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Fenton Reagent Oxidation and Decolorizing Reaction Kinetics of Reactive Red SBE

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Abstract

Fenton reagent was employed to treat and decolorize the wastewater of Reactive Red SBE by on-line spectrophotometry. The effects of initial FeSO₄ concentration, initial H₂O₂ concentration, pH, reactive red SBE and temperature on the decoloration of reactive red SBE were investigated. The results show that Fenton oxidize process follows pseudo first order kinetics in the first stage and reaction activation energy is 2.608kJ/mol. The decolorizing reaction rate constants (k) increase with the rise of FeSO₄ concentration, H₂O₂ concentration, temperature, but decrease with the rise of reactive red SBE, and the optimum pH is 3. Initial FeSO₄ concentration and initial H₂O₂ concentration against k are linear correlation.

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Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).*Keywords:* Fenton reagent; Reactive Red SBE; kinetics; decolorizing reaction rate constant

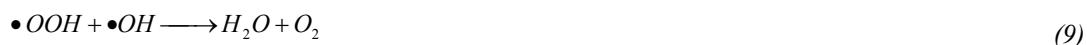
1. Introduction

Nowadays, many reactive dyestuffs are designed by scientists to express a good characteristic about high resistance to fading caused by chemical, biological and light-induced oxidation [1] because of their resistant to oxidation and biodegradation, so the synthetic reactive dyestuffs are widespread applied in several industries including textile, paper, printing, cosmetics and pharmaceuticals [2]. But the dyeing process consumes excessive water and one of the largest groups of dye mills discharges abundant wastewater with residual dyes. Dyestuff wastewater does not been decolorized when treated aerobically by municipal sewage systems [3] due to their complex structure and synthetic origin. Obviously, one of

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the vital problems regarding dye industries is the colored effluent which contains visible pollutants [4] and less than 1ppm of dyestuffs can cause notable water coloration [5]. Dyestuffs wastewater can be removed by chemical and physical methods including adsorption, photocatalytic oxidation [6], coagulation-flocculation and electrochemical methods, and so on. Fenton’s reagent is homogenous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions in an acidic environment [7] and Eqs. (1)—(10) are the main inorganic reactions in the solution [8]. In this paper, Fenton reagent was employed to treat and decolorize the wastewater of Reactive Red SBE (RR SBE) by on-line spectrophotometry. The effects of FeSO₄ concentration、H₂O₂ concentration、pH、reactive red SBE and temperature on the discoloration of reactive red SBE were investigated.



2. Experimental

2.1. Apparatus and chemical reagent

Materials: RR SBE (Reactive Red SBE, Fig. 1) was obtained from Jiangsu Shenxin dyestuffs Co. Ltd. (China) and used without further purification. H₂O₂ (30%), FeSO₄ and H₂SO₄ at least analytical grade were purchased from Beijing Chemical Reagents Co. Ltd. Apparatus: UV-2102PC UV-Vis spectrophotometer (Shanghai, China), peristaltic pump, current colorimetric container and computer compose online monitoring system. Magnetic stirrer (Rongsheng Apparatus Co. Ltd.) can advantage to mix reactive materials.

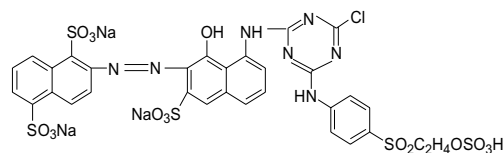


Fig. 1 Chemical structure of Reactive red SBE

2.2. Procedures

Fenton process was performed in a beaker containing 200 ml solution, in which the specified concentration of selected dyestuff was remained. 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.

3. Results and discussion

3.1. Determination of experimental wavelength

Fig. 2 shows the UV-Vis spectrums of all reactive materials from 190—700nm. The spectrums of H_2SO_4 , Fe^{2+} , Fe^{3+} , H_2O_2 in 500—600 nm have not absorption but Reactive Red SBE in this area has a strong absorption, and maximum adsorption peak is 543 nm. So 543 nm in the visible region is determined the experimental wavelength. The criterion equation of absorbance against Reactive SBE concentration in the 543 nm at neutral pH is $A=0.02251C-0.00178$, $R^2=0.9999$ and we found UV-Vis spectrum of Reactive Red SBE has not been influenced by different acid ambient in the experiment. So the criterion equation can be used in acid and neutral circumstance.

