Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.22966

141 (2019) 301–309
February

Degradation kinetics of Reactive Dark Blue B-2GLN with Fenton oxidation process

Aifang Gao[a,b,c,*], Aiguo Li[a], Weiping Wang[a]

[a]*School of Water Resources and Environment, Hebei GEO University, Shijiazhuang, 050031, China, Tel. +86 311 87208362, email: llhx2006@126.com (A. Gao), 10067454@qq.com (A. Li), 2393718268@qq.com (W. Wang)*
[b]*Hebei Province Collaborative Innovation Center for Sustainable Utilization of Water Resources and Optimization of Industrial Structure, Shijiazhuang, China*
[c]*Hebei Key Laboratory of Sustained Utilization and Development of Water Resources,Shijiazhuang, China*

Received 22 December 2017; Accepted 14 August 2018

ABSTRACT

Online spectrophotometric method was employed to monitor the degradation of Reactive Dark Blue B-2GLN (RDB B-2GLN) solution with Fenton oxidation process. The effect of initial $FeSO_4$ concentration, initial H_2O_2 concentration, pH value, and initial dye concentration on chroma removal has been studied. The kinetic mechanics was estimated. The results show that: under the preparation conditions of the optimum dosage of H_2O_2 2.635 mM, pH 2.7, Fe^{2+} dosage 0.0696 mM, and the initial dye concentration 16 mg/L, the color removal rate of Reactive Dark Blue B-2GLN is about 85.04% after 300 s. The intrinsic reaction rate constant of ·OH with RDB B-2GLN in aqueous solution is 2.62×10^{11} M^{-1} s^{-1}. The molecule structure of RDB B-2GLN is decomposed and not mineralized completely by Fenton's reagent (300 s). The intermediate product and possible degradation mechanism of RDB B-2GLN is predicted by GC-MS analysis. Online spectrophotometric method is an accurate, quick, and feasible technique to monitor color removal rate of RDB B-2GLN in Fenton process.

Keywords: Fenton oxidation, Reactive Dark Blue B-2GLN, Spectrophotometry, kinetics, degradation, wastewater

1. Introduction

Reactive azo dyes are extensively used in textile industry due to their chemical stability and versatility [1,2]. They contain one or more azo groups with aromatic rings mostly substituted by sulfonate groups [3]. Azo dyes are resistant to water, light, oxidizing agents and biodegradation under aerobic conditions [4,5]. The reactive dye wastewater discharged from various chemical industries contains a great deal of organic effluent [6]. The very low concentrations dyes in effluent can also give rise to visible chroma and undesirable feeling in our living environment [7]. Moreover, some are toxic and carcinogenic and mutagenic for human beings [1]. Because of the inability of conventional physical, chemical and biological methods to degrade completely dye wastewater [1,7], it is very necessary to find an effective treatment method of azodye wastewater in order to degrade organic pollutants.

Advanced oxidization processes (AOPs) are promising technique for the degradation of organic contaminants in industrial wastewater [8–16]. Such oxidation mechanisms produce strong oxidants such as hydroxyl radicals (·OH) [17–19]. Hydroxyl radicals are powerful non-selective oxidants with high oxidizing potential, and react with dissolved species, removing chromaticity and reducing chemical oxygen demand. The hydroxyl radicals easily attack the unsaturated functional group of dye molecule and the chromophore is destroyed and decolorized [20]. Ultimately, AOPs decompose organic pollutants

---

*Corresponding author.

1944-3994 / 1944-3986

to CO_2, H_2O and inorganic salt within aqueous environments [21–23].

The Fenton oxidation process is a homogeneous advance oxidation process and an attractive treatment for the decolorization and degradation of reactive dyes due to its efficiency, fast reaction speed and moderate investment. The Fenton process can produce highly oxidative hydroxyl radical from an acidic mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) [20] by the reaction $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$. Some studies have been investigated on the decolorization and degradation of dyes using the Fenton oxidation process. For example, Sun et al. [24] discussed the effect of some parameters on the decolorization of azo dye Orange G using Fenton reagent and determined the optimum decolorization parameters. Fu et al. [25] reported the decolorization kinetics of Acid Red 73 follows the first-order kinetic model. Karatas et al. [23] used Fenton reagent to treat Reactive Blue 114 dye in aqueous solutions and obtained 90% decolorization rate. Su et al. [26] studied Fenton process to treat Reactive Black 5, Reactive Blue 2, and Reactive Orange 16 and all dyes were decomposed under the optimized experimental conditions. Xu et al. [8] investigated Fenton oxidation kinetics of mixed dyes wastewater and salt effect by online spectrophotometry.

Online spectrophotometric monitoring technique is an accurate, fast and convenient method to investigate instantaneous absorbance variation of dye at different reaction time during dye wastewater treatment [1,8]. It can reduce the experimental error and improve experimental efficiency. In the present paper, we choose Reactive Dark Blue B-2GLN (RDB B-2GLN) as a model pollutant which used in textile industry of Hebei. The RDB B-2GLNdye is an aromatic azo compound and one of tricolor reactive dye. Fenton oxidation was applied for decomposition of RDB B-2GLN solution and online spectrophotometric method was selected as the analysis method to monitor color removal. The experimental condition was controlled by various parameters, including the ferrous ions catalyst (Fe^{2+}) dosage, hydrogen peroxide (H_2O_2) dosage, initial dye concentration, and the pH value. The decolorization kinetics performance of Fenton oxidation was studied based on experimental data. The kinetic model of azo dye degradation with Fenton's reagent was established. The possible degradation mechanism of RDB B-2GLN was predicted based on the degradation intermediate products that were determined by GC-MS analysis.

2. Experimental Section

2.1. Reagents

Reactive Dark BlueB-2GLN (RDB B-2GLN) was purchased from Shijiazhuang Dyestuffs Company (China), and the RDB B-2GLN solution was prepared by dissolving a requisite quantity of dye in double-distilled water. The structure of RDB B-2GLN is listed in Fig. 1. Hydrogen peroxide H_2O_2 (30% in water), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), and sulfuric acid H_2SO_4were of reagent grade and purchased from Shijiazhuang Xiandai Chemical Reagent Company (China).

