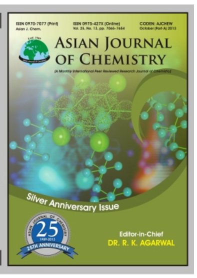
Asian Journal of Chemistry; Vol. 25, No. 14 (2013), 7989-7992

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14888



On-line Spectrophotometric Method for Decolourizing Reaction Kinetics of Reactive Black 5 by Fenton Oxidation

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(*Received*: 3 December 2012; *Accepted*: 29 July 2013) AJC-13856

Fenton oxidation was employed to treat and decolourize the modeling wastewater of reactive black 5 by online spectrophotometry. The effects of initial $FeSO_4$ dosage, initial H_2O_2 dosage, pH value, initial reactive black 5 and temperature on the colour removal and decolourizing reaction rate constant were investigated. The results show that Fenton oxidation follows pseudo first order kinetics in the first stage and reaction activation energy is 3.451 kJ mol^{-1}. The optimum initial H_2O_2 and pH was 2.118 mM and 3, respectively. Initial $FeSO_4$ dosage against k_{ap} presents a linear correlation: $k_{ap} = 0.1354\ [Fe^{2+}]_o$. Intrinsic reaction rate constant of reactive black 5 and ˇOH is $7.528 \times 10^{11}\ M^{-1}\ s^{-1}$.

Key Words: Fenton oxidation, Reactive black 5, Kinetics, Reaction rate constant.

INTRODUCTION

Dyestuff brings our life beautiful. Therefore it is wide-ranging applied in the many industries. In recent report, each year about 12 % of synthetic textile dyes were lost during producing processes[1]. A large part of them directly discharged to the environment without any treatment. Wastewater in dye and textile industry had strong colour, high COD and a relatively low BOD/COD ratio[2]. Nowadays, there are many approaches to deal with colouring wastewater, such as biodegradation, chemical coagulation, photocatalytic oxidation and chemical oxidation, *etc*.

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 (ˆOH) to oxidize contaminants in acid aqueous[3]. The ˆOH serves as very powerful, effective and nonspecific oxidizing agent, second only to fluorine in oxidizing powder[4] to destruct chemical structure of organic. The mechanism of Fenton oxidation process could be described as some complex redox reactions in eqs. (1)-(6) in treatment of dye (D).

In this study, Fenton's reagent was employed to treat modeling compound of textile wastewater of reactive black 5 by online spectrophotometric system[5]. The purpose of this research is to find out the best reaction condition for maximum colour removal and reaction rate in dyeing wastewater and established the kinetic model of dyeing degradation during Fenton oxidation process.

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + \bullet OH + OH^- ,\ k_1 = 76\ M^{-1}s^{-1} \quad (1)$$

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

$$Fe^{2+} + \bullet OH \xrightarrow{k_3} Fe^{3+} + OH^- ,\ k_3 = 3.2 \times 10^8\ M^{-1}s^{-1} \quad (3)$$

$$H_2O_2 + \bullet OH \xrightarrow{k_4} \bullet OOH + H_2O ,\ k_4 = 1.0 \times 10^{10}\ M^{-1}s^{-1} \quad (4)$$

$$\bullet OH + \bullet OOH \xrightarrow{k_5} H_2O + O_2 ,\ k_5 = 2.7 \times 10^7\ M^{-1}s^{-1} \quad (5)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_6} Fe^{2+} + H^+ + \bullet OOH ,\ k_6 = 0.01\ M^{-1}s^{-1} \quad (6)$$

EXPERIMENTAL

Reactive black 5 was obtained from Jiangsu Shenxin Dye Company (China) and used without further purification. Modeling wastewater of reactive black 5 was prepared by dissolving requisite quantity of the dyestuffs in double distilled water. $FeSO_4 \cdot 7H_2O$, H_2SO_4 and H_2O_2 (30 % in H_2O) were of analytical grade and purchased from Beijing Chemical Reagent Company.