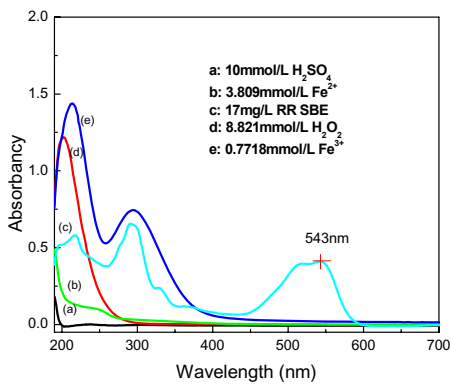


Fig.2 UV-Vis spectrum of reactants

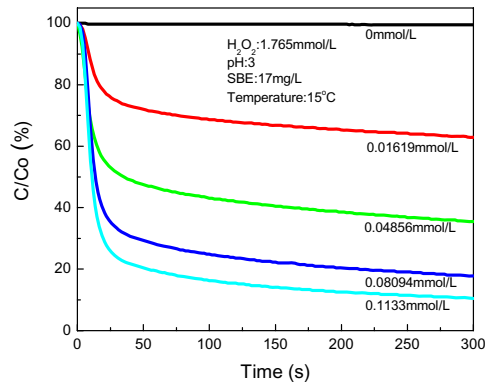


Fig.3 Effect of initial Fe^{2+} concentration

3.2. Influence of initial Fe^{2+} concentration

Tab. 1 Effect of initial Fe^{2+} concentration to k and $t_{1/2}$ of SBE decolorization by Fenton's reagent

$[Fe^{2+}]_0$ /mmol/L	k /s ⁻¹	$t_{1/2}$ /s	R^2	Removal (%) in 300 s
0.01619	0.01632	42.47	0.9916	37.07
0.04856	0.03655	19.00	0.9916	64.53
0.08094	0.05920	11.71	0.9893	82.20
0.1133	0.07592	9.130	0.9898	89.56

The curve of decolorization of Reactive Red SBE against time at different initial concentrations of Fe^{2+} which are used concentrations of 0, 0.01616, 0.04856, 0.08094 and 0.1133 mmol/L is showed in Fig. 3. From the Fig. 3, we can be seen clearly degradation speed rate and removal efficiency have a great increase with the rise of Fe^{2+} concentrations. The results denote that its probably can be divided two regions for

the Fenton oxidation process to degradate dye. At he beginning of the reaction, coloration of Reactive Red SBE decrease rapidly. However in the second region (≥ 30 s), decoloration process is very slow. These experimental phenomena can be explained in two aspects. The reduce of Fe^{2+} and H_2O_2 concentration can decrease the reaction rate and intermediate products during the Fenton oxidation process engage in the reaction. From many reports, Fenton oxidation process follows pseudo first order kinetics [8, 9]. From the integral curves decolorization of Reactive Red SBE in Fig.3 degradation process do not submit first order rate law, but in the first region (≤ 30 s) the experimental results follow first order rate law, $\ln(\text{Co}/\text{C})=kt$, and calculated results are showed in Tab. 1. From Tab.1 , the decolorizing reaction rate constants (k) and removal efficiency in 300 s have a great increase with the rise of initial Fe^{2+} concentration. Initial Fe^{2+} concentrations against k is linear correlation, $k=0.6627[\text{Fe}^{2+}]_0+0.0033$, $R^2=0.9963$.