2.2. Apparatus set-up

Fig. 2 shows the online spectrophotometric system. Reaction unit (degradation device) includes a digital magnetic stirrer apparatus (Shanghai Instrument company, China), and 250 mL beaker. Optical measuring unit contains UV-Vis spectrometer (UNICO 2802, Shanghai, China), cycle peristaltic pump and cuvette (1 mL). The velocity of the model wastewater in system was 22 mL/min. Recording unit was a computer and the monitoring frequency was 12 min^{-1} during the reaction process.

2.3. Degradation procedures

The amount of 200 mL simulated wastewater, which was made up with certain concentration of RDB B-2GLN and ferrous ion, was added into a 250 mL vessel. The designed pH value was adjusted with H_2SO_4. The pH-meter was used to monitor the pH value. Meanwhile, the magnetic stirrer and pump were employed. With the help of peristaltic pump, the simulated dye wastewater was pressed into the cuvette of the UV-Vis spectrophotometer. The maximal absorption peak of dye was recorded by spectrophotometer. The certain concentration H_2O_2 was added into the wastewater, and the computer began to record experimental absorbance results.

2.4. IC method

Inorganic ions (Cl^-, NO_3^- and SO_4^{2-}) in aqueous solution were measured by Metrohm-881 Ion Chromatography (IC) with conductivity detector, tower type IC column (4 × 250 mm) and MagIC Net software. The eluent was a mixture

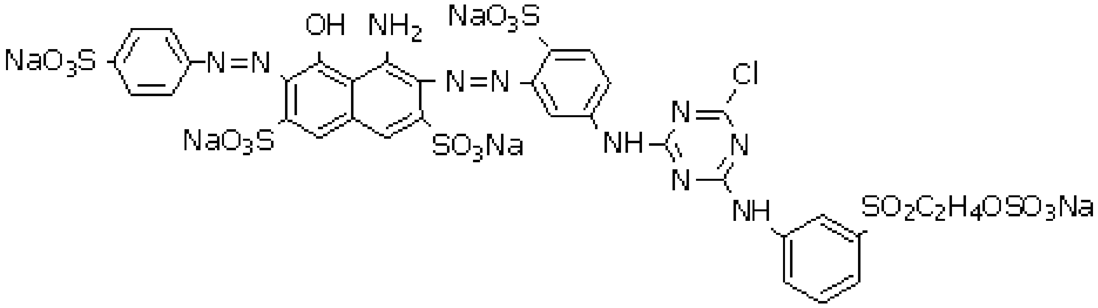


Fig. 1. Reactive Dark Blue B-2GLN (RDB B-2GLN).

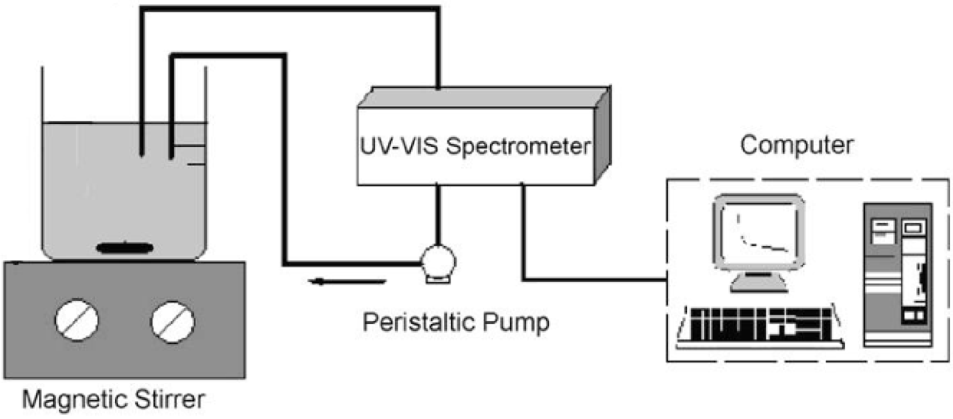


Fig. 2. Online spectrophotometric system.

of Na_2CO_3 (1.8 mmol/L) and $NaHCO_3$ (1.7 mmol/L). The eluent flow rate was 1.0 mL/min.

2.5. GC-MS analysis

Organic matter in the sample was measured by gas chromatography-mass spectrometry (Thermo THERMOFISHER ISQ GC-MS). The analytical conditions are as follows: 60ºC, 10ºC/min, 240ºC, 15 min, column flow rate 1.0 mL/min, ion source 250°, transmission line 250°, vaporization 250°. Scanning mode: full scan, scan range: 25–450. Four bar mass analyzer with EI source and SIM mode, scanning rate: up to 11,111 u/s in the whole mass range (1.2–1100 u).

2.6. Feasibility analysis of online spectrophotometric technique

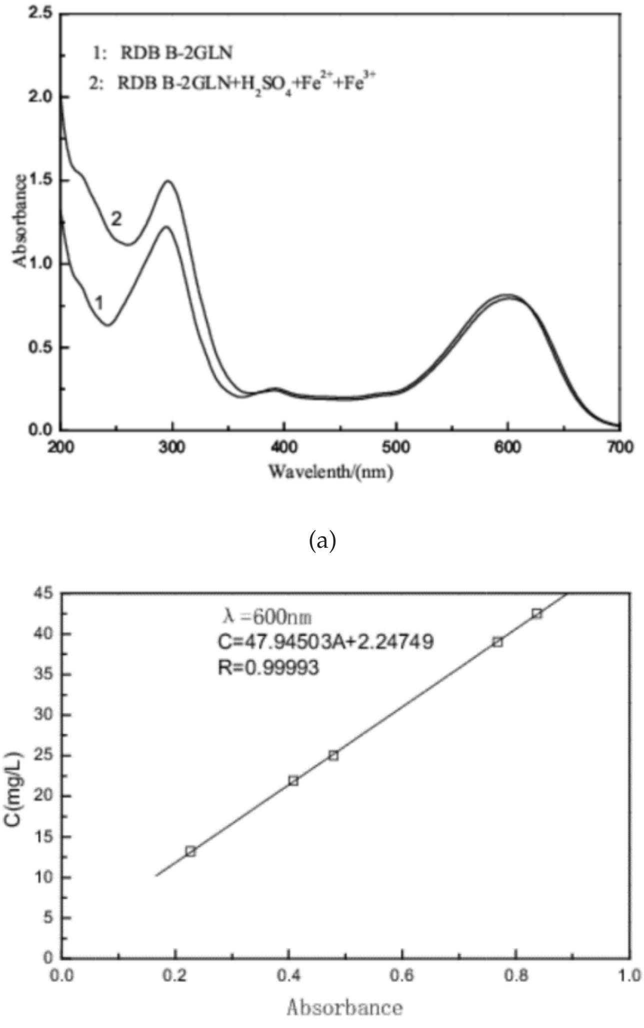
The decolorization of RDB B-2GLN dye was analyzed by online spectrophotometry method during Fenton oxidation process. RDB B-2GLN has a maximum adsorption peak at 600 nm.