Fig. 1 shows online spectrophotometric system. This system can be integrated by three parts *i.e.*, reaction unit, optical measuring unit and recording unit. Reaction unit contains a magnetic stirrer apparatus (Rongsheng Instrument company, China), thermometer, 250 mL beaker and temperature controller. Magnetic stirrer apparatus has another function of heating solution. Optical measuring unit includes UV-visible spectrometer, peristaltic pump and current colourimetric container (UNICO 2012PC, Shanghai, China). Current velocity of wastewater in system is 18.5 mL L^{-1}. Recording unit is a computer and monitoring frequency is 6 min^{-1}.

Fenton oxidation process was performed using 200 mL solution, which contained specified concentration of selected

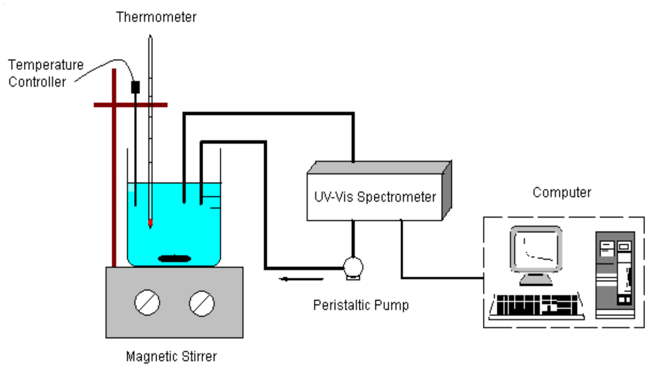

Fig. 1. Online spectrophotometric system

dyestuff in beaker. The calculated $FeSO_4$ concentration and pH adjustment using H_2SO_4 were added to the wastewater. At the same time, stir and pump were applied. Wastewater was pressed into the UV-visible spectrophotometer by peristaltic pump. The maximal absorption peak of reactive black 5 was 599 nm monitored by UV-visible spectrophotometer. When the calculated H_2O_2 concentrations were added into the wastewater and computer which was linked with spectrophotometer began to record instant absorbance.

RESULTS AND DISCUSSION

In many early reports, Fenton oxidization process apparently followed first-order kinetics[6,7], $\ln(C_0/C) = k_{ap}t$. The slope k_{ap} is the decolourizing reaction rate constant. In this paper, the k_{ap} is one of the important parameters to evaluate degradation efficiency. Another parameter was the colour removal (R) in 300 s:

$$R = \frac{C_0 - C_{300}}{C_0} \times 100\% \quad (7)$$

Time-dependent degradation of reactive black 5: The change in C/C_0 value of dyes *versus* irradiation time is shown in Fig. 2. C represents the concentration of dye in t sec and C_0 is the initial concentration. Fenton oxidation process can be prepared by two regions to treat reactive black 5 from Fig. 2. At beginning of the reaction ($t \geq 50s$), decolourization is faster and in the second region ($t \geq 50s$), decolourizing rate is significantly retarded as the reaction time is extended. These experimental phenomena can be explained by two aspects. Decrement of Fe^{2+} and H_2O_2 concentration can decrease the reaction rate during Fenton process. In another way, intermediate products during the Fenton oxidation process engage in the reaction and restrain mainly reaction to proceed. From the Fig. 2, Fenton oxidization process apparently follows first-order kinetics in the early stage.

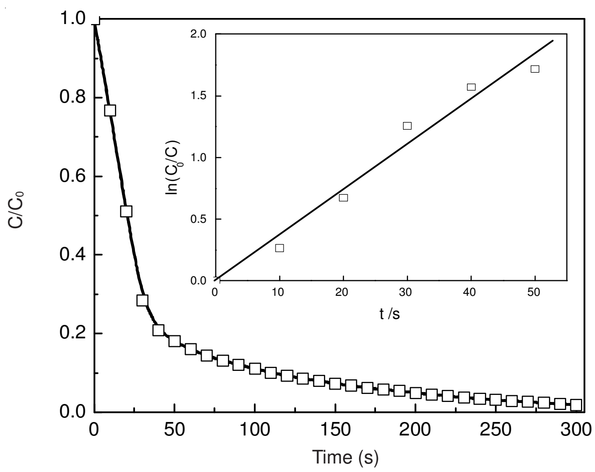

Fig. 2. Time-dependent degradation of reactive black 5 ($[RB\ 5]_o$ = 17 mg/L, $[Fe^{2+}]_o$ = 0.09711 mM, $[H_2O_2]_o$ = 2.118 mM, pH = 3, T = 15 ºC)

