Kinetic study of Reactive Black 5 degradation by Fe$^{2+}$/S$_2$O$_8^{2-}$ process via interactive model-based response surface methodology

Jun-Ming Hong, Yu-Feng Xia, Chung-Chuan Hsueh and Bor-Yann Chen

ABSTRACT

This study aimed to kinetically discover optimal conditions on characteristics of Reactive Black 5 decolorization/degradation via ferrous (Fe$^{2+}$)-activated potassium persulfate (PS). Monod-like kinetics and interactive model-based response surface methodology (RSM) were applied to fitting and predict optimize treatment. Biodegradability of the intermediates was also tested by shaking culture with two species (Proteus hauseri ZMd44 and Shewanella sp. WLP72). Results showed that the optimal degradation efficiency was predicted (through RSM) as pH 3.72, (PS) = 0.39 mM, and (Fe$^{2+}$) = 0.29 mM. The transformation products (α-4-hydroxymandelic acid, benzoic acid, benzene, formic acid, oxalic acid and acetic acid) were less toxic than the original dye solution. According to those results, clean-up of dye pollutants by the Fe$^{2+}$/S$_2$O$_8^{2-}$ process is feasible as a pre-processing for the biodegradation, and the predicted optimal conditions are meaningful for further industry utilization.

Key words | azo dye, biodegradability analysis, decolorization, ferrous, SO$_4^{2-}$

INTRODUCTION

The textile dyeing industry generates a considerable amount of dye-bearing wastewater (WW). Thus, residual dyes in WW inevitably released to the environment pose significant threat to living organisms globally (Peng et al. 2008). Azo dyes are the most popularly used textile dyes (>60%), and the removal of these dyes from WW has been of utmost priority under US EPA regulations (Chen et al. 2017). Azo dyes or derived intermediates (e.g., aromatic amines) are potentially cytotoxic and possibly mutagenic to organisms (Stylidi 2004). Conventional physical, chemical, and biological methods are usually not efficient for degrading recalcitrant azo dyes (Rodriguez et al. 2014). Thus, exploring cost-effective methods to degrade textile dyes is important for sustainable development.

Advanced oxidation processes (AOPs) are used to effectively treat dye-bearing WW by destroying recalcitrant organic contaminants, because the hydroxyl radical and/or other radicals are highly active for degradation (Anipsitakis & Dionysiou 2003). An example of an AOP is the Fenton-associated reaction (e.g., electro-Fenton, photo-Fenton, and photoelectro-Fenton) (Khataee et al. 2014; Antonin et al. 2015; Li et al. 2015a, 2015b). TiO$_2$-mediated photocatalysis (Wetchakun et al. 2015) and other oxidative reactions using potassium permanganate (Aleboyeh et al. 2009) and Co$^{2+}$/oxone reagent (Yu et al. 2015) have been examined for dye degradation. Dye is usually removed at acidic pH levels (ca. 3) in Fenton processes, because the decolorization rates of dyes are relatively slow under alkaline condition. Moreover, Fenton-like systems are not very promising because of the required high levels of H$_2$O$_2$ (Kasiri et al. 2008) or electric energy (Panizza & Oturan 2011; Solano et al. 2015). Methods using TiO$_2$-mediated photocatalysis are still not economically feasible for large-scale treatment (Kansal et al. 2010) and present a potential safety hazard due to the nano-particles (Li et al. 2016).

Persulfate (PS)-catalyzed techniques are used to degrade several pollutants (Liang et al. 2013; Zhao et al. 2015; Ayoub & Ghauch 2014; Monteaugu et al. 2015; Yan et al. 2015). These techniques provide alternatives for dye mineralization (Xu & Li 2010). As one of the strongest oxidants in aqueous phases ($E^0 = 2.01$ V) and compared with H$_2$O$_2$ ($E^0 = 1.76$ V), PS is highly soluble, appropriate for numerous reactants, relatively stable, inexpensive, and more persistent in the subsurface than peroxide (Liang et al. 2007). An application based on the activation of PS ion (S$_2$O$_8^{2-}$) to generate sulfate radicals (SO$_4^{2-}$) for reactivity ($E^0 = 2.5$–$3.1$ V vs. NHE)
exhibits great potential for contaminant degradation (Xu & Li 2010). Readily available ferrous ions can effectively activate PS to generate SO$_4^{2-}$ radicals for oxidation, as shown by the following mechanisms (Li et al. 2015a, 2015b):

$$
Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + Fe^{3+} \quad (k = 27 \, \text{M}^{-1} \, \text{s}^{-1})
$$

(1)

$$
SO_4^{\bullet-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad (k = 4.6 \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1} \text{ (22 \, ^\circ \text{C}}, \text{ pH} = 3 - 5)\quad (2)
$$

However, if Fe$^{2+}$ is in excess, Fe$^{2+}$ would significantly scavenge SO$_4^{2-}$ and inhibit radical oxidation of contaminants (Equation (2)). Quenching of SO$_4^{2-}$ by Fe$^{2+}$ can be a major side reaction (e.g., at higher concentrations of Fe$^{2+}$) based on the reaction rate constant between SO$_4^{2-}$ and Fe$^{2+}$ (Equation (2)). A threshold amount of Fe$^{2+}$ is required to effectively activate PS, whereas excessive Fe$^{2+}$ is detrimental to degradation. Thus, the main factors affecting degradation performance are pH, concentration of PS and ferrous ions, and the concentration of target pollutant. The concentration of dyes during dye degradation via AOPs could significantly affect the decontamination efficiency (He et al. 2007; Medien & Khalil 2010; Ghoreishian et al. 2014). Kusic et al. reported the optimal conditions of different PS activation methods (Fe$^0$/PS and Fe$^{2+}$/PS) through response surface methodology (RSM) (Kusic et al. 2011). The current study attempted to discover the interactions of the main factors with the decolorization performance of reactive black 5 (RBk5) and RSM was used to quantitatively confirm the individual and interactive effects of the operating parameters (i.e., proton and PS and Fe(II) concentration) on the efficiency of treating 0.05 and 0.10 mM RBk5. Additionally, the biodegradability of RBk5 transformation products treated by the Fe$^{2+}$/PS process is rarely reported. Therefore, the feasibility of the biodegradation of these intermediates was comprehensively assessed.