After adding H_2SO_4, Fe^{2+}, Fe^{3+}, the absorption ranges have almost no change (Fig. 3). Therefore, we chose 600 nmas monitoring wavelength in the present study. Instant absorbance results recorded by computer were transformed to concentrations of dye based on the criterion equation. The relationship of the absorbance (A) at 600 nm against concentration (C) of RDB B-2GLN is C = 47.94503A+2.24749 (R = 0.99993).

3. Results and discussion

3.1. Time-dependent degradation of RDB B-2GLN

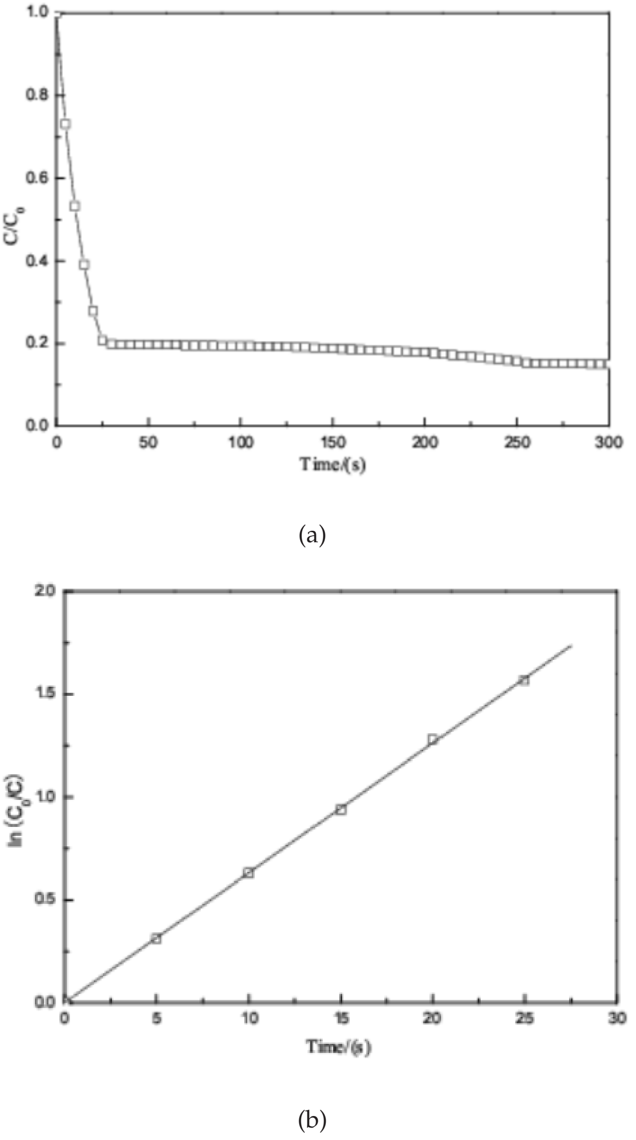
The change of C/C_0 value of RDB B-2GLN dye against reaction time is listed in Fig. 4. C_0 and C represent the initial concentration and the instant concentration of reactive azo dye, respectively. As seen from Fig. 4a, Fenton oxidation process of RDB B-2GLN solution undergoes two stages. The decolorization is very fast at the first stage (less than 25 s), and it is fairly slow at the second stage. This experimental phenomenon may be explained from two reasons. Firstly, the catalyst $FeSO_4$ and hydrogen peroxide insolution



(a)

(b)

Fig. 3. Comparison of dye UV–Vis spectra between dye and dye (+H_2SO_4+ Fe^{2+}+ Fe^{3+}).



(a)

(b)

Fig. 4. Relation of time and degradation of RDB B-2GLN ([RDB B-2GLN]$_0$ = 16 mg/L, [Fe^{2+}]$_0$ = 0.0696 mM, [H_2O_2]$_0$ = 2.635 mM, pH = 2.7, T = 27°C).

is consumed during Fenton oxidation. Secondly, intermediate products or byproducts that produced in the reaction decreased apparent rate of dye degradation. We can see from Fig. 4b, at the first stage (during the first 25 s) the Fenton oxidization process obviously abode by first-order kinetics ($\ln(C_0/C) = k_{ap}t$).The slope (k_{ap})represents the first-order rate constants. In this paper, the decolorizing reaction rate constant (k_{ap}) and decolorization rate [$R = (C_0 - C)/C_0 \times 100\%$] were examined in 300 sunder various reaction conditions, such as the $FeSO_4$ concentration, initial dosage of H_2O_2, pH value, and initial concentration of RDB B-2GLN.

3.2. Influence of $FeSO_4$ concentration

The relationship of different $FeSO_4$ concentrations and the rate constant k_{ap} and the decolorization rate R of RDB B-2GLN is shown in Fig. 5. When Fe^{2+} concentration increases from 0.0167 to 0.0696 mM, the decolorization rate *R* increases from 33.19% to 85.04%, and the rate constant k_{ap} increases from 0.01443 to 0.06265 s^{-1}. However, the decolorization rate *R* first slows down and then levels off when Fe^{2+} concentration continues to increase, while rate constant K_{ap} has a slight increase at higher Fe^{2+} concentration during Fenton oxidation. This experimental phenomenon manifests that high Fe^{2+} concentration does not effect decolorization of RDB B-2GLN in the Fenton oxidation process. This may be because the excess ferrous ion Fe^{2+} competes with the dye molecules for the hydroxyl radical ·OH ($Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$) [11,27]. Therefore, the initial Fe^{2+} concentration of 0.0696 mM can be chosen as an optimum dosage for efficiently RDB B-2GLN decolorizing from aqueous solutions.