Effect of initial Fe^{2+} dosage: A series of Fe^{2+} dosage influence on R and k_{ap} has been investigated in Fig. 3. The R increases from 74.1 % to 95.22 % with the addition of Fe^{2+} dosage from 0.03237 to 0.09711 mM. However R was only 96.10 % when Fe^{2+} catalyst is improved 0.1618 mM. This experimental phenomenon suggests that high Fe^{2+} dosage does not effect decolourization of reactive black 5 in the Fenton oxidation process due to Fe^{2+} ion competing ´OH with dye molecules[8], which can be expressed by the eqn. 3. Therefore, 0.09711 mM of initial Fe^{2+} dosage can be used as an optimum dosage. Initial Fe^{2+} dosage against k_{ap} shows a linear correlation from the Fig. 3, $k_{ap} = 0.1354[Fe^{2+}]_o$, $R^2 = 0.9917$. This result expresses that Fe^{2+} as a catalyst can accelerate the decomposition of H_2O_2 obviously and produce ˆOH.

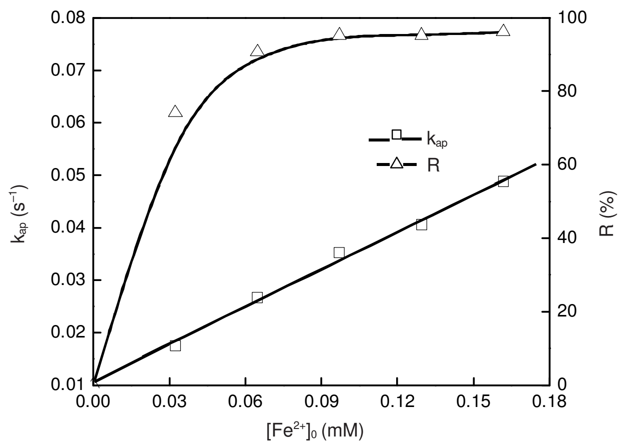

Fig. 3. Influence of initial Fe^{2+} concentration; ($[RB\ 5]_o$ =17 mg/L, $[H_2O_2]_o$ = 2.118 mM, pH = 3, T = 15 ºC)

Effect of initial H_2O_2 dosage: Another important point considered in Fenton oxidation was the amounts of hydrogen peroxide[9]. Fig. 4 shows the change of R and k_{ap} with various amounts of initial H_2O_2. The R and k_{ap} increase from 92.01

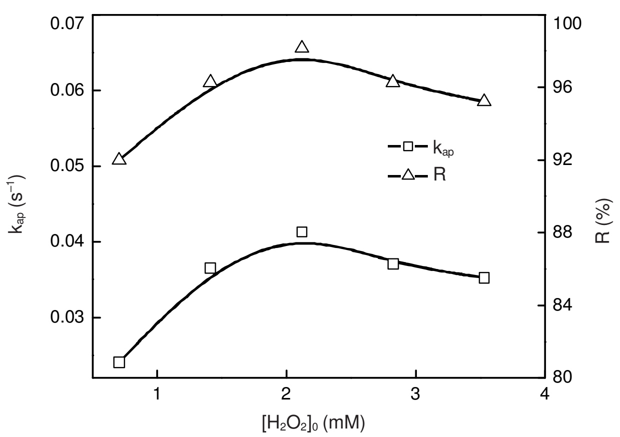

Fig. 4. Influence of initial H_2O_2 concentrations; ($[RB\ 5]_o$ = 17 mg/L, $[Fe^{2+}]_o$ = 0.09711 mM, pH = 3, T = 15 ºC)