3.3. Influence of initial H_2O_2 concentration

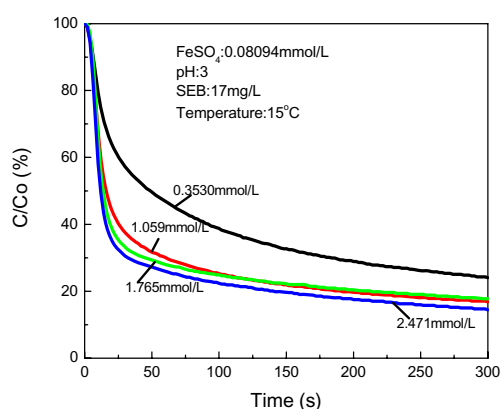


Fig 4 Effect of initial H_2O_2 concentration

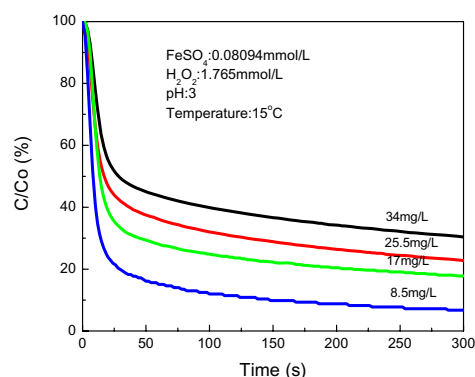


Fig.5 Effect of initial reactive red-SBE concentration

The curve of decolorization of Reactive Red SBE against time at different initial concentrations of H_2O_2 which are used concentrations from 0.3530 to 2.471 mmol/L is showed in Fig. 4 while keeping the FeSO_4 dose, pH, Reactive Red SBE dose and Temperature constant at 0.08094 mmol/L, 3, 17 mg/L and 15 °C. The first order kinetics constants were simulated in Tab. 2, which carried through during the early stage. As can be seen from th Fig. 4 and Tab. 2, the addition of H_2O_2 from 0.3530 to 1.059 mmol/L increases the decolourization from 75.93% to 83.17% at 300 s and further increase from 1.059 to 2.471 mmol/L causes small significant change in decolourization. At the high dosage of H_2O_2 the decrease in decolourization is due to the hydroxyl radical scavenging effect of H_2O_2 (Eq. 10) and recombination of hydroxyl radicals (Eq. 7) [10]. From Tab. 2, the decolorizing reaction rate constants (k) increase with the rise of initial H_2O_2 concentrations. k against initial H_2O_2 concentration is linear correlation, $k=0.02508[\text{H}_2\text{O}_2]_0+0.01753$, $R^2=0.9959$.

Tab. 2 Effect of initial H₂O₂ concentration to k and t_{1/2} of SBE decolorization by Fenton's reagent

[H ₂ O ₂] ₀ /mmol/L	k /s ⁻¹	t _{1/2} /s	R ²	Removal (%) in 300 s
0.3530	0.02577	26.90	0.9937	75.93
1.059	0.04630	19.00	0.9894	83.17
1.765	0.05920	11.71	0.9893	82.20
2.471	0.08049	8.612	0.9978	85.51

3.4. Influence of initial Reactive Red SBE concentration

Tab. 3 Effect of reactive red-SBE concentration to k and t_{1/2} of SBE decolorization by Fenton's reagent

Reactive Red SBE /mg • L ⁻¹	k /s ⁻¹	t _{1/2} /s	R ²	Removal (%) in 300 s
8.5	0.08547	8.10	0.9927	93.30
17	0.05920	11.71	0.9893	82.20
25.5	0.04780	14.50	0.9892	77.21
34	0.03635	19.07	0.9886	69.61

Fig. 5 shows the curves of decolorization of Reactive Red SBE against time at different initial concentrations of Reactive Red SBE which are used concentrations of 8.5, 17, 25.5, 34 mg/L. Tab.3 shows the decolorizing reaction rate constant (k) and the half-value period (t_{1/2}) according to the experimental data in the first region at different initial concentrations of Reactive Red SBE. The figure and table clearly reveal that the increase in dye concentration decreases the removal efficiency and the decolorizing reaction rate constant. Increase of dye concentration from 8.5 to 34 decrease k from 0.08547 to 0.03635 s⁻¹ and the decolorization from 93.30% to 69.61% in 300s. The increase in dye concentration increases the number of dye molecules in the water and not the hydroxyl radical, so the removal rate decreases.