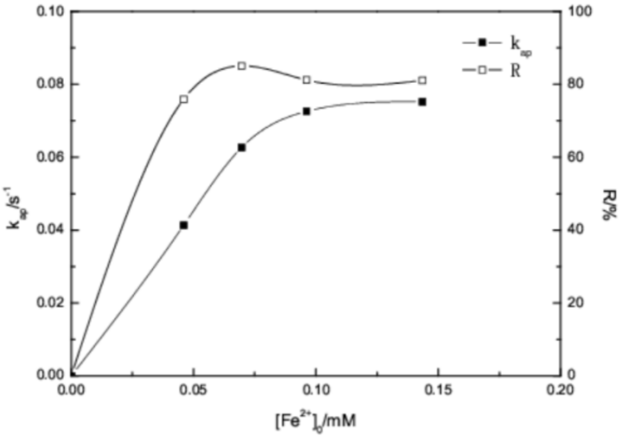


Fig. 5. Influence of initial Fe^{2+} concentration ([RDB B-2GLN]$_0$ = 16 mg/L, [H_2O_2]$_0$ = 2.635 mM, pH = 2.7, T = 27°C).

3.3. Influence of initial H_2O_2 concentration

The high oxidative hydroxyl radical is generated by the reaction of ferrous ion Fe^{2+} with H_2O_2 [28,29]. Fig. 6 displays the effect of the decolorization rate R of RDB B-2GLN and the decolorizing rate constant k_{ap} on various H_2O_2 concentrations. The decolorization rate increases from 44.26% to 85.04% with the H_2O_2 concentration rising from 0.907 to 2.635 mM. The range of k_{ap} is between 0.03637 s^{-1} and 0.06265 s^{-1} with H_2O_2 concentration from 0.907 to 2.635 mM. The experimental result suggests that R and k_{ap} of reactive azo dye RDB B-2GLN increase remarkably under certain concentration. This result can be explained by the enhancement in the quantum yield of formation of ·OH radical [1,30]. However, when H_2O_2 concentration further increases to 4.508 mM, the decolorization rate and decolorizing rate constant go down to 76.30% and 0.05277 s^{-1}, respectively. Both fluctuate at higher H_2O_2 concentration in oxidation process. At the higher H_2O_2concentrations (greater than 2.635 mM), the decrease of the decolorization rate is due to excess H_2O_2 consuming ·OH (H_2O_2 + ·OH →·OOH + H_2O) [31] and generating the hydroperoxyl radical ·OOH (·OOH as a scavenger of hydroxyl radical, ·OH + ·OOH → H_2O + O_2) [30,32]. Hydroperoxyl radical promotes the radical chain reactions, but its oxidation

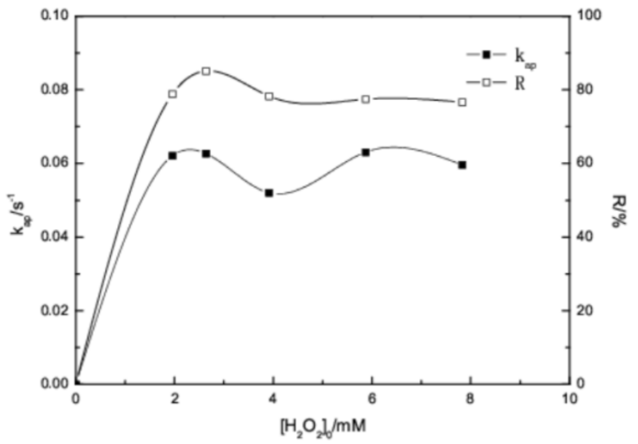


Fig. 6. Influence of initial H_2O_2 concentration ($[RDB\ B\text{-}2GLN]_0$ = 16 mg/L, $[Fe^{2+}]_0$ = 0.0696 mM, pH = 2.7, T = 27ºC).

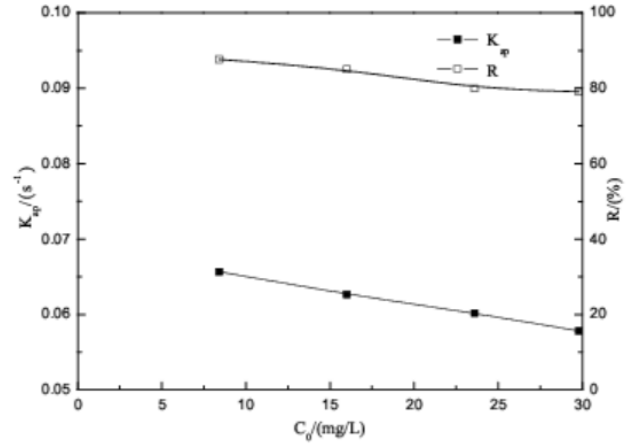


Fig. 7. Influence of initial dye concentration ($[Fe^{2+}]_0$ = 0.0696 mM, $[H_2O_2]_0$ = 2.635 mM, pH = 2.7, T = 27ºC).

potential is much lower than that of ·OH. For this reason, hydroperoxyl radical does not contribute to the oxidative destruction of RDB B-2GLNdye molecule in the aqueous solution [30]. Therefore, we choose 2.635 mM as an optimum H_2O_2 dosage of the decolorization of azo dye RDB B-2GLN in Fenton oxidation process.

3.4. Influence of initial RDB B-2GLN concentration

In order to investigate the influence of initial dye concentration on decolorization rate and the decolorizing reaction constant k_{ap}, the azo dye concentrations ranging from 8.4 to 29.8 mg/L are listed in Fig. 7. When the RDB B-2GLN concentration is 8.4, 16.0, 23.6, and 29.8 mg/L, the decolorization rate and the decolorizing reaction constant are 87.7%, 85.0%, 80.0%, 79.1% and 0.066, 0.063, 0.060, 0.058, respectively. As seen from Fig. 7, there is a slight change in the decolorization rates in the selected dye concentration range. It is also observed that the lower the dye concentrations were, the higher the decolorization rate and the decolorizing reaction constant would be. This is because the rise of dye concentration in aqueous solution increases the number of dye molecules in the aqueous, while the hydroxyl radical concentration keeps the same. So the decolorizing rate (k) and the apparent decolorizing constant (k_{ap}) decrease with increasing dye concentration [33].