to 98.17 % and 0.0241 to 0.0413 s^{-1} respectively with the dosage of H_2O_2 from 0.7060 mM to 2.118 mM. Further increasing H_2O_2 dosage to 3.529 mM, the R and k_{ap} decrease to 95.22 % and 0.03525 s^{-1}, respectively. Thus, the 2.118 mM of initial H_2O_2 dosage can be used as the optimum dosage. The increase of H_2O_2 dosage accelerated the produce of ˆOH. However, H_2O_2 of higher concentration could adsorb ˆOH (eqn. 4 and eqn. 5), as a result of reducing rate of H_2O_2. The more concentration of H_2O_2, the more power adsorbed function[10].

Effect of pH: The pH of the solution plays an important role on decolourizing of dyes using Fenton oxidation[11]. The influence of pH on decomposition of reactive black 5 by Fenton oxidation is shown in Fig. 5. Three is the optimum pH from the Fig. 3. At low pH (pH < 3) the colour removal and reaction rate was limited because ˆOH is consumed by the excessive H^+ as eqn. 8. When pH higher than 3, Fenton oxidizing ability is decreased, not only by the decomposition of H_2O_2 but also the deactivation of the ferrous catalyst with the formation of ferric hydroxo complexes[12] and the reduction of ˆOH (eqn. 1) according to the Le Châtelier principle, which should be taken into consideration.

$$\cdot OH + H^+ + e^- \rightarrow H_2O \quad (8)$$

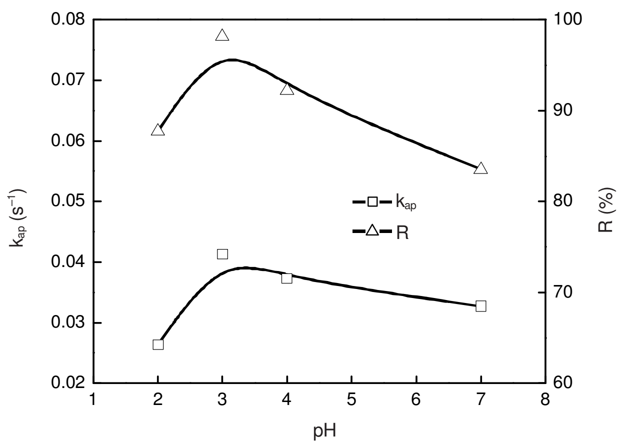

Fig. 5. Influence of pH; ($[RB\ 5]_o$ = 17 mg/L, $[Fe^{2+}]_o$ = 0.09711 mM, $[H_2O_2]_o$ = 2.118 mM, T = 15 °C)

Effect of temperature: Temperature is a key parameter impacting on the reaction rate and the product yield. Fig. 6 shows the k_{ap} increases from 0.0365 to 0.04088 s^{-1} with the

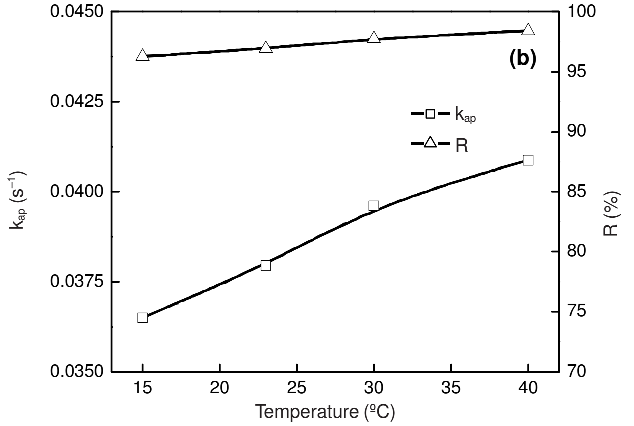

Fig. 6. Influence of temperature; ($[RB\ 5]_o$ = 17 mg/L, $[Fe^{2+}]_o$ = 0.09711 mM, $[H_2O_2]_o$ = 1.412 mM, pH = 3)

