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Decolorization of Reactive Black 5 from Synthetic Dye Wastewater by Fenton Process

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Abstract

Reactive Black 5 (RB5) is an azo dye commonly used in industries. Its toxicity and non-biodegradability require an effective treatment process. In this study, the oxidation of RB5 wastewater by Fenton process was observed. The experiments were conducted with synthetic RB5 wastewater in a 1-liter batch reactor with a stirrer. The effects of initial ferrous (Fe^{2+}) concentration and pH on RB5 removal were studied. The results showed high removal efficiency (>90%). Increasing the concentration of Fe^{2+} could increase the RB5 decolorization by Fenton process. The decline of of remaining Fe^{2+} let to the genertation hydroxyl radicals (•OH) from hydrogen peroxide (H_2O_2). The initial degradation rate of RB5 decolorization was increased from 0.0023 to 0.0754 mM/min. In contrast, the RB5 decolorization of RB5 was decreased when the pH was increased from 3 to 5. The optimal condition of the RB5 removal was determined as follows: pH 3, 5 mM of H_2O_2, and 0.5 mM of Fe^{2+}. At this condition, the almost complete delorization of RB5 by Fenton process was achieved within 30 minutes.

Keywords: Decolorization; Dye wastewater treatment; Fenton process; Reactive Black 5

1. Introduction

Textile industry is one of the most important export industries of Thailand. The industries use large amount of water and chemicals for finishing and dying processes (Sirianuntapiboon and Srisornsak, 2007). Wastewater from dyeing and finishing factories is a also significant source of environmental pollution due to the fact that colour is usually the first contaminant to be recognized in these wastewaters.

The high strength of colored effluents may become visual eyesores and causes aesthetic pollution, eutrophication and perturbations in aquatic life. In addition, colour-containing dyestuffs have been found to be toxic and carcinogenic to aquatic organisms (Puvaneswari *et al.*, 2006; Gad-Allah *et al.*, 2009; Hassan and Nemr, 2017). Due to their toxicity and

slow degradation, these dyes are classified as environmentally hazardous materials. The release of colored wastewater poses a major problem for the industry as well as a threat to the environment.

Reactive Black 5 (RB), a well-known representative of azo dyes (-N=N-) and also consisted of reactive groups and chromophore groups illustrated in Figure 1, has been commonly used in industries. RB5 is non-biodegradable and persistent compound in aquatic environment, therefore, the purification of RB5 wastewater have to be studied the effective treatment before disposal to environment.

Advanced oxidation processes (AOPs) are an alternative approach that provides the destruction of hazardous organic compounds via hydroxyl radical (•OH), which is a highly reactive oxidant (E^o= 2.8 V) and non-selective oxidant which is capable of destroying a wide range of organic pollutants in water and wastewater (Zoh *et al*., 2002; Titus *et al*., 2004; Farre *et al*., 2006; Saritha *et al*., 2007; Guinea *et al*., 2008; Sun *et al*., 2008). Fenton process is one of the AOPs that uses a mixture of hydrogen peroxide (H_2O_2) and Fe^{2+} to generate •OH. There are several advantages of Fenton process such as a fast reaction of all advanced oxidation processes, Fe^{2+} and H_2O_2 are not expensive and non-poisonous, the process take easily control (Bautista *et al*., 2007).

This technology has been used for detoxification, decolorization, removal of non-biodegradable effluents and treatment of high polluted wastewater from different sources such as cosmetics (Bautista *et al*., 2007), landfill leachate (Zhang *et al*., 2005), textile (Meric

et al., 2004), pharmaceuticals and personal care products (Pi *et al*., 2014). Therefore, the RB5 wastewater could possibly be treated by Fenton process. The aim of this research is to investigate the RB5 oxidation by Fenton process. The important factors affecting the treatment, which are Fe^{2+} concentration and initial pH, were also studied.

2. Meterials and Methods

2.1 Chemicals and materials

Reactive Black 5 was kindly supplied from DyStar Ltd.Co. The structure of RB5 (Commercial name: Remazol Black B, Color Index: 20525, Formular: $C_{26}H_{21}Na_4N_5O_{19}S_6$, Molecular weight: 991.8 g/mol and λ_{max}: 597 nm) was presented in Figure 1. