K. 2012. Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils. Chem. Engg. J., 213(4): 295-317.

Xu, H., Zhang, D. and Xu, W. 2008. Monitoring of decolorization kinetics of Reactive Brilliant Blue X-BR by online spectrophotometric method in Fenton oxidation process. J. Hazard. Mater., 158(2-3): 445-453.