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Optimization of Fenton–SBR treatment process for the treatment of aqueous dye solution

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ABSTRACT

The degradation of dye C.I.Reactive brilliant blue 4 (RB4) was evaluated by using a combined process of Fenton's reagent and sequencing batch reactor (SBR). Fenton treatment was confirmed effective to enhance biodegradability and reduce acute toxicity of RB4 solution by Zahn–Wellens test (ZWT) and MicrotoxTM bacterial bioluminescence assay. As for the initial RB4 concentration of 100 mg/L, the optimum doses for Fenton oxidation were found out to be 0.52 mmol/L of Fe^{2+} and 5.2 mmol/L of H_2O_2 dose at pH 3. Under these conditions, the obtained total organic carbon (TOC) and color removal were 44.2 and 100%, respectively. To fully exert the potential of biotreatment of SBR and save the costs of chemical reagents, the dose of Fenton reagent was reduced to Fe^{2+} 0.39 mmol/L and H_2O_2 3.9 mmol/L. Thus, the polish step for Fenton's effluent was conducted by SBR, and the overall TOC removal percent can be achieved at 73.5%.

Keywords: Reactive brilliant blue 4; Fenton; Bacterial bioluminescence assay; Zahn–Wellens test; Sequencing batch reactor

1. Introduction

Textile and dyeing industry may cause serious environmental problems. Over 700,000 tons of approximately 10,000 types of dyestuff are produced annually worldwide [1]. From this amount, 20–30% of the total dyes consumption is reactive dyes [2]. Generally, the discharged wastewater which has strong color, high value of chemical oxygen demand (COD), and extremely low biochemical oxygen demand (BOD) to COD ratio may cause esthetically displeasing and disturb the biological process in water body and the weak ecosystem [3]. Therefore, it is urgent to find an effective method to solve these serious problems to meet the increasingly stringent standards of wastewater discharge. At present, many methods have been developed to eliminate the detrimental environmental effects of dyeing wastewater. Among all these methods, biotreatment, physical, and chemical treatments are mostly common in practical application. Evidently, biotreatment processes are considered to be one of the mostly economical methods, but single biological treatment unit is not capable of degrading the dyeing wastewater efficiently due to its nature of recalcitrance and strong

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color [4,5]. Some researchers [6] have reported that partial degradation and decolorization of dyeing wastewater could be achieved by the combination of anaerobic and aerobic treatment, but there aroused some problems of low organic pollutants removal efficiency and vast investment of the structures and reactors [7]. Some other auxiliary applications such as chemical oxidation are used to modify the chemical characteristics of dyes to render them amenable and less toxic to biodegradation process. It was also reported that chemical treatment followed by biological unit (chemical treatment prior to biological unit) could give better results rather than single biological and biological prior to the chemical treatment [8].

Among several alternatives, Fenton treatment is one of the most feasible chemical methods used in dyeing wastewater degradation due to its ease of operation and high efficiency. Fenton process can be generated with the interaction of ferrous ion and hydrogen peroxide in aqueous solution. The generated hydroxyl radicals have extremely high oxidizing ability, which can attack and destroy the structure of the molecules of organic substrate through the complex chain redox reactions [9,10]. Actually, the use of Fenton reagent could be effective to achieve not only strong oxidation of organic substrate, but also the removal capacity due to the coagulation effect contributed by the formation of ferric-hydroxo complexes [11,12]. It is apparent that higher concentration of dyeing wastewater consumes more ferrous ion and hydrogen peroxide, which results in higher cost of reagent and the subsequent disposal of Fenton sludge. Furthermore, it is not economical for the sole application of Fenton reagent to degrade the dyeing wastewater completely.

In the present work, combined process of Fenton and sequencing batch reactor (SBR) treatment was applied to treat the aqueous solution containing dye of C.I.Reactive blue 4 (RB4). RB4, a commercial reactive dye based on anthraquinone group as chromophore and dichlorotriazine group as reactive group is commonly used for the dyeing cotton fibers. Similar to some previous studies for the treatment of dyeing simulated wastewater [13], Fenton oxidation was used as a pretreatment to decoloration and improve the biodegradability of the RB4 solution. Subsequently, biotreatment of SBR was adapted as a polishing step for the final purification. In addition, oxidation, coagulation, and precipitation effects on the degradation of RB4 solution have been evaluated separately in Fenton process. Zahn–Wellens test (ZWT) and acute bacterial bioluminescence assay were used to evaluate the biodegradability and acute toxicity of the dye solution and the Fenton effluents.