3.5. Influence of pH value

The pH value plays an important role on dye degradation in Fenton process [33]. The influence of pH value on decomposition of RDB B-2GLN by Fenton oxidation is shown in Fig. 8. When the pH value increases from 2 to 2.7, the dye decolorization rate and k_{ap} increase from 76.57% to 85.04% and from 0.04229 to 0.06265 s^{-1}, respectively. However,when the pH value further increases to 5.0, the decolorization rate and k_{ap} decrease to be 64.32% and 0.04716 s^{-1}, respectively. The decolorization rate of RDB B-2GLN at pH 2.7 is higher than those of other pH values. Therefore, the pH value of 2.7 is considered the optimum value for the decolorization of azo dye RDB B-2GLN during Fenton oxidation. The reason may be explained as below. When the pH value is lower than 2.7, the ·OH is consumed by the excessive hydrogen ion ($\cdot OH + H^+ + e^- \rightarrow H_2O$) [27,33,34], and thus the decolorization rate and rate constant k_{ap} are relatively small. When the pH value is higher than 2.7 in Fenton process, because of the self-decomposition of hydrogen peroxide (H_2O_2) and deactivation of the ferrous catalysts, which formed ferric hydroxide complexes leading to a reduction in the amount of ·OH radical [35], the Fenton oxidizing ability also decreased. The dye color removal decreases rapidly after pH 3. These results show that the Fenton oxidation has the best activity in a weakly acidic environment. Similar experimental results are reported Table 1. We have compared various initial dye concentrations, H_2O_2 dosages, pH value and Fe^{2+} dosages with Fenton oxidation in the papers.

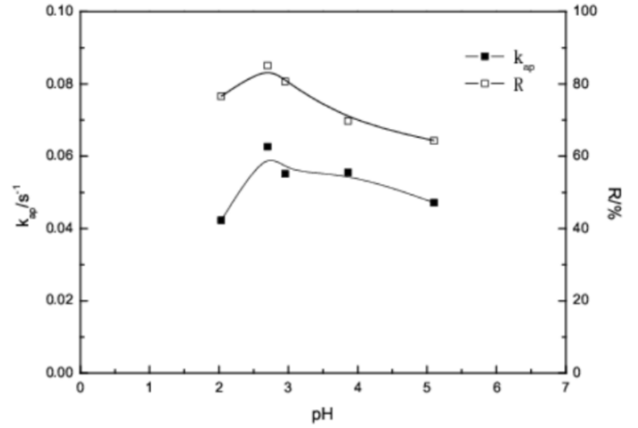


Fig. 8. Influence of pH value ($[RDB\ B\text{-}2GLN]_0$ = 16 mg/L, $[Fe^{2+}]_0$ = 0.0696 mM, $[H_2O_2]_0$ = 2.635 mM, T = 27ºC).

3.6. Kinetics study

The kinetics can be described as pseudo-first order with respect to the dye concentration. That is: $-dc/dt = k_{ap}t$, $\ln C_0/C = k_{ap}t$.

Table 1
The results of various azo dyes in Fenton oxidation process

Dye type	Initial concentration	Optimum H_2O_2 dosage	Optimum pH	Optimum Fe^{2+} dosage	Sources
Reactive Red 6B	4×10^{-5} M	2.5×10^{-3} M	3.85	3.5×10^{-5} M	[11]
Peach Red	0.2 mM	30 mM	3.0	0.6 mM	[15]
Orange G	6.63×10^{-5} M	1.0×10^{-2} M	4.0	3.5×10^{-5} M	[24]
C.I. Acid Red 73	200 mg/L	2.0 mM	3.0	$[ZVI]_0$=0.3 g/L	[25]
Reactive Yellow B-4RFN	16 mg/L	3.98 mM	3.8	0.0512	[36]
Disperse Yellow 119 and Disperse Red 167	100 mg/L 100 mg/L	75 mg/L 100 mg/L	3 3	50 mg/L 75 mg/L	[37]
Acid Red 66 and Direct Blue 71	2.94×10^{-5} M	7.50×10^{-4} M 5.00×10^{-3} M	3.5	2.50×10^{-5} M	[1]
Amido Black 10B	50 mg/L	0.50 mM	3.5	0.025 mM	[35]
Reactive Black 5 and Reactive Orange 16	74.07 g carrier/L,	100 mg/L	3.0	2 mg/L	[26]
Reactive Dark Blue B-2GLN	16 mg/L	2.635 mM	2.7	0.0696 mM	This study

The mechanism for degradation of RDB B-2GLN dye is expressed in Eqs. (1)–(9) [38]. The reactions rate of degradation of dye may be defined as:

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

$$\text{RDB B-2GLN} + \cdot OH \xrightarrow{k_2} \text{Product}_{\text{oxid}} \quad (2)$$

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

$$H_2O_2 + \cdot OH \xrightarrow{k_4} \cdot OOH + H_2O, \ k_4 = 4.5 \times 10^7\ M^{-1}\,s^{-1} \quad (4)$$

$$\cdot OH + \cdot OOH \xrightarrow{k_5} H_2O + O_2, \ k_5 = 6.6 \times 10^{11}\ M^{-1}\,s^{-1} \quad (5)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_6} Fe^{2+} + H^- + \cdot OOH, \ k_6 = 0.02\ M^{-1}\,s^{-1} \quad (6)$$

$$Fe^{3+} + \cdot OOH \xrightarrow{k_7} Fe^{2+} + H^+ + O_2, \ k_7 = 3.1 \times 10^5\ M^{-1}\,s^{-1} \quad (7)$$

$$Fe^{2+} + \cdot OOH \xrightarrow{k_8} Fe^{3+} + HO_2^-, \ k_8 = 1.2 \times 10^6\ M^{-1}\,s^{-1} \quad (8)$$

The reaction rate of dye can be defined as:

$$-\frac{d[\text{RDB B-2GLN}]}{dt} = k_2[\cdot OH][\text{RDB B-2GLN}] \quad (9)$$

According to the steady-state assumption, we can obtain [·OH] as follow:

$$\frac{d[\cdot OH]}{dt} = k_1[Fe^{2+}][H_2O_2] - k_2[\cdot OH][\text{RDB B-2GLN}] - k_3[Fe^{2+}][\cdot OH] - k_4[H_2O_2][\cdot OH] - k_5[\cdot OH][\cdot OOH] = 0 \quad (10)$$

$$\frac{d[\cdot OOH]}{dt} = k_4[H_2O_2][\cdot OH] + k_6[Fe^{3+}][H_2O_2] - k_5[\cdot OH][\cdot OOH] - k_7[Fe^{3+}][\cdot OOH] - k_8[Fe^{2+}][\cdot OOH] = 0 \quad (11)$$