**MATERIALS AND METHODS**

**Materials and chemicals**

RBk5 (C$_{26}$H$_{21}$N$_5$Na$_4$S$_6$, MW = 991.82 g mol$^{-1}$) (Zhang et al. 2012) was obtained from Everlight Chemical Ltd (Taiwan). All chemicals were of reagent grade and used without further purification. Milli-Q water, with a resistivity of 18.25 MΩ cm$^{-1}$ (Millipore Milli-Q system), was used to prepare the solution. Sodium PS (Na$_2$S$_2$O$_8$, 99%) and ferrous sulfate (FeSO$_4$·7H$_2$O) were obtained from Sigma-Aldrich Inc. Moreover, 1,10-phenanthroline, potassium iodide, and ethanol were purchased from the National Chemical Reagent Co. (Xiamen, China). Concentrated sulfuric acid (>98.0%) and sodium hydroxide (>96.0%) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China) and diluted to 1 M for initial pH adjustment.

**Batch experiments**

RBk5 was degraded in a 100 mL shake flask under mechanical stirring at room temperature (25 ± 1 °C). The initial pH levels were adjusted by 1 M sodium hydroxide (NaOH) or sulfuric acid (H$_2$SO$_4$). The effect of initial pH was determined by inspecting the dye degradation at pH 2.0–12.0 (±0.05), and the effect of initial pH on the shift in absorbance was measured. A pH buffer was not added to the flask to prevent interference from the buffer solution. The results showed no significant differences in the tested pH range. The initial pH was adjusted to 4.0 in the remaining experiments. Seven different mole ratios of Fe$^{2+}$ to PS, namely, 1:4, 1:2, 1:1, 1:5:1, 2:1, 3:1, and 4:1, were tested to study the effect of Fe$^{2+}$-activated PS, and (Fe$^{2+}$) or (PS) was controlled at 0.2 mM. The effect of dye concentration was determined by testing 0.025, 0.050, 0.075, and 0.100 mM RBk5 at pH 4.0, (PS) = 0.2 mM, and (FeSO$_4$) = 0.2 mM.

Blank experiments were conducted prior to all experiments (e.g., PS/RBk5, Fe$_{2+}$/RBk5, and Vis$_{600 \, \text{nm}}$/RBk5) to ensure that no decolorization (<0.5%) had occurred (data not shown). Decolorization of RBk5 was determined by on-line continuous monitoring with absorbance at $\lambda_{\text{max}}$ (Hach, DR3900), because the decolorization was performed rapidly.

**Analysis**

Decolorization percentage was established by measuring the absorbance in the visible spectra at the characteristic wavelength of RBk5 ($\lambda_{\text{max}} = 600$ nm) via a UV-vis spectrophotometer. The UV-vis results were confirmed by high performance liquid chromatography (Waters) (Figures S1–S3, available with the online version of this paper). The concentration of PS anions was determined by spectrophotometric determination with potassium iodide (Liang et al. 2008), whereas total iron and ferrous iron were measured with 1,10-phenanthroline at 510 nm (Rice et al. 2012). The pH level and...
oxidation reduction potential (ORP, the index of the tendency of a chemical species to donate/acquire electrons and thereby be oxidized or reduced) were monitored using a pH meter (SP-2100, Suntex, Taiwan) equipped with a pH electrode and a silver chloride and saturated calomel electrode, respectively. Chemical oxygen demand (COD) was determined using rapid digestion spectrophotometric determination (Hach, DR3900).

The initial degradation rate of RBk5 was investigated using the first-order kinetics (Equations (3) and (4)). The decolorization percentage DE (%) of RBk5 was calculated using Equation (5) as follows:

$$\frac{dC}{dt} = -k_1 C(0) = C_0$$  \hspace{1cm} (3)

$$\ln \frac{C}{C_0} = -k_1 t$$  \hspace{1cm} (4)

$$DE = \frac{C_0 - C}{C_0} \times 100\%$$  \hspace{1cm} (5)

where $C_0$ is the initial concentration of RBk5 (mM), $C$ is the RBk5 concentration at time $t$ (s), and $k_1$ is the first-order rate constant (s$^{-1}$).

**Experimental design**

A central composite design (CCD) consisting of 17 experimental sets was performed, including the center point in triplicate. CCD combined with RSM was used to determine the optimal conditions of initial pH, and concentration of iron activator ($Fe^{2+}$) and oxidant ($K_2S_2O_8$) to develop empirical models to apply $Fe^{2+}/S_2O_8^{2-}$ processes to degrade RBk5.

Experimental data were analyzed using Design-Expert 8.0.6 software and fitted to a second-order polynomial equation. The following function (Equation (6)) was employed to obtain the interactive relationships between dependent and independent variables (Arslan-Alaton et al. 2009):

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j$$  \hspace{1cm} (6)

where $b_0$ is the average value of the experimental response, $b_i$ is the main effect of the coded variable $X_i$, $b_{ii}$ is the quadratic effect of the coded variable $X_i$, and $b_{ij}$ is the interaction effect between the respective coded variables.

Initial $Fe^{2+}$ and PS concentrations and initial pH of the WW were considered as the independent process-specific variables, whereas DE and $k_1$ were considered as the dependent variables (i.e., output responses). Values of the independent variables and their variation limits were determined based on the related scientific literature and the experimental results obtained in pretest studies conducted with azo dye. The results are presented in Table 1 for (RBk5)$_0$ = 0.05 mM and 0.10 mM.

**Biodegradability test**

The acute toxicity of the reaction solution was determined with two species (Proteus hauseri ZMd44 and Shewanella sp. WLP72) which had been cultured in the laboratory for more than five generations. Prior to the tests, 200 mg L$^{-1}$ RBk5 was decolorized through the $Fe^{2+}/S_2O_8^{2-}$ process under different molar ratios ([PS]/[Fe$^{2+}$]) = 0.5:1, 1:1, 2:1, and 4:1; (Fe$^{2+}$) = 0.2 mM; pH 4; reaction time = 30 min), and 50 mL of treated RBk5 solution was added into 50 mL of Luria-Bertani medium (LB broth, Miller, Difco). The pH level was then adjusted to pH 7 by phosphate buffer. The acute toxicity experiments were conducted in 150 mL Erlenmeyer flasks using pre-cultured P. hauseri ZMd44 and Shewanella sp. WLP72 species, and the samples were divided into five groups. Synchronous growth activity and maximum metabolic function were ensured in the same growth phase for bioassay by inoculating 5% (v/v) cultured broth on fresh sterile LB medium. A cell culture was harvested at approximately mid-exponential growth phase (ca. 4 h) for further toxicity assessment. Four groups were used for the test, while one group was used for the blank (200 mg L$^{-1}$ RBk5 not decolorized). All samples were incubated aerobically at 30 °C and centrifuged at 200 rpm. The specific growth rates in the exponential growth phase were determined through the measured OD$_{600}$, which was determined by removing the supernatant of 1 mL of culture after centrifugation and diluting the microbial sediment to 1 mL using sterile deionized water.

| Table 1 | Experimental design of level setting for three independent variables (a) (RBk5)$_0$ = 0.05 mM; (b) (RBk5)$_0$ = 0.10 mM |
|---|---|---|---|---|---|---|---|
| Input variable | Symbol | Range and levels |
| (a) | Initial pH $X_1$ | 2.37 2.67 2.97 3.27 3.57 | | |
| (b) | Initial pH $X_1$ | 2.37 2.67 2.97 3.27 3.57 | | |
| PS (mM) $X_2$ | 0.13 0.26 0.39 0.52 0.65 | | |
| PS (mM) $X_2$ | 0.13 0.26 0.39 0.52 0.65 | | |
| $Fe^{2+}$ (mM) $X_3$ | 0.13 0.26 0.39 0.52 0.65 | | |
| $Fe^{2+}$ (mM) $X_3$ | 0.13 0.26 0.39 0.52 0.65 | | |
RESULTS AND DISCUSSION

Effect of UV–visible spectral changes

Time courses of spectral profiles were monitored (Figure 1(a)) to discover whether decolorized intermediates (e.g., aromatic amines) were generated. RBk5 was decolorized by ca. 90% within 10 min (Figure 1(b)). Despite the complexity, RBk5 concentrations at any time $t$ following a single impulse and RBk5 addition can be described by $C = \sum_{i=1}^{n} C_i e^{-\lambda_i t}$, where $\lambda_i$ and $C_i$ denote eigenvalues and concentrations of reactant and intermediate(s) species, respectively. Initial rates at all intermediate concentrations were determined to be zero (Notari 1987). RBk5 concentration is known to behave according to linear kinetics, because the equation is empirically adequate. The RBk5 profiles followed the model of bioexponential disposition (Chen 2002). That is, the degradation of RBk5 might have occurred in two steps, namely, fast decolorization of RBk5 in the first 2 min and then slow degradation for a longer period of ca. 30 min. Intermediary products were likely more inhibitory of chemical stability than raw compound RBk5. Thus, the first step was the predominant overall reaction, and its rate constant may follow Monod-like kinetics. That is, the rate of reaction in RBk5 during the first step is a first-order reaction. The reaction order in RBk5 diminished continuously from maximum to zero as intermediate concentrations continually increased.

The spectral profiles of RBk5 before and after oxidation could be detected at the visible wavelength regions (e.g., 600 nm as signal wavelength of azo linkage in RBk5). The characteristic peak at 600 nm decreased rapidly within 2 min, and then the absorbance of peaks was attenuated to minimal values (Figure 1). This result implied that the conjugate structure (–N=N–) of RBk5 was destroyed, leading to rapid color removal. Two peaks at 336 and 322 nm occurred after 30 s of decolorization reaction, and the absorbance decreased slowly afterward. Hence, RBk5 was degradation, and derived intermediates formed. The time-series profile of COD was measured (Figure 1(c)) to investigate the mineralization of RBk5 by Fe$^{2+}$/PS treatment. COD was rapidly reduced in the first 2 min and then decreased slowly in the next 50 min. This phenomenon was in accordance with the trend of RBk5 decolorization. The results indicated that the decolorization and mineralization of RBk5 were synchronous. By comparing with other research, the advantages of the proposed approach were obvious since high efficiency can be achieved in short time (as shown in Table S1, available with the online version of this paper).

In the research of Zhang and coworkers, 90% efficiency can be achieved in 120 min by the photocatalytic process (Zhang et al. 2012); however, lower efficiency of biodegradation was achieved by a graphene-TiO$_2$ triggered reaction (Hsueh et al. 2009; Li et al. 2013; Zhang et al. 2015). In contrast, high decolorization percentage of 98% could be obtained by the Fe$^{2+}$/S$_2$O$_8^2$ – process in 30 min in this research. As known, the rate of oxidation and reduction...
for RBK5 dyes is strongly related to the degradation pathway of azo dyes. To deeply understand the mechanism of reaction, the byproducts and intermediate products were analyzed by gas chromatography–mass spectrometry (GC-MS, Varian 240-MS); the results are shown in Figure S4 (available online). Three compounds were elucidated as byproducts and intermediate products formed during the degradation of RBK5 (Table S2, available online), after 10 min reaction. DL-4-hydroxymandelic acid (RT = 55.05 min) is identified as a major product in the Fe²⁺/PS process, which supports the fission of the −N=N— group. Then the DL-4-hydroxymandelic acid could be further degraded to benzoic acid (RT = 43.74 min) and benzene (RT = 33.68 min). However, after 40 min reaction, all the benzodiazepine material was completely decomposed. The cleavage of the benzene ring formed some intermediates of formic acid, oxalic acid and acetic acid (as shown in Table S2). Finally, all the byproducts will be mineralized to CO₂ and water. By comparing with the results of Zhang et al. (2015), smaller molecules can be achieved in this research, which indicates the complete degradation. The photodegradation results in the desulfonation of dyes (Zhang et al. 2015) rather than the fission of the −N=N— group (this research). The difference in the degradation pathway explains the difference in efficiency.