2. Materials and methods

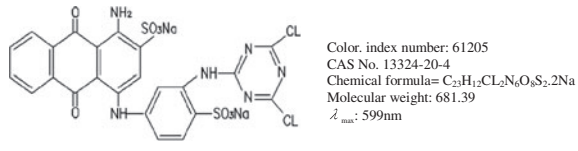
2.1. RB4 aqueous solution and reagents

Commercial dye of RB4 was supplied by ShangHai ZhenFeng Dyes Company (Shanghai, China) without any further treatment. The mixed aqueous solutions were prepared by dissolving requisite quantity of RB4 in pure water. The initial concentration of RB4 for mostly experiments was 100 mg/L. The molecular structure and some characteristics of RB4 are illustrated in Fig. 1. Table 1 depicts the characteristics of the RB4 aqueous solution at the concentration of 100 mg/L.

Ferrous sulfate ($FeSO_4{\cdot}7H_2O_2$), H_2O_2(30%, W/W) was obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Sulfuric acids (H_2SO_4), sodium hydroxide (NaOH) were supplied by LinFeng Chemical Reagent Company (Shanghai, China). Diethylene glycol (DEG) was obtained from Sinopharm Chemical reagent Company (Shanghai, China). All the chemicals were of analytical grade and used without any further purification. Pure water was used throughout the experiments

2.2. Fenton+SBR procedure

The overall treatment consisted of two stages, Fenton oxidation and the subsequent biotreatment of SBR. At the beginning runs of Fenton oxidation, jar tests were used to obtain the optimum parameters. Fenton tests (oxidation and coagulation/precipitation stages) [14] were carried out in a beaker with an effective capacity of 2 L. The quantitative ferrous sulfate was added to RB4 solution, then pH was adjusted to prospective value by using H_2SO_4 (1 mol/L) and NaOH (3 mol/L). Following the pH adjustment, quantified 30% (w/w) hydrogen peroxide was quickly added to the mixture and the oxidation occurred. The mixed solution was stirred at a speed of 60 r/min during the 120 min reaction. After the oxidation stage, pH of the mixed solution was adjusted to 8.0–8.5 by dosing of NaOH (3 mol/L) solution. After the settlement of Fenton sludge, the obtained supernatant was then analyzed again and stored in a tank as the influent of SBR treatment.



Color. index number: 61205
CAS No. 13324-20-4
Chemical formula= $C_{23}H_{12}CL_2N_6O_8S_2.2Na$
Molecular weight: 681.39
λ_{max}: 599nm

Fig. 1. Molecular structure and characteristics of RB4.

Table 1
Characteristics of RB4 solution

Parameters	Concentration (mg/L)	TOC (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Conductivity (μs/cm)	pH
Value	100	40.3	85.6	<5	2,300	6.8

The experimental SBR reactor was composed of a cylindrical vessel equipped with an air diffuser. The effective working volume was 12 L (internal diameter 20 cm, effective height of 40 cm). The SBR system was operated in a cyclical manner, where each cycle comprised periods of filling, reaction with aeration, settlements, and discharge of the clarified effluent. Each cycle was operated for 8, 12, and 16 h, respectively. Each cycle had 6, 10, and 14 h of aerobic reaction and another 2 h for filling (0.5 h), settlements (1 h), and discharge (0.5 h), respectively. Air diffusers provided the dissolved oxygen (DO) in the range of 2–4 mg/L for biooxidation in the aqueous solution. In the steady operation state, mixed liquor suspend solid (MLSS) was in the range of 3–4 g/L. Temperature and pH values were controlled in the range of 18–20 and 7.0–7.8° C, respectively. KH_2PO_4 and NH_4Cl were added to SBR reactor with the dose of 30 and 100 mg/day to maintain the activity of the micro-organisms. Fig. 2 depicts the process of the combined process of Fenton oxidation and SBR.

2.3. Analytical methods

The degradation of RB4 in aqueous solution was monitored by determinations of total organic carbon (TOC) using a TOC analyzer (Shimadzu, TOC-$_{CPN}$, Japan). The evolution of UV–vis absorption spectra during the Fenton oxidation was recorded by a UV–vis spectrophotometer (UV-2450, Shimadzu, Japan) in the range of 200–800 nm. And the degree of RB4 solution decolorization was calculated on the basis of the following equation [15]:

$$\text{Decolorization percent}(\%) = \left[\left(\frac{A_0 - A_t}{A_0}\right)\right] \times 100\% \quad (1)$$

where A_0 is the initial absorbance of the RB4 solution at the wavelength of 595 nm, A_t is the absorbance of the RB4 solution at the wavelength of 595 nm after Fenton treatment.