On account of k_6 being negligible, compared with k_7, k_8, k_4 and k_5, so Eq. (11) can be written as:

$$k_5[\cdot OH][\cdot OOH] = k_4[H_2O_2][\cdot OH] - k_7[Fe^{3+}][\cdot OOH] - k_8[Fe^{2+}][\cdot OOH] \quad (12)$$

k_7 and k_8 were also negligible compared with k_4, Eq. (12) can be written as:

$$k_5[\cdot OH][\cdot OOH] = k_4[H_2O_2][\cdot OH] \quad (13)$$

According to Eqs. (10) and (13), we obtain:

$$\frac{d[\cdot OH]}{dt} = k_1[Fe^{2+}][H_2O_2] - k_2[\cdot OH][\text{RDB B-2GLN}] - k_3[Fe^{2+}][\cdot OH] - 2k_4[H_2O_2][\cdot OH] = 0 \quad (14)$$

$$[\cdot OH] = \frac{k_1[Fe^{2+}][H_2O_2]}{k_2[\text{RDB B-2GLN}] + k_3[Fe^{2+}] + 2k_4[H_2O_2]} \quad (15)$$

Combining Eqs. (9) with (15), we obtained:

$$-\frac{d[\text{RDB B-2GLN}]}{dt} = \frac{k_2k_1[Fe^{2+}][H_2O_2][\text{RDB B-2GLN}]}{k_2[\text{RDB B-2GLN}] + k_3[Fe^{2+}] + 2k_4[H_2O_2]} \quad (16)$$

Thus, Eq. (16) deduces to

$$\frac{[H_2O_2][\text{RDB B-2GLN}]}{(-d[\text{RDB B-2GLN}]/dt)} = \frac{[\text{RDB B-2GLN}]}{k_1[Fe^{2+}]} + \frac{k_3}{k_2k_1} + \frac{2k_4[H_2O_2]}{k_2k_1[Fe^{2+}]} \quad (17)$$

Fenton oxidation process follows first-order kinetics, it can be described:

$$-\frac{d[\text{RDB B-2GLN}]}{dt} = k_{ap}[\text{RDB B-2GLN}] \quad (18)$$

The k_{ap} is apparent reaction rate constant, we combine Eqs. (17) with (18) and obtain:

$$\frac{[H_2O_2]_0}{k_{ap}} = k[\text{RDB B-2GLN}]_0 + B \quad (19)$$

$$B = \frac{k_3}{k_2k_1} + \frac{2k_4[H_2O_2]_0}{k_2k_1[Fe^{2+}]_0}$$

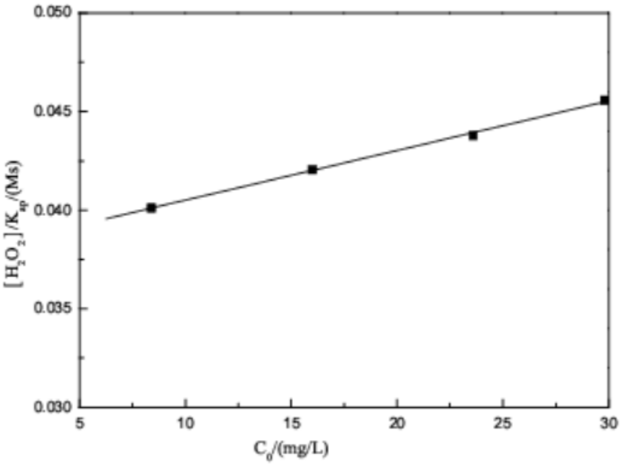


Fig. 9. The relationship between $[H_2O_2]/k_{ap}$ and $[RDB\ B\text{-}2GLN]_0$ ($[Fe^{2+}]_0$ = 0.0696 mM, $[H_2O_2]_0$ = 2.635 mM, pH = 2.7, T = 27°C).

The experimental results are displayed in Fig. 9. The linear relationship between $[H_2O_2]_0/k_{ap}$ and $[RDB\ B\text{-}2GLN]_0$ ($R^2 > 0.99$) fits well. According to the intercept (B), the intrinsic rate constant (k_2) of RDB B-2GLN reacting with ·OH is $2.62 \times 10^{11}\ M^{-1}\ s^{-1}$.

3.7. Product analysis of Fenton oxidation

In order to analyze the products of the Fenton oxidation for RDB B-2GLN, the UV-Vis spectrum, ion chromatography (IC), and gas chromatography-massspectrometry (GC-MS)were used to investigate intermediates or byproducts. We chose the reaction conditions as: the dosage of Fe^{2+} is 0.0696 mM; the dosage of H_2O_2 is 2.635 mM; RDB B-2GLN concentration is 16 mg/L; pH value is 2.7; temperature is 27°C; the reaction time is 300 s.

3.7.1. UV-Vis spectrum

Fig. 10 lists the UV-Vis spectra of dyes before and after the Fenton oxidation process.

Before the reaction (at 0 s), RDB B-2GLN dye has the intensive absorption in the range of 500–700 nm with the maximum absorbability at λ_{max} = 600 nm. However, after the Fenton oxidation reaction (at 300 s), there is no absorbability in visible area (400–700 nm), but only observed in UV range. The chemical structure of RDB B-2GLN dye is destroyed by Fenton reagent, and degradation of RDB B-2GLN wastewater can effectively be realized. However, strong absorbance in ultraviolet region indicates that some intermediates or byproducts may be produced after Fenton oxidation process. Therefore, RDB B-2GLN dye is not mineralized completely by Fenton reagent.

3.7.2. Analysis of IC

Inorganic products were analyzed by ion chromatography. We find that there are a number of SO_4^{2-} ions in solution. SO_4^{2-} concentration is 11.7 mg/L. It illustrates that the chemical structure of RDB B-2GLN is damaged by Fenton process. A certain amount of NO_3^- and Cl^- ions exists in oxidation process. Cl^- concentration is 3.57 mg/L. NO_3^- concentration is 5.38 mg/L and NO_2^- concentration is less than 0.002 mg/L indicating that the oxidation reaction is not thorough in less than 300 s in aqueous solution. Therefore, RDB B-2GLNhas not been mineralized in 300 s by Fenton oxidation process.