Real textile WW (CODCr = 307–1,120 ppm; biochemical oxygen demand = 66.0–199 ppm; suspended solids = 104–114 ppm; pH = 10.62–11.16; chromaticity = 200–1,000; RBK5 = 200–1,000 ppm) from Eastern Asia (Xiamen, China) Corporation Ltd was also analyzed to further demonstrate the effect of treatment using Fe-activated PS. Chemical characterization of WW is shown in the inserted table in Figure 1(d). Besides RBK5, Reactive Blue 171 (RB171) and Reactive Green 19 (RG19) are the main organics in the WW. The concentration of all the dyes changed with the operation process. According to the result in Figure 1(d), the main adsorption band of real textile WW was located at 600 nm and increasing the reaction time led to decreased intensity of the adsorption band. This phenomenon indicated the strong activity of Fe-activated PS for oxidation, regardless of the complexity of the real textile WW.

Optimal operation variables

Effect of pH

The decolorization profile followed the bioexponential model (Figure 2). RBK5 could be decolorized rapidly in the first 2 min once ferrous sulfate was added, and then decolorization tended to be steady (Notari 1987; Zhang et al. 2012). The effect of initial pH for the Fe²⁺/PS process is presented in Figure 2(a). The most favorable pH levels

![Figure 2](https://iwaponline.com/wst/article-pdf/76/7/1754/450095/wst076071754.pdf)

**Figure 2** | Effect of (a) pH; (b) PS; and (c) Fe²⁺ on the efficiency of the Fe²⁺/PS-catalyzed decolorization process.
for RBk5 degradation were at ca. pH 3–4. Alkaline pH levels (ca. pH 9–12) were not favorable for the reactions involved in RBk5 degradation. High DE (DE > 80% in 10 min) was observed at pH 2–7, indicating that the Fe$^{2+}$/S$_2$O$_8^{2-}$ process could still be performed within a wide range of acidic pHs. The fastest $k_1$ of RBk5 was observed at ca. pH 4.0, and increasing or decreasing pH levels would lower decolorization performance. However, second-stage RBk5 DE ($t > 2$ min) was slightly slower at pH 4.0 than at pH 3.0. This phenomenon is probably caused by the fact that additional SO$_4^{2-}$ could be formed with acid-catalyzation in acidic pH levels (Equations (7) and (8)), as follows (Saien et al. 2011):

\[ \text{S}_2\text{O}_8^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_8^- \]  

(7)

\[ \text{HS}_2\text{O}_8^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{H}^+ \]  

(8)

Moreover, the amount of free Fe$^{2+}$ declined because of the formation of Fe$^{2+}$ complexes at pH > 4.0 (Equation (9)) (Rao et al. 2014):

\[ \text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{+} + \text{H}^+ \]  

(9)

The degradation efficiency drastically decreased from 89.79% to 53.83% in 10 min (inserted box in Figure 2(a)) when pH was increased from 4.0 to 9.0. Then, decolorization was almost terminated at alkaline pH levels (e.g., pH 12). Further increase in pH levels led to the precipitation of Fe(OH)$_2$. Both FeOH$^+$ and Fe(OH)$_2$ had much lower catalytic activity toward PS ions, thereby producing fewer sulfate radicals (Rao et al. 2014). The $k_1$ value of RBk5 was lower at pH 2.0 than at pH 3.0, which can be explained by two points. First, complex (Fe(H$_2$O)$_2$)$^{2+}$ formed at low pH levels (Masomboon et al. 2009), leading to a deficiency of free Fe$^{2+}$ to activate PS ions in the solution and fewer sulfate radicals. Second, since PS could be acid-activated, higher SO$_4^{2-}$ was generated in highly acidic conditions, and this process could favor radical scavenging reactions, instead of radical with RBk5 reactions (Peyton 1993). Possible chemical scavenging reactions (i.e., Equations (10)–(13)) to compete with SO$_4^{2-}$/RBk5 interaction are as follows (Saien et al. 2011):

\[ \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}^+ \]  

(10)

\[ \text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \]  

(11)

\[ \text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} \]  

(12)

\[ \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \]  

(13)

The pH levels may decline, because H$^+$ was propagated from the reaction shown in Equation (10), and OH$^-$ was consumed via Equation (11). The pH level and ORP changed rapidly during the first stage (<2 min) when pH$_0$ was between pH 4 and pH 9, and the final pH ($\text{pH}_f$) was ca. 3.5 (data not shown). The $\text{pH}_f$ was almost identical with pH$_0$ at $\text{pH}_0 < 3$. This result does not imply that the Equation (10) reaction does not occur in strong acidic media, but rather confirms that the amount of released H$^+$ is so low such that significant reduction is appropriate under alkaline and natural pH conditions only (pH 4–9) (Saien et al. 2011). However, when initial pH$_0$ was much higher than 7, Fe$^{2+}$ inevitably precipitated as Fe(OH)$_2$, 1, and apparently Fe$^{2+}$/S$_2$O$_8^{2-}$ AOP was terminated. Given that the pH$_f$ value for bisulfate ion (HSO$_4^-$) was 2.0 (Ghoreishian et al. 2014), at pH $\leq$ 2.0, the released H$^+$ via Equation (10) could react with SO$_4^{2-}$ and form HSO$_4$. That is, pH did not significantly change when initial pH$_0$ was 2.0 probably because of the significant amounts of protons provided for the reaction.