COD, BOD_5, MLSS, and mixed liquor volatile suspended solids were determined by the methods of the Chinese national environmental protection agency standard [16]. The pH measurements were performed using a pH meter (Model-PHs-3C, Leici, Shanghai). DO is measured by a portable DO meter. (Orion, 310D-1, USA) The method of dehydrogenase (DHA) was measured in accordance with the procedures described by Chen and Gu [17]

2.4. Toxicity evaluation and ZWT

Acute toxicity of the dye solution was assessed using a commercial Microtox™ bacterial bioluminescence assay, which was evaluated by the determination of the inhibitory effects on the marine photobacterium *Vibrio fischeri*. Analysis was conducted in accordance with the standard procedures recommended by the manufacturer (Strategic Diagnostics

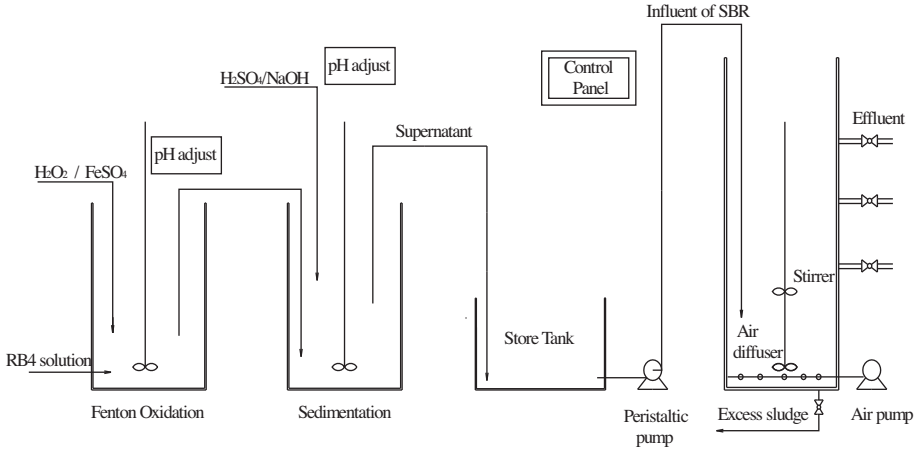


Fig. 2. Schematic of the combined Fenton + SBR process.

Inc, USA). The inhibition or stimulation effect of samples on the photobacterium was analyzed by measuring the loss or gain in light emission by a portable analyzer. The results were subsequently compared with a toxicant-free control (2% sodium chloride solution). Eqs. (2) and (3) expressed the calculations:

$$\text{Inhibition effect } (\%)\text{:Light Loss} = \left[\left(\frac{C_t - S_t}{C_t}\right)\right] \times 100, \text{ when, } C_t > S_t \quad (2)$$

$$\text{Stimulation effect } (\%)\text{:Light Gain} = \left[\left(\frac{S_t - C_t}{C_t}\right)\right] \times 100, \text{ when, } S_t > C_t \quad (3)$$

where C_t is the luminescence intensity of control sample after the reaction time of 15 min; S_t is the luminescence intensity of test sample after the reaction time of 15 min. Samples from Fenton treatment were previously filtered (0.2 μm filter) before the toxicity testing. Each assay was performed in duplicate.

The biodegradability of the original and the corresponding Fenton effluents was evaluated by the ZWT. The tests were carried out according to the protocol of Directive 88/302/EEC. The parallel control substrate of DEG was used as the indicator of bioactivity of the micro-organisms. Degradation was monitored by TOC determination of the sample solution at regular time intervals. Eq. (4) expressed the calculation of the degradation [18].

$$D_T = [1 - (C_T - C_B)/(C_A - C_B A)] \times 100 \quad (4)$$

where D_T = biodegradation (%) at time T, C_A = TOC value in the test mixture measured 3 h after the start of the test (mg/L), C_T = TOC value in the test mixture at time T of sampling (mg/L), C_B = TOC value of the blank at time T of sampling (mg/L), C_{BA} = TOC value of the blank, measured 3 h after the beginning of the test (mg/L). Samples analyzed are considered biodegradable when the biodegradation percentage is over 70%.

3. Results and discussions

3.1. Optimum operating conditions of Fenton treatment

3.1.1. Effect of pH on the oxidation stage of Fenton treatment

This part of experiments was carried out at different initial pH value of 1.5, 3, 5, and 6, whereas the concentration of RB4, H_2O_2, and Fe^{2+} were controlled at 100 mg/L, 5.20 and 0.52 mmol/L, respectively. Fenton oxidation is a highly acid medium dependent process since pH plays a critical role in the mechanism of OH· formation [19]. Fig. 3 shows the significant effect of pH on the degradation of RB4. The measured TOC removal percent was 20.1, 27.4, 21.8, and 9.8% for the corresponding pH value of 1.5, 3.0, 5.0, and 6.0, respectively. The results showed the optimal pH value was 3, at which the highest TOC removal percent of 27.4% was obtained. Generally, high pH decreases the concentration of soluble Fe^{3+} and obstructs the regeneration of Fe^{3+}–Fe^{2+} [20]. In addition, the hydrogen peroxide is unstable and easy to be decomposed, thus leading to a reduction of ·OH radicals. On the other hand, when pH value is lower than 2, some complex iron species $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, and $[Fe(OH)(H_2O)_5]^{2+}$ were formed. And the oxidation process is declined because the formed complex species reacted relatively slow with hydrogen peroxide [21]. Moreover, high H^+ concentration acts as scavengers to ·OH more obviously, which hinders the oxidation as well [22].