rise of temperature from 15 to 40 ºC. However, the R presents only a little increase from 96.27 to 98.41 %. This result demonstrated that higher temperature increases the reaction rate between Fe^{2+} and H_2O_2, therefore increasing the rate of production of oxidizing species such as ˆOH or high-valence iron species. However, the quantity of oxidizing agent (H_2O_2) does not increase and Fe^{2+} is easily hydrolyzed while H_2O_2 is very unstable and decomposed by itself in higher temperature. Therefore the colour removal has not a big change with the rise of temperature. According to Arrhenius formula ($\ln k_{ap} = -\frac{Ea}{RT} + \ln A$), the dependence of $\ln k_{ap}$ on -1/T[13] can be linear fit to calculate the activation energy (E_a) in the similar temperature range. The E_a is 3.451 kJ mol^{-1} ($R^2 > 0.99$).

Kinetics study: According to the reference[14], relationship between initial H_2O_2 concentration and initial reactive black 5 concentration is as follow:

$$\frac{[H_2O_2]_0}{k_{ap}} = K[D]_0 + B \quad (9)$$

$$B = \frac{k_3}{k_1k_2} + \frac{2k_4[H_2O_2]_0}{k_1k_2[Fe^{2+}]_0} \quad (10)$$

The result shows in Fig. 7 about the linear relationship between $\frac{[H_2O_2]_0}{k_{ap}}$ and $[RB\ 5]_0$ ($R^2 > 0.99$). According to the intercept (B), calculated intrinsic rate constant (k_2) of reactive black 5 and ˆOH is 7.528 × 10^{11} M^{-1} s^{-1}. From the Fig. 7, it is observed that the lower dyes concentration, the higher k_{ap} for degradation process. The rise of dye concentration in aqueous increased the number of dye molecules in the water but ˆOH, so the colour removal and reaction rate (k_{ap}) decreases.

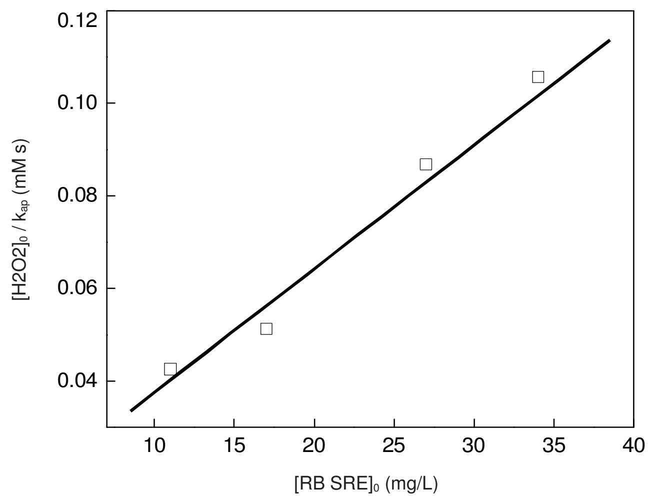

Fig. 7. Relationship between $[H_2O_2]_o/k_{ap}$ and $[RB\ 5]_o$; ($[Fe^{2+}]_o$ = 0.09711 mM, $[H_2O_2]_o$ = 2.118 mM, pH = 3, T = 15 ºC)

Conclusion

Fenton oxidation process can rapidly deal with modeling wastewater of reactive black 5 and follows pseudo first order kinetics in the first stage. The optimum initial H_2O_2 and pH was 2.118 mM and 3, respectively. Initial $FeSO_4$ concentration against k_{ap} presents a linear correlation: $k_{ap} = 0.1354[Fe^{2+}]_o$. The reaction activation energy of Fenton oxidation is 3.451 kJ mol^{-1} and intrinsic rate constant of reactive black 5 and ˆOH is 7.528×10^{11} $M^{-1}s^{-1}$.

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