**Effect of PS dosage**

Increasing the concentration of PS from 0.05 mM to 0.20 mM enhanced the degradation process (i.e., decolorization percentage increased from 41.29% to 88.87% in 10 min; Figure 2(b)). However, further increase in PS dosage did not significantly increase RBk5 decolorization. This phenomenon was similar to the finding when trichloroethane was degraded using a ferrous-activated PS process (Liang et al. 2004). Increasing the PS concentration from 0.2 mM to 0.8 mM resulted in the slight enhancement of RBk5 decolorization from 88.87% to 95.02% (within 10 min). Thus, the optimal concentration of PS was chosen at 0.2 mM for cost-effective consideration.

PS was activated by Fe$^{2+}$ to generate sulfate radicals via Equation (1) to decolorize RBk5. Higher PS concentration would result in more collision with Fe$^{2+}$ to generate more SO$_4^{2-}$. Then, the more opportunities to attack the RBk5 molecules, the higher the DE. Moreover, higher probability of collision between PS and Fe$^{2+}$ caused significant reductions in Fe$^{2+}$ (Jiang et al. 2013). Consequently, less SO$_4^{2-}$ was quenched by Fe$^{2+}$, enhancing DE as the concentration of PS increased. Meanwhile, higher SO$_4^{2-}$ generation led to higher radical concentrations, which could favor the reaction with radicals (e.g., ·OH in Equations (10)–(13)) instead of radical with RBk5. However, adding more S$_2$O$_8^{2-}$ ions led to a
low variation in DE and $k_1$, probably because of the recombination of excessive generated •OH radicals to form less-reactive H$_2$O$_2$ molecules (Saien et al. 2011).

**Effect of Fe$^{2+}$**

The DE of RBk5 increased from 76.91% to 88.61% with an increase in Fe$^{2+}$ concentration from 0.05 mM to 0.2 mM (Figure 2(c)). Further increase in Fe$^{2+}$ to 0.8 mM decreased the DE of RBk5 to 60%.

High concentration of Fe$^{2+}$ had advantages and disadvantages in the generation and existence of SO$_4$$^±$/$C_0$. Higher dosage of Fe$^{2+}$ ions improved the generation rate of SO$_4$$^±$/$C_0$, and this condition accelerated the decomposition of RBk5. Dye degradation improved as Fe$^{2+}$ dosage increased. However, Fe$^{2+}$ can also act as an effective scavenger of SO$_4$$^±$/$C_0$, significantly reducing DE (Miao et al. 2015). Therefore, the optimal concentration of Fe$^{2+}$ was chosen at 0.2 mM.

The variation in (Fe$^{2+}$) was monitored during the reaction with different initial (Fe$^{2+}$)$_0$ ranging from 0.05 mM to 0.8 mM. Fe$^{2+}$ was consumed rapidly, and its concentration was reduced sharply in the first 2 min. The PS degradation rate was enhanced from 10.45% to 88.47% with increased Fe$^{2+}$ concentration (data not shown). This result was consistent with the finding of Liang et al. (2004), who showed that further increase in Fe$^{2+}$ ions could have proportional augmentations to PS decomposition.

**The kinetic model of $k_1$**

Thus, for the operation variables, the effect of pH on $k_1$ could be modeled via diprotic acid-base equilibria (Equation (14)), as described in the Appendix (available with the online version of this paper):

$$k_1 = \frac{k_{max}}{1 + (H^+)/K_1 + K_2/(H^+)}$$

(14)

and the optimal pH at $(H^+) = \sqrt{K_1K_2}$.

The effects of PS and Fe$^{2+}$ on $k_1$ are determined using Michaelis–Menten or Monod-like kinetics, as follows (Equation (15)):

$$k_1 = \frac{k_{max}(A)}{K_s + (A)}$$

(15)

where $(A)$ represents the concentration of PS or Fe$^{2+}$, and $K_s$ is the half-velocity constant (i.e., the value $(S)$ when $k/k_{max} = 0.5$).

The curves of the model predictions (Figure 3) show that pH $> 7.0$ is apparently not appropriate, possibly because of precipitate formation (e.g., Fe(OH)$_2$↓). Kinetic modeling of Equations (14) and (15) could be simulated as follows:

$$k_1 = \frac{1.29}{1 + (H^+)/5.56 \times 10^{-3} + 5.26 \times 10^{-6}/(H^+)}$$

(16)

The optimal concentration of $H^+$ for maximal $k_1$ was as follows:

$$(H^+) = \sqrt{K_1K_2} = 2.05 \times 10^{-4} \text{ (i.e., pH = 3.69)}$$

Moreover, according to the aforementioned mechanisms of PS catalyst–multiple species systems (Berrington de Gonzalez & Cox 2005), the plausible model of $k_1$ based
upon PS and Fe$^{2+}$ effect is shown in Equations (17) and (18):

$$k_1 = \frac{8.81(PS)}{1.30 + (PS)}$$

(17)

$$k_1 = \frac{1.91(Fe^{2+})}{0.14 + (Fe^{2+})}$$

(18)

In summary, the interactive model with a correlation factor of $\phi = 0.74$ could be presented as shown in Equation (19), as follows:

$$k_1 = 0.74 \times \frac{1.29}{1 + ((H^+)/3.56 \times 10^{-8}) + (5.26 \times 10^{-8}/(H^+))} \times \frac{8.81(PS)}{1.30 + (PS)} \times \frac{1.91(Fe^{2+})}{0.14 + (Fe^{2+})} \quad (r^2 = 0.924)$$

(19)

**Effect of RBk5 concentration**

Apparently, initial dye concentration could crucially affect the efficiency of decolorization, because pollutant concentration is of great importance to WW treatment (Ghoreishian et al. 2014). The DE gradually decreased with increased initial dye concentrations (Figure 4). After 10 min of reaction, decolorization of 0.025, 0.050, 0.075, and 0.10 mM RBk5 reached 92.32%, 88.87%, 86.70%, and 77.32%, respectively. The $k_1$ values sharply decreased with increased RBk5 concentration as indicated in the inserted box in Figure 4. The efficiency of the process based on the amount of dye decolorized generally increased with increased initial concentrations (He et al. 2007).