3.5. Influence of pH

The pH of the solution is an important parameter for Fenton process [11]. Fig. 6 shows the curves of decolorization of Reactive Red SBE against time at different pH (2, 3, 7). Tab. 4 shows the decolorizing reaction rate constant (k) and the half-value period (t_{1/2}) according to the experimental data in the first region at different pH. As can be seen from the Fig. 6 and Tab. 4, pH 3 is found to be the optimum pH for both processes. However, pH 2 and pH 7 also have a good decolorizing removal. The decolorizing reaction rate constants are similar in these three reaction conditions. In many early reports, dye can not be degraded using Fenton reagent at neutral medium [11, 12]. Our results are different from early reports.

Tab. 4 Effect of pH to k and t_{1/2} of SBE decolorization by Fenton’s reagent

pH	k /s ⁻¹	t _{1/2} /s	R ²	Removal (%) in 300 s
2	0.05897	11.75	0.9898	78.11
3	0.05920	11.71	0.9893	82.20
7	0.05708	12.14	0.9903	73.51

3.6. Influence of temperature

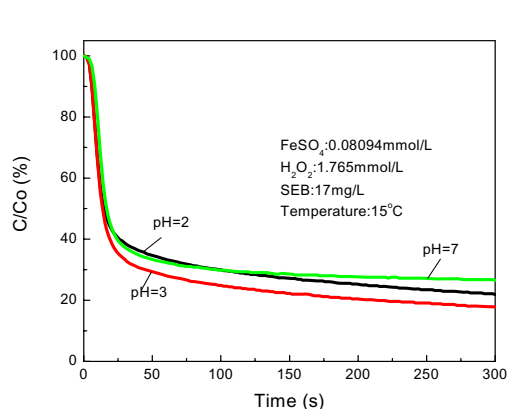


Fig.6 Effect of pH

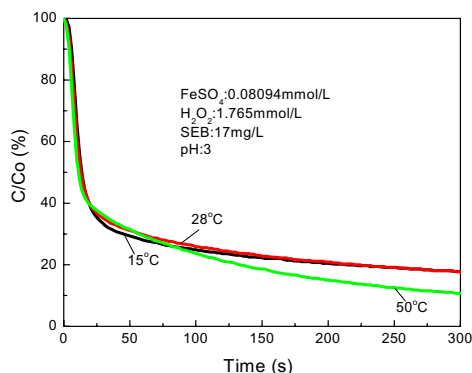


Fig.7 Effect of temperature

For the change of temperature condition from 15 to 50 oC, the curves of SBE decreased with time from 0 to300 s show in Fig 7, while initial concentration of Fe²⁺、H₂O₂、Reactive Red SEB and pH value remained constant. The first order kinetics constants were simulated in Tab.5, which carried through during the early stage. It is shown that decolorization rate and removal efficiency could be increased with

the raise of reaction temperature. According to the expression $\ln k = -\frac{Ea}{RT} + \ln A$, reaction activation energy (Ea) could be calculated of 2.608 kJ/mol. As for the relationship between temperature and Ea, reaction occurred instantly during room temperature when value of Ea less than 63kJ/mol. Therefore, pollution water of Reactive Red SEB could be degraded when using Fenton technique in room temperature. Moreover, this method conforms to condition in reality.

Tab. 5 Effect of temperature to k and t_{1/2} of SBE decolorization by Fenton’s reagent

θ / $^{\circ}$ C	k / s^{-1}	$t_{1/2}$ /s	R^2	Removal (%) in 300 s
15	0.05920	11.71	0.9893	82.20
28	0.06331	10.95	0.9930	82.22
50	0.06678	10.38	0.9877	89.27

4. Conclusion

Fenton reagent can rapidly damage chemical structure of Reactive Red SBE and decolorization of dye wastewater is effectively achieved. However there are some intermediates and by products existed in the Fenton process. So mineralization process is not completely. Fenton oxidization process follows pseudo first order kinetics in the first stage. Reaction activation energy (E_a) is 2.608 kJ/mol. The decolorizing reaction rate constants (k) increase with the rise of $FeSO_4$ concentration、 H_2O_2 concentration、temperature, but decrease with the rise of reactive red SBE, and the optimum pH is 3. Initial $FeSO_4$ concentration and initial H_2O_2 concentration against k are linear correlation.

Acknowledgements

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