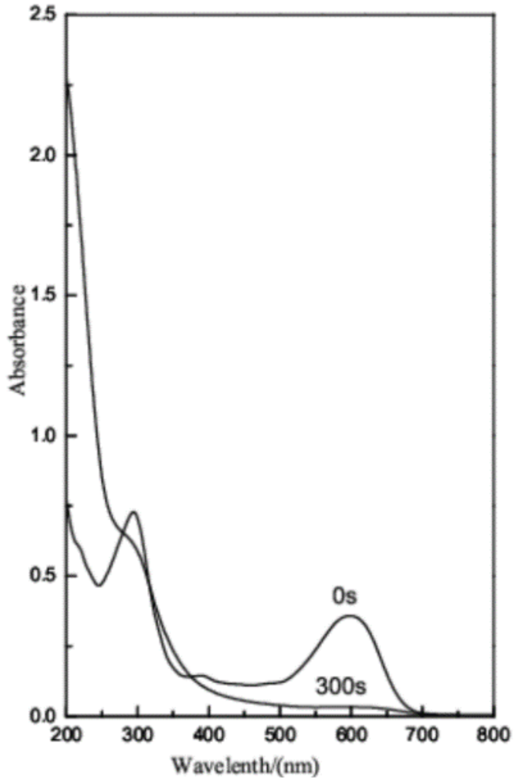
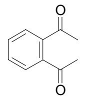
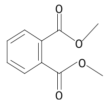
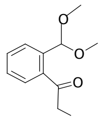
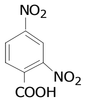


Fig. 10. UV–Vis spectral of dyes during Fenton oxidation.

3.7.3. Analysis of GC-MS and the possible degradation pathway of RDB B-2GLN

In order to predict the degradation pathway of azo dye RDB B-2GLN, the intermediate and by-products were analyzed by GC-MS after Fenton oxidation and the results are shown in Table 2. The GC-MS analysis indicates that the molecule structure of RDB B-2GLN can be effectively destroyed. However, several colorless intermediate or by-products are produced, the intermediates are dimethyl phthalate and benzoic acid, 2-(1-oxopropyl)-, methyl ester (retention time: 15.67). There were also less by-products such as 1,2-diacetylenzene (6.86), and 2,4-dinitrobenzoic acid (17.43) in aqueous. According to GC-MS results, RDB B-2GLN isn't completely mineralized by Fenton's reagent in limited 300 s. The possible pathway of degradation of RDB B-2GLN is as follows: the Reactive Dark Blue B-2GLN dye contains some C-N and C-S bonds which have low bond energy. When ·OH reacts with RDB B-2GLN, it is easy to be destroyed, including the cleavage of a nitrogen double bond. Therefore, the highly active hydroxyl radicals firstly attack and oxidize these chemical bonds, and then decom-

Table 2
Identified intermediates of degradation of RDB B-2GLN withFenton oxidation

Retention n/min	Chemical formula	Structure skeleton symbol
6.86	1,2-diacetylenzene	
15.67	dimethyl phthalate	
15.67	benzoic acid, 2-(1-oxopropyl)-, methyl ester	
17.43	2,4-dinitrobenzoic acid	

pose RDB B-2GLN to produce derivatives of naphthalene, benzene and triazine.Secondly, the derivatives of naphthalene were further oxidized by hydroxyl radical to form a product dominated by dimethyl phthalate, 2-(1-oxopropyl)-, methyl ester, and 1,2-diacetylenzene. The benzene-based compounds can be further degraded to 2,4-dinitrobenzoic acid and aliphatic compounds. The derivatives of triazines reacted to produce 2, 4, 6-hydroxyl-1, 3, 5-triazine, and ultimately could be further mineralized to produce CO_2 and H_2O.

4. Conclusions

Online spectrophotometric technique is a feasible and convenient monitoring technique for studying color removal of reactive azo dye RDB B-2GLN by Fenton process. The color removal process can be divided into two stages: the first stage (25 s) has faster decolorization, while the second stage is fairly slower.

The optimum conditions are found that initial H_2O_2 concentration is 2.635 mM, the optimal $FeSO_4(Fe^{2+})$ concentration is 0.0696 mM, and the pH value is 2.7. The lower the dye concentration, the higher the decolorization rate and k_{ap}. According to the mechanism of Fenton oxidation process, a kinetic modeling has been obtained to acquire intrinsic reaction rates of ·OH and dyes. The intrinsic rate constant of RDB B-2GLN in solution is 2.62×10^{11} M^{-1} s^{-1} with Fenton process.

Fenton oxidation process can rapidly decompose RDB B-2GLN in 300 s, and decolorization of dye wastewater is measured by the UV-Vis, IC, and GC-MS analysis. However, there are some intermediates or byproducts existing in the Fenton oxidation process. The possible degradation mechanism is discussed. The mineralization is not completely performed in limited 300 s with Fenton oxidation process.

Acknowledgements

The work is partly supported by the Young Talent Plan of Hebei Province 2016, the Excellent Youth Foundation of Hebei Province Department of Education of China (Grant No. Y2011110), and the Project of water conservancy scientific research and extension in Hebei Province in 2016 (Grant No. Z2016070).

References

[1] S. Tunç, T. Gürkan, O. Duman, 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. Eng. J., 181–182 (2012) 431–442.

[2] N.K. Daud, M.A. Ahmad, B.H. Hameed, Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe–Montmorillonite K10 catalyst, Chem. Eng. J., 165 (2010) 111–116.

[3] Y.L. Song, J.T. Li, H. Chen, Degradation of C.I. Acid Red 88 aqueous solution by combination of Fenton's reagent and ultrasound irradiation, J. Chem. Technol. Biotechnol., 84 (2009) 578–583.

[4] S. Wang, A comparative study of Fenton and Fenton-like reaction kinetics in decolorization of wastewater, Dyes Pigm., 76 (2008) 714–720.

[5] K. Barbusinski, J. Majewski, Discoloration of azo dye Acid Red 18 by Fenton reagent in the presence of iron powder, Pol. J. Environ. Stud., 12 (2003) 151–155.

[6] The World's Worst Pollution Problem: Assessing Health Risks at Hazardous Waste Sites. Blacksmith Institute, New York, USA. 2012.

[7] M. Siddique, R. Farooq, G.J. Price, Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19, Ultrason. Sonochem., 21 (2014) 1206–1212.

[8] H. Xu, D. Zhang, T. Yu, F. Wu, H. Li, Studying Fenton oxidation kinetics of mixed dyes wastewater and salt effect by online spectrophotometry, Desal. Water Treat., 102 (2018) 340–348.