As the concentration of RBk5 increased, the radical provided for degradation approached saturated levels. Increasing dye concentration only increased the number of dye molecules, but not the radicals available for reaction concentration. Therefore, the removal rate should be reduced (Lucas & Peres 2006). Moreover, the competition between dye intermediates and RBk5 for SO$_4$$^-$$^2$ became intense because of the high oxidation capability of SO$_4$$^-$$^2$. These factors contributed to such a decreased rate constant with an increase in initial concentration.

**RSM analysis**

Decolorization performance via the Fe$^{2+}$/PS system was dependent on the initial concentration of RBk5 (Figure 4). However, a few studies mentioned optimal dye decolorization at numerous operation concentrations. In this study, the optimal color removal of RBk5 was investigated through RSM. Table 2 summarizes two sets of experimental designs.
Table 2 | Experimental design matrix and response based on experimental runs and predicted values on decolorization rate (DE; %) proposed by CCD design

<table>
<thead>
<tr>
<th>Run</th>
<th>pH (X1)</th>
<th>PS (X2)</th>
<th>Fe2+ (X3)</th>
<th>Y' (0.05 mM)</th>
<th>Y'' (0.10 mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level</td>
<td>Level</td>
<td>Level</td>
<td>Experimental</td>
<td>Predicted</td>
</tr>
<tr>
<td>1</td>
<td>−1</td>
<td>−1</td>
<td>−1</td>
<td>89.86</td>
<td>89.58</td>
</tr>
<tr>
<td>2</td>
<td>−1</td>
<td>−1</td>
<td>+1</td>
<td>87.98</td>
<td>87.51</td>
</tr>
<tr>
<td>3</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>92.86</td>
<td>91.79</td>
</tr>
<tr>
<td>4</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>90.25</td>
<td>89.90</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
<td>88.12</td>
<td>87.26</td>
</tr>
<tr>
<td>6</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>87.72</td>
<td>87.57</td>
</tr>
<tr>
<td>7</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>90.78</td>
<td>90.05</td>
</tr>
<tr>
<td>8</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>91.46</td>
<td>89.99</td>
</tr>
<tr>
<td>9</td>
<td>−1.73</td>
<td>0</td>
<td>0</td>
<td>90.58</td>
<td>90.53</td>
</tr>
<tr>
<td>10</td>
<td>+1.73</td>
<td>0</td>
<td>0</td>
<td>88.84</td>
<td>89.79</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>−1.73</td>
<td>0</td>
<td>87.76</td>
<td>88.19</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>+1.73</td>
<td>0</td>
<td>91.48</td>
<td>92.67</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>−1.73</td>
<td>86.48</td>
<td>87.59</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>+1.73</td>
<td>85.71</td>
<td>86.22</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>92.59</td>
<td>92.53</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>92.34</td>
<td>92.53</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>92.68</td>
<td>92.53</td>
</tr>
</tbody>
</table>

for 0.05 and 0.10 mM RBk5, and the response results of DE for 0.05 and 0.10 mM RBk5 (Y' and Y'', respectively) are discussed. The predicted values were evidently consistent with the experimental data.

A second-order polynomial model (Equation (6)) was fitted according to the 17 experimental sets of data presented in Table 2. The approximating function was obtained in terms of the coded factors, and this function described the DE for 0.05 and 0.10 mM initial RBk5 concentration as indicated in Equations (20) and (21), respectively.

\[
Y' = 92.53 - 0.42 X_1 + 1.29 X_2 - 0.40 X_3 + 0.14 X_1 X_2 + 0.60 X_1 X_3 + 0.044 X_2 X_3 - 0.67 X_1^2 - 0.70 X_2^2 - 1.88 X_3^2 \tag{20}
\]

\[
Y'' = 91.51 + 0.57 X_1 + 1.79 X_2 - 0.89 X_3 + 0.19 X_1 X_2 + 0.76 X_1 X_3 - 0.14 X_2 X_3 - 0.50 X_1^2 - 1.29 X_2^2 - 1.33 X_3^2 \tag{21}
\]

Checking the adequacy of a model is an integral part of overall data analysis because the approximating model functions would yield poor or misleading results if the fit is inadequate (Korbahti 2007). Analysis of variance (ANOVA) results of the established model for DE are shown in Table 3 (DE' and DE'' for 0.05 and 0.10 mM RBk5, respectively). The mean squares were obtained by dividing the sum of the squares of each of the two sources of variation, that is, the model and the error (residual) variance, by the respective degrees of freedom (DF). The model F-value was calculated by dividing the model mean square by the residual mean square.

Values of Prob > F (p value) less than 0.050 imply that the model is statistically significant, whereas values >0.1000 usually imply non-significance. In this case, Prob > F-values of 0.0087 and 0.0149 denote that the DE of the employed models was significant. The model F-values of 7.05 and 5.84 imply that the model was significant (Table 3). Generally, a smaller p value of a parameter implies higher significance in the model (Yetilmezsoy et al. 2009). Obtained p values of the model components indicated that the quadratic effects of each parameter are more significant than the effects of their interactions.

Three-dimensional response surfaces were also provided to investigate the interactive effect of two variables.
on DE as shown in Figure 5(a) and 5(b) for 0.05 and 0.10 mM RBk5, respectively. The maximum predicted value is illustrated as the surface confined in the smallest ellipse in the contour diagram. Elliptical contours were obtained in the case of perfect interaction between the independent variables.