3.1.2. Effects of H_2O_2 and Fe^{2+} dosage on Fenton oxidation

Dosages of H_2O_2 and iron salt are the most important parameters that have to be taken into account for the cost. The effect of H_2O_2 concentration on the degradation efficiencies was studied in the range of 2.6–20.8 mmol/L and the catalyst of Fe^{2+} used was simultaneous changed in the range of 0.26–2.08 mmol/L. As shown in Fig. 4, TOC removal was 13.7, 26.2, 32.2, and 33.3% for the corresponding initial H_2O_2 concentration of 2.60, 5.20, 15.60, and 20.8 mmol/L, respectively. The increasing concentration of H_2O_2 from 2.60 to 5.2 mmol/L was positive for the degradation of

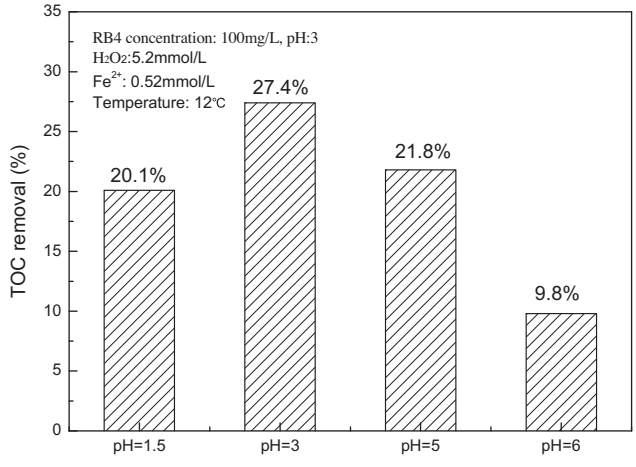


Fig. 3. Effect of pH value on TOC removal.

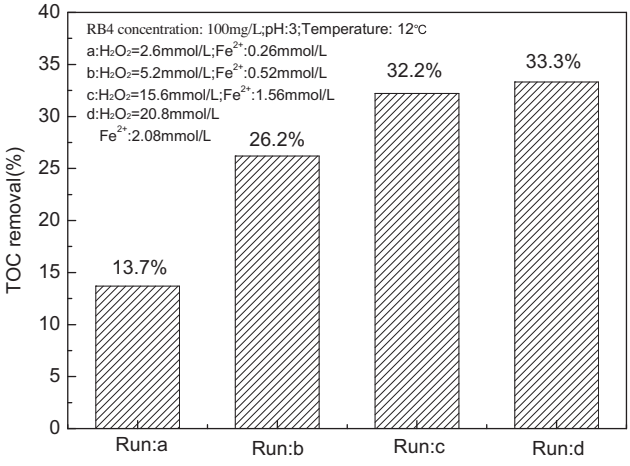


Fig. 4. Effect of different dosages of H_2O_2/Fe^{2+} concentration on TOC removal.

RB4. However, higher H_2O_2 concentration of 15.60 and 20.8 mmol/L cannot contribute the desired increase in RB4 degradation efficiency. The lowest TOC removal of 13.7% indicated that the use of H_2O_2 was far from enough to complete oxidation due to the insufficient HO· radicals. However, too high concentration of H_2O_2 performs practically infeasible and also caused partial reaction of hydroxyl radical scavenging [23]. Furthermore, the generation of less reactive ·OOH radicals which contribute less to the oxidative degradation of organic substrates may occur due to the superfluous H_2O_2 [24].

The ferrous ion initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. Fig. 5 shows the results under the same conditions except for the variation of Fe^{2+} concentration of 1.04, 0.52, and 0.26 mmol/L. And the corresponding molar ratio of H_2O_2/Fe^{2+} were 5, 10, and 20, respectively. It can be seen that suitable Fe^{2+} concentration results in the most efficient catalytic performance and highest TOC removal percent. The result indicated that the optimum concentration of $FeSO_4$ was 0.52 mmol/L, in which could obtain the highest TOC removal of 24.0%. Due to the deficient Fe^{2+} concentration of 0.26 mmol/L, the corresponding TOC removal was 14.6%. In this case, oxidation proceeded relatively slowly and incompletely because of the decrease of the catalytic ability of decomposing the hydrogen peroxide and the insufficient yield of ·OH. When Fe^{2+} concentration was raised to 1.04 mmol/L, the TOC removal percent was only 22.8%. Compared with Fe^{2+} concentration of 0.52 mmol/L, higher Fe^{2+} concentration did not help to further increase the TOC removal percent. The results revealed that the overdose of Fe^{2+} leads to OH· radical scavenging and the decrease of oxidation efficiency [25]. It could be seen that the suitable dosages are H_2O_2 5.2 mmol/L and Fe^{2+} 0.52 mmol/L when the concentration of RB4 was 100 mg/L.

3.1.3. Evaluation of coagulation and precipitation effects on TOC removal

Batch experiments were conducted to evaluate the coagulation and precipitation effects on TOC removal. Fenton processes were performed under the same conditions except for the variation of Fe^{2+} dosage of 5.2, 1.04, 0.52, and 0.26 mmol/L. After the oxidation stage, the mixed solution was analyzed immediately. Subsequently, the mixtures were adjusted to pH 8.0 and settled for 1 h. After the coagulation/precipitation stage, the supernatant was decanted and the TOC

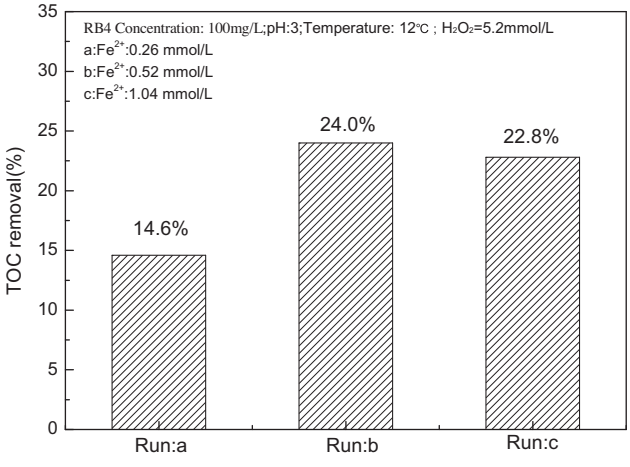


Fig. 5. Effect of Fe^{2+} concentrations on TOC removal.

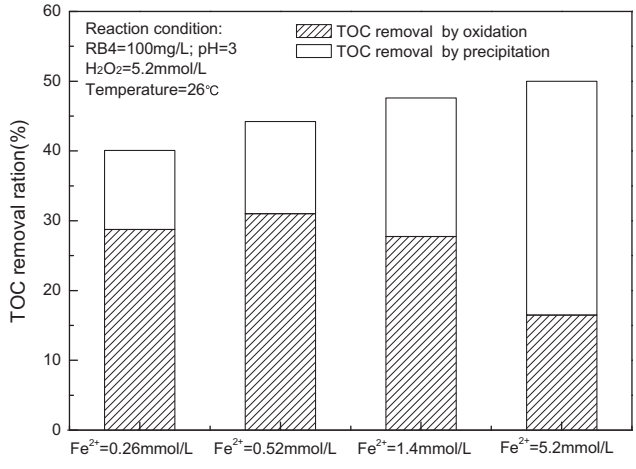


Fig. 6. TOC removal by Fenton oxidation and precipitation under different dosages of Fe^{2+}.

value was measured. Fig. 6 shows TOC removal percentage contributed by oxidation and coagulation/precipitation stages under different concentrations of iron salts. It could be seen that overall TOC removal percentages were 40.1, 44.2, 47.6, and 50.0%, where the corresponding Fe^{2+} concentrations were 0.26, 0.52, 1.04, and 5.2 mmol/L, respectively. Thus, the proportion of TOC removal percent contributed by coagulation/precipitation was 11.3, 13.2, 19.8, and 33.5%, and the corresponding oxidative contribution was 28.8, 31.0, 27.8, and 16.5%, respectively.

It is evident that more iron salts generate more ferric hydroxides particles which can agglomerate forming macroscopic flocs .The macroscopic flocs of Fe $(OH)_3$ were beneficial to form denser and bigger flocculation, which can accelerate the sedimentation and strengthen the sweep and enmeshment of organic matters by adsorption and the bridge formation mechanism [26]. Thus, the coagulation and precipitation effects of overdose iron salts may occupy a leading position in Fenton process, which is not the expected result. Moreover, too much Fe^{2+} yields more Fenton sludge which is less economic and infeasible in practical application.