[9] M.D.G. Luna, M.L. Veciana, J.I. Colades, C.C. Su, M.C. Lu, Factors that influence degradation of acetaminophen by Fenton processes, J. Taiwan Inst. Chem. Eng., 45 (2014) 565–570.

[10] H. Xu, M. Li, J. Zhang, Preparation, characterization, and photocatalytic studies on anatase nano-TiO_2 at internal air lift circulating photocatalytic reactor, Mater. Res. Bull., 48 (2013) 3144–3148.

[11] H. Xu, T.L. Yu, J.X. Wang, M. Li, Y.N. Liu, Online monitoring of Fenton-Mediated Reactive Red 6B oxidation kinetics, Environ. Prog. Sustain., 34 (2015) 1019–1027.

[12] B. Arjunan, M. Karuppan, A review on Fenton and improvements to the Fenton process for wastewater treatment, J. Environ. Chem. Eng., 2 (2014) 557–572.

[13] H. Xu, F. Wu, M. Li, Z. Liang, Application of response surface methodology for optimization of nano-TiO_2 preparation using modified sol-gel method, J. Sol-Gel Sci.Techn., 67 (2013) 394–405.

[14] D. Rubio, E. Nebot, J.F. Casanueva, C. Pulgarin, Comparative effect of simulated solar light, UV, UV/H_2O_2 and photo-Fenton treatment (UV-Vis/H_2O_2/$Fe^{2+,3+}$) in the escherichiacoli inactivation in artificial seawater, Water Res., 47 (2013) 6367–6379.

[15] M.W. Chang, J.M. Chern, Decolorization of Peach Red Azo dye, HF_6 by Fenton reaction: initial rate analysis, J. Taiwan Inst. Chem. E., 41 (2010) 221–228.

[16] H. Xu, T. Yu, J. Liu, Photo-degradation of Acid Yellow 11 in aqueous on nano-ZnO/Bentonite under ultraviolet and visible light irradiation, Mater. Lett., 117 (2014) 263–265.

[17] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review, Chem. Eng. J., 284 (2016) 582–598.

[18] E. Basturk, M. Karatas, Advanced oxidation of Reactive Blue 181 solution: A comparison between Fenton and Sono-Fenton Process, Ultrason. Sonochem., 21 (2014) 1881–1885.

[19] Y. Segura, F. Martínez, J.A. Melero, R. Molina, R. Chand, D.H. Bremner, Enhancement of the advanced Fenton process (Fe^0/H_2O_2) by ultrasound for the mineralization of phenol, Appl. Catal., B: Environ., 113–114 (2012) 100–106.

[20] F. Emami, A.R. Tehrani-Bagha, K. Gharanjig, F.M. Menger, Kinetic study of the factors controlling Fenton-Promoted destruction of a non-biodegradable dye, Desalination, 257 (2010) 124–128.

[21] O.U. Inmaculada, M.C. Anuska, L.R. Juan, E. Santiago, Advanced technologies for water treatment and reuse, AIChE J., 61 (2015) 3146–3158.

[22] E. Basturk, M. Karatas, Decolorization of antraquinone dye Reactive Blue 181 solution by UV/H_2O_2 process, J. Photochem. Photobio. A: Chem., 299 (2015) 67–72.

[23] M. Karatas, Y.A. Argun, M.E. Argun, Decolorization of antraquinonic dye: Reactive Blue 114 from synthetic wastewater by Fenton process: kinetics and thermodynamics, J. Ind. Eng. Chem., 18 (2012) 1058–1062.

[24] S.P. Sun, C.J. Li, J.H. Sun, S.H. Shi, M.H. Fan, Q. Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study, J. Hazard. Mater., 161 (2009) 1052–1057.

[25] F. Fu, Q. Wang, B. Tang, Effective degradation of C.I. Acid Red 73 by advanced Fenton process, J. Hazard. Mater., 174 (2010) 17–22.

[26] C.C. Su, M.P. Asa, C. Ratanatamskul, M.C. Lu, Effect of operating parameters on decolorization and COD removal of three reactive dyes by Fenton's reagent using fluidized-bed reactor, Desalination, 278 (2011) 211–218.

[27] H. Zheng, Y.X. Pan, X.Y. Xiang, Oxidation of acidic dye Eosin Y by the solar photo-Fenton processes, J. Hazard. Mater., 141 (2007) 457–464.

[28] S. Venny, H.K. Ng. Gan, Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils, Chem. Eng. J., 213 (2012) 295–317.

[29] I. Nitoi, T. Oncescu, P. Oancea, Mechanism and kinetic study for the degradation of lindane by Photo-Fenton process, J. Ind. Eng. Chem., 19 (2013) 305–309.

[30] B.H. Hameed, T.W. Lee, Degradation of Malachite Green in aqueous solution by Fenton process, J. Hazard. Mater., 164 (2009) 468–472.

[31] A. Sinha, S. Chakrabarti, B. Chaudhuri, S. Bhattacharjee, P. Ray, S.B. Roy, Oxidative degradation of strong acetic acid liquor in wastewater emanating from hazardous industries, Ind. Eng. Chem. Res., 46 (2007) 3101–3107.

[32] K. Sehested, E. Bjergbakke, O.L. Resmussen, Reactions of H_2O_2 in the pulse-irradiated Fe^{2+}-O_2 system, J. Chem. Phys., 51 (1969) 3159–3166.

[33] M. Muruganandham, M. Swaminathan, Decolorization of reactive orange 4 by Fenton and photo-Fenton oxidation technology, Dyes Pig., 63 (2004) 315–321.

[34] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm., 71 (2006) 236–244.

[35] J.H. Sun, S.P. Sun, G.L. Wang, P.L. Qiao, Degradation of azo dye Amido Black 10 B in aqueous solution by Fenton oxidation process, Dyes Pigm., 74 (2007) 647–652.

[36] A. Gao, Z. P, W. Wang, F. Li, Online monitoring of decolorization kinetics of reactive yellow B-4RFN in Fenton process, Fresen. Environ. Bull., 26 (2017) 3415–3421.

[37] F. Çiner, Ö. Gökkuş, Treatability of dye solutions containing disperse dyes by Fenton and Fenton-solar light oxidation processes, Clean-Soil Air Water, 41 (2013) 80–85.

[38] H. Kušić, N. Koprivanac, A.L. Božić, I. Selanec, Photo-assisted Fenton type processes for the degradation of phenol: A kinetic study, J. Hazard. Mater., B136 (2006) 632–644.