The normal probability plot and internally standardized residuals are shown in the Figure 6(a) and 6(c) for 0.05 mM RBk5 and Figure 6(b) and 6(d) for 0.10 mM RBk5. The normal probability plot is an important diagnostic tool used to detect and describe systematic deviations from assumptions that errors are normally distributed and independent of each other and that error variances are homogeneous (Yetilmezsoy et al. 2009). No serious violations were found in the assumptions underlying the analysis, and the residuals were independent (Figure 6(a) and 6(b)). Further check of model adequacy was performed by correlating the internally studentized residuals against the predicted values (Figure 6(c) and 6(d)). This plot tests the assumption of constant variance that points are randomly scattered, lying within the top and bottom limits for outlier detection. Thus, the developed DE was successful in capturing the correlation between the influencing parameters of the Fe$^{2+}$/S$_2$O$_8^{2-}$ process to predict the degradation of RBk5 model WW.

This model could be obtained using Taylor’s expansion, and the polynomial model may describe the kinetic model in the domain near operation conditions. Here, the function (DE) could be written as follows:

\[
f(X_1, X_2, X_3) = f(X_1 + \delta X_1, X_2 + \delta X_2, X_3 + \delta X_3) \\
\equiv f(X_1, X_2, X_3) + \frac{\partial f}{\partial X_1} |\delta X_1| + \frac{\partial f}{\partial X_2} |\delta X_2| + \frac{\partial f}{\partial X_3} |\delta X_3| \\
+ \frac{\partial^2 f}{\partial X_1 \partial X_2} (\delta X_1)(\delta X_2) + \frac{\partial^2 f}{\partial X_1 \partial X_3} (\delta X_1)(\delta X_3) + \frac{\partial^2 f}{\partial X_2 \partial X_3} (\delta X_2)(\delta X_3) \\
+ \sum_{n=0}^{3} \sum_{i=1}^{n} \sum_{j=1}^{n} O(\delta X_1^n X_2^i X_3^j) \\
\]  

(22)

where $\delta X_1$, $\delta X_2$, and $\delta X_3$ denote the deviations of variables $X_1$, $X_2$, and $X_3$, respectively. Thus, the empirical polynomial model (i.e., contour analysis) could technically describe the system behavior (not just curve-fitting).
According to Equation (22), Equation (6) could be presented as follows:

\[ f(X_1, X_2, X_3) \cong b_0 + \sum b_iX_i + \sum b_{ij}X_i^2 + \sum b_{ij}X_iX_j \]  (23)

The optimum conditions obtained according to the model in Equations (20) and (21) are shown in Table 4. Random experiments were also conducted to test the feasibility of the RSM model, and the results are shown in Table 5. Good agreement was found between the experimental data and predicted results.

Table 4 shows that the optimal conditions of RBk5 decolorization were dependent on concentration of RBk5. Highly acidic conditions were favorable to decolorize 0.05 mM RBk5. However, the optimal decolorization of 0.10 mM RBk5 was performed at relatively high pH level,
where (PS) and (Fe$^{2+}$) were just less than twice the results at 0.05 mM RBk5, indicating that the RBk5 could be more readily and efficiently decolorized at high concentration. That is, more SO$_4^{2-}$ could be consumed by RBk5 when at high RBk5 concentration. Consequently, less SO$_4^{2-}$ was quenched by Fe$^{2+}$ (Jiang et al. 2013). Thus, the degradation and utilization efficiency of PS and Fe$^{2+}$ both increased.

<table>
<thead>
<tr>
<th>(RBk5)</th>
<th>$X_1$</th>
<th>$X_2$ (mM)</th>
<th>$X_3$ (mM)</th>
<th>Predicted</th>
<th>Actual</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 mM</td>
<td>3.72</td>
<td>0.39</td>
<td>0.29</td>
<td>93.19</td>
<td>93.28</td>
<td>-0.25</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>4.55</td>
<td>0.72</td>
<td>0.53</td>
<td>92.43</td>
<td>92.56</td>
<td>-0.80</td>
</tr>
</tbody>
</table>

Table 5 | The random experimental results for the feasibility test of RSM

<table>
<thead>
<tr>
<th>(RBk5)</th>
<th>$X_1$</th>
<th>$X_2$ (mM)</th>
<th>$X_3$ (mM)</th>
<th>Predicted</th>
<th>Actual</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 mM</td>
<td>4.0</td>
<td>0.20</td>
<td>0.20</td>
<td>89.09</td>
<td>88.87</td>
<td>-0.25</td>
</tr>
<tr>
<td>0.05 mM</td>
<td>4.0</td>
<td>0.20</td>
<td>0.30</td>
<td>90.53</td>
<td>87.34</td>
<td>-1.34</td>
</tr>
<tr>
<td>0.05 mM</td>
<td>5.0</td>
<td>0.30</td>
<td>0.40</td>
<td>89.75</td>
<td>88.68</td>
<td>-0.99</td>
</tr>
<tr>
<td>0.05 mM</td>
<td>3.0</td>
<td>0.30</td>
<td>0.20</td>
<td>91.39</td>
<td>90.36</td>
<td>-1.13</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>4.0</td>
<td>0.40</td>
<td>0.20</td>
<td>91.59</td>
<td>91.26</td>
<td>-0.36</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>3.5</td>
<td>0.7</td>
<td>0.5</td>
<td>91.96</td>
<td>92.48</td>
<td>+0.57</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>3</td>
<td>0.60</td>
<td>0.80</td>
<td>87.45</td>
<td>86.54</td>
<td>-1.04</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>4.5</td>
<td>0.50</td>
<td>0.70</td>
<td>89.85</td>
<td>89.28</td>
<td>+0.58</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>5</td>
<td>0.40</td>
<td>0.60</td>
<td>88.32</td>
<td>86.92</td>
<td>-1.59</td>
</tr>
<tr>
<td>0.10 mM</td>
<td>4.0</td>
<td>0.80</td>
<td>0.60</td>
<td>92.00</td>
<td>91.26</td>
<td>+1.00</td>
</tr>
</tbody>
</table>

Figure 6 | Model for DE diagnostic: (a) and (b) the internally studentized residuals and normal % probability plot for DE of 0.05 mM and 0.10 mM RBk5, respectively. (c) and (d) Predicted and plot of studentized residuals for DE of 0.05 mM and 0.10 mM RBk5, respectively.
This finding is of great importance when considering the industrial application to WW decolorization.