3.2. Decolorizaiton by Fenton process

Fig. 7 depicts the evolution of color removal in 120 min. Initially, the generated OH·radicals attack the molecule of RB4 and result in rapid breaking of chromophore group of anthraquinone. It could be seen that the color removal percent that can be attained was 96.3% in the first 40 min and almost 100% after 120 min. With the decreased oxidation ability and the increasing organic substrate of oxidized intermediates in the mixed solution, the subsequent decolorizing rate slows down. That is to say, TOC removal lags far behind color decolorization in Fenton oxidation. The phenomena can also be illustrated by the evolution of UV–vis spectral analysis. Fig. 8 shows the typical evolution of UV–vis absorption spectra during Fenton oxidation. It can be seen that the original absorbance peak bands at 599, 370, and 296 nm decrease markedly in 30 min. That indicates the molecular structure is absolutely damaged by the generated OH·radicals. As for color removal, the remarkable absorption band at 599 nm, attributing to the chromophore group of RB4 molecular, is almost completely vanished in less than 30 min. However, the absorbance in ultraviolet and visible regions indicates that some intermediates still exist in the mixed solution. That is to say Fenton process cannot mineralize RB4 absolutely.

3.3. Toxicity assessments and ZWT

To assess the acute toxicity of RB4 aqueous solution and Fenton effluents, tests were conducted through the variation of the natural luminescence of the marine photobacterium *V. fischeri*. Table 2 shows the results of the tests. With the increasing RB4 concentration from 25 to 100 mg/L, the inhibition effects on the *V. fischeri* became more significant. On comparison, the inhibition percentages of the Fenton effluent were 6 and 10%, corresponding to the initial RB4 concentrations of 50 and 100 mg/L. It can be deduced that Fenton oxidation intermediates such as 1, 2-diacetylenzene, 2,5-diritrobenzoic, and phallic acid [27] were less toxic than the original substance of RB4. As for the water sample of SBR effluent, the observed luminous ability of photobacterium *V. fischeri*

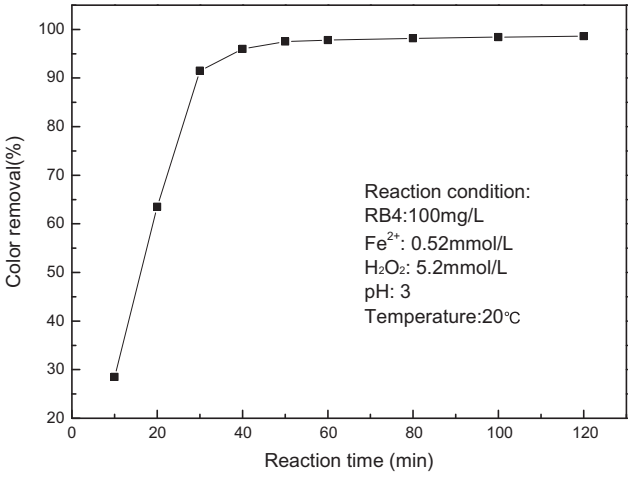


Fig. 7. Color removal by Fenton oxidation as a function of reaction time.

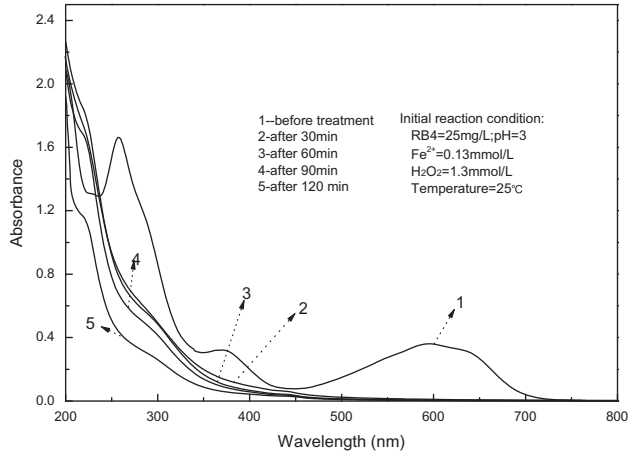


Fig. 8. UV–vis spectra of RB4 solution before and after different Fenton treatments time.

increased by 7%. The result indicated that the effluent was not only nontoxic but the substrate can also be assimilated by the photobacterium.

ZWT was applied to evaluate the potential of aerobic biodegradation degree of RB4 solution and Fenton effluent. The control substrates of DEG solution (TOC: 100 mg/L), initial RB4 solution (Concentration: 100 mg/L), and the Fenton effluent (Initial RB4 concentration: 100 mg/L) were prepared to conduct ZWTs. Fig. 9 shows the results of the test. DEG, as the control substrate, achieved almost 80% biodegradation in less than six days. This indicated the active sludge was effective and the tests were valid. It can be seen from the results that raw RB4 substrate almost cannot be degraded by micro-organisms. ZWT of raw RB4 solution was terminated in 15 days due to the death of the micro-organisms. Compared with the raw RB4 solution, Fenton effluent can be partly degraded by the micro-organisms. It took almost 20 days to reach the TOC removal percent of 70%, which was the recommended biodegradability standard. Compared with the raw RB4 solution, the intermediates achieved an increase of BOD_5/COD from 0.06 to 0.28. It indicates that Fenton oxidation can render the RB4 solution relatively easy biodegradable. The results indicate that ZWT can determine the biodegradability of an organic substrate more accurately due to its similar operating conditions of the sludge biotreatment process [28].

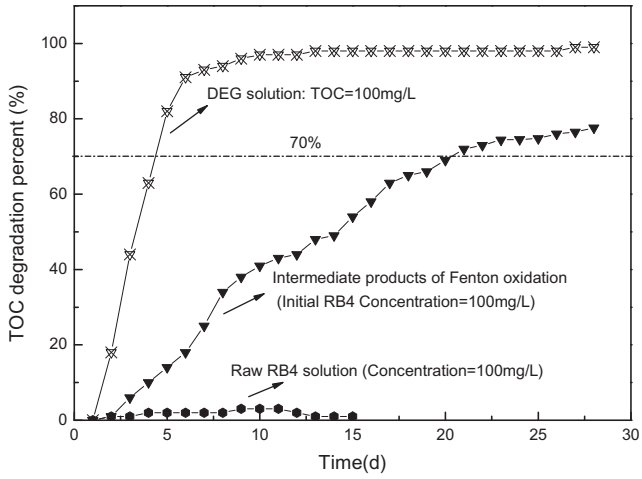


Fig. 9. Results of ZWT.

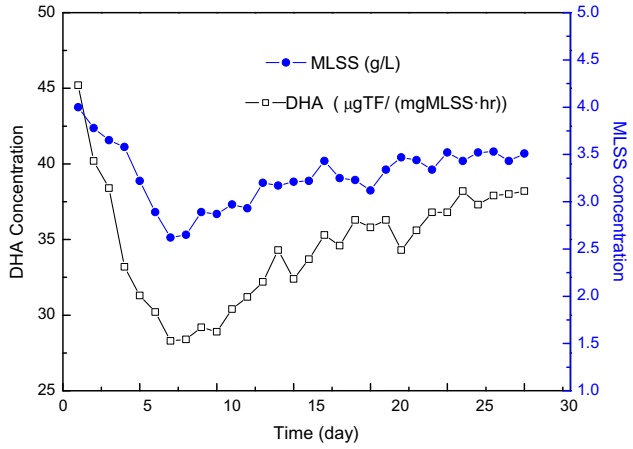


Fig. 10. MLSS and DHA evolutions of the acclimation stage.

3.4. SBR treatment

3.4.1. Stabilization of SBR

The reactor was initially inoculated with 4.0 g/L of MLSS obtained from a secondary sedimentation tank of a domestic treatment plant. DO concentration was controlled in the range of 2–3 mg/L. DHA, a special oxidation–reduction enzyme which participates in the main stream of electron transport from organic substrates to molecular oxygen, was used to indicate the stabilization and activity of the micro-organisms. The evolutions of DHA are illustrated in Fig. 10. In the first seven days, the DHA concentration decreased significantly from 45.2 to 28.4 gTF/(mg MLSS h) due to the inhibition effect of the Fenton intermediates. At

Table 2
Inhibition or stimulation effects on the marine photobacterium *V. fischeri*

Index	Water sample (initial dye concentration, mg/L)	TOC (mg/L)	pH	Average luminescence inhibition/stimulation ratio
1	RB4-(25)	10.4	7.0	−17%
2	RB4-(50)	23.5	7.0	−34%
3	RB4-(100)	43.0	7.0	−41%
4	RB4 after Fenton treatment (50)	14.4	7.0	−6%
5	RB4 after Fenton treatment (100)	28.3	7.0	−10%
6	RB4 after Fenton/SBR treatment	8.0	7.0	+7%

(−, means the inhibition effects, + means the stimulation effects).

the same time, a marked decline of MLSS concentration was observed. This reduction in MLSS from 4.0 to 2.6 g/L could be attributed to the low activity of unacclimated activated sludge micro-organisms. It also can be seen from Fig. 10 that SBR system came into a relatively stable state with the DHA concentration ranging from 33.3 to 38.3 gTF/(mg MLSS h) in the last 10 days. It should be noted that MLSS concentration began to increase after seven days, and kept in the range of 3.2–3.5 g/L. Based on the stabilized MLSS and DHA concentrations, the average TOC removal percent was about 74.3%. It indicated that the bacteria were adapted metabolically to the substrates of Fenton effluents.

3.4.2. TOC removal by SBR

After the acclimation stage, SBR system was fed with different Fenton effluents to evaluate the potential of biotreatment of SBR. The TOC removal results of each combined Fenton and SBR processes were summarized in Table 3. It can be seen that runs 1–3 achieved TOC removal of 39.55% by Fenton process. Due to the improved BOD_5/COD index of 0.28 of Fenton effluents, the overall TOC removal was 78.7, 81.3, and 82.7%, corresponding to SBR cycle time of 8, 12, and 16 h, respectively. Compared with the results of run 1, run 3 only achieved an increasing TOC removal of 4.0%. Thus, it can be deduced that the organic substrate was consumed in a large proportion in 8 h cycle due to the increased BOD_5/COD index of 0.28. It is not feasible to raise TOC removal by extending the reaction time. On the contrary, runs 7–9 exhibited different results of SBR treatment. In Fenton process, the reduced Fe^{2+}/H_2O_2 dosage of 0.26/2.6 mmol/L resulted in relatively low BOD_5/COD index of 0.19. When working under the conditions, the percentages of biodegradation contributed by SBR were 52.4, 57.5, and 65.8%, and the corresponding overall TOC removal percentages were 63.8, 67.7, and 74.0%, respectively. As for moderate dosage of H_2O_2 3.9 mmol/L and Fe^{2+} 0.39 mmol/L of runs 4–6, Fenton treatment contributed 30.4% TOC removal of RB4 solution. And the overall TOC removal percentages were 73.7, 75.6, and 78.1%, corresponding to different SBR cycle time of 8, 12, and 16 h, respectively.

It is interesting to point out that runs 1, 4, 5, 6, and 9 attained similar TOC removal percentages of 78.7, 73.7, 75.6, 78.1, and 74.0%, respectively. Actually, the percentage of organic substrates removal was limited by the nature of the supernatant and the operation conditions of SBR process. Under the conditions of relatively sufficient Fe^{2+} and H_2O_2 doses, Fenton treatment can generate more biocompatible intermediates. On the other hand, biomass metabolites became more effective due to the prolonged SBR cycle time. Thus, it is important to seek the balance point of the dose of Fenton reagent and operation parameters of SBR. From one perspective, large Fenton dose may cause bigger costs and generate more solid waste of Fenton sludge. Furthermore, too long cycle time of SBR results in vast initial investment of structure and high aeration energy consumption during practical application. Considering the two aspects, Fe^{2+} dose of 0.39 mmol/L, H_2O_2 dose of 3.9 mmol/L, and SBR cycle time of 8 h are the favorable operation parameters of Fenton-coupled SBR process.

4. Conclusion

Results demonstrated that the aqueous solution containing reactive dye of RB4 can be successfully treated by the combined process of Fenton and SBR. With the use of Fenton's reaction as a primary

Table 3
TOC removal results of each combined Fenton and SBR process

Run	Fenton process				SBR treatment		Overall TOC removal percent (%)
	Fe^{2+}/H_2O_2 (mmol/L)	Initial TOC (mg/L)	Supernatant		SBR cycle/aeration time (h)	Effluent TOC (mg/L)	
			TOC(mg/L)	BOD_5/COD			
1	0.52/5.2	40.5	24.5	0.28	8/6	8.6	78.7
2	0.52/5.2	40.5	24.5	0.28	12/10	7.6	81.3
3	0.52/5.2	40.5	24.5	0.28	16/14	7.0	82.7
4	0.39/3.9	40.5	28.2	0.22	8/6	10.7	73.7
5	0.39/3.9	40.5	28.2	0.22	12/10	9.9	75.6
6	0.39/3.9	40.5	28.2	0.22	16/14	8.9	78.1
7	0.26/2.6	40.5	30.8	0.19	8/6	14.7	63.8
8	0.26/2.6	40.5	30.8	0.19	12/10	13.1	67.7
9	0.26/2.6	40.5	30.8	0.19	16/14	10.5	74.0

treatment, the RB4 solution became decolourized and more biodegradable, as well as less toxic. The results also found that Fenton treatment cannot mineralize RB4 completely and the TOC removal rate lags far behind color decolorization. To completely exert the efficiency of SBR and saving the cost of dosage, the optimum operation parameters of Fe^{2+}, H_2O_2 dose, and cycle time of SBR were 0.39, 3.9 mmol/L, and 8 h, respectively. At these conditions, the combined Fenton process and SBR could obtain the overall TOC removal percentage of 73.7% and almost 100% color removal.

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