Moreover, Yates’s algorithm was applied to consider the main and interactive effects. The effects of 2$^3$ factorial designed are shown in Table 6. The pH level showed a remarkable negative impact on the Fe$^{2+}$/S$_2$O$_8^{2-}$/C$_0$ process. By contrast, the effect of pH level was positive for 0.10 mM RBk5 treatment, suggesting that the treatment of 0.10 mM RBk5 had high efficiency at wider pH ranges. Taking all the parameters into consideration, the best operating conditions were defined as pH 3.72, (PS) = 0.39 mM, and (Fe$^{2+}$) = 0.29 mM, which resulted in the maximum decolorization percentage and possibility for industrial application.

**Biodegradability test**

Considering aquatic ecological security, the toxicity of transformation products should be tested because of possible increased biotoxicity (Duarte et al. 2013). As the results of GC-MS show (Figure S4 and Table S2), the transformation products of the PS process were DL-4-hydroxymandelic acid, benzoic acid, benzene, formic acid, oxalic acid and acetic acid, respectively. Considering the toxicity of benzene, the toxicity of the treated dye solution was monitored by inhibiting the growth of two species (P. hauseri ZMd44 and Shewanella sp. WLP72). The specific growth rates ($\mu$, h$^{-1}$) in the exponential growth phase were calculated using the value of OD$_{600}$. Higher specific growth rates of the microbes indicated lower acute toxicity of the solution. The lowest growth rates of ZMd44 and WLP72 were found in the raw RBk5 solution (Figure 7). The $\mu$ value of ZMd44 and WLP72 under the different degradation conditions are shown in Table 7. The results showed that the microbes grew much better in the degraded solution than in the raw solution, implying that all generated products were less toxic than the original dye during the homogeneous photo-Fenton process (de Luna et al. 2014). Moreover, the biggest $\mu$ indicated that the best operation ratio of PS/Fe$^{2+}$ was 2:1. The COD

<table>
<thead>
<tr>
<th>Estimated effect</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>$X_1X_2$</th>
<th>$X_1X_3$</th>
<th>$X_2X_3$</th>
<th>$X_1X_2X_3$</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE'</td>
<td>-0.7175</td>
<td>2.9175</td>
<td>-1.0525</td>
<td>0.2825</td>
<td>1.1925</td>
<td>0.0875</td>
<td>0.4525</td>
<td>0.6547</td>
</tr>
<tr>
<td>DE''</td>
<td>1.305</td>
<td>2.995</td>
<td>-1.85</td>
<td>0.37</td>
<td>1.525</td>
<td>-0.285</td>
<td>-1.05</td>
<td>0.9548</td>
</tr>
</tbody>
</table>

Figure 7 | The biodegradability of RBk5 decolorization intermediates under different molar ratio of PS/Fe$^{2+}$.

<table>
<thead>
<tr>
<th>(PS)/(Fe$^{2+}$)</th>
<th>Blank</th>
<th>0.5:1</th>
<th>1:1</th>
<th>2:1</th>
<th>4:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZMd44</td>
<td>0.04016</td>
<td>0.04619</td>
<td>0.05052</td>
<td>0.1058</td>
<td>0.06479</td>
</tr>
<tr>
<td>WLP72</td>
<td>0.02766</td>
<td>0.03427</td>
<td>0.03717</td>
<td>0.07037</td>
<td>0.04478</td>
</tr>
</tbody>
</table>
removal rate was also determined after decolorization for further verification. COD removal rates of 38.62%, 63.51%, 72.15%, and 56.47% were achieved when the molar ratios of PS/Fe$^{2+}$ were 0.5:1, 1:1, 2:1, and 4:1, respectively. The toxicity test shows that PS/Fe$^{2+}$ treatment is a suitable method for complete decolorization and detoxification. Moreover, the biodegradation process progressed better at PS/Fe$^{2+}$ molar ratio of 2:1.

**CONCLUSION**

Decolorization of azo dye RBk5 by Fe$^{2+}$-activated PS has been optimized using interactive model-assisted PS. Three variables (i.e., pH, PS concentration, and ferrous concentration) were defined as significant factors for decolorization. However, the decolorization was more favorable at pH 2–7, and the effect of (PS)/(Fe$^{2+}$) was highly significant. The oxidative reaction apparently followed Monod-like kinetic characteristics. The effects of independent variables and their interactions on decolorization percentage of RBk5 were clearly elucidated using the RSM. Comparison of decolorizations of 0.05 and 0.10 mM RBk5 indicated that decolorization could be performed in moderate pH levels under high concentrations of RBk5. The biodegradability test showed that the decolorization intermediates were less toxic than the original dye solution, and the optimal molar ratio of PS/Fe$^{2+}$ for detoxification and mineralization was 2:1.

**ACKNOWLEDGEMENTS**

This work was financially supported by Fujian province Science and Technology project Foundation (2014Y4006), Xiamen Technology project Foundation (3502Z20140057, 3502Z20153025, 3502Z20151256), Quanzhou Technology project Foundation (2016Z074), the Fundamental Research Funds for the Central Universities (ZQN-PY217) and China Postdoctoral Science Foundation (2015M582032).

**REFERENCES**


Kasiri, M. B., Aleboyeh, H. & Aleboyeh, A. 2008 Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous
photo-Fenton catalyst. Applied Catalysis B: Environmental 84, 9–15.


First received 15 November 2016; accepted in revised form 2 June 2017. Available online 16 June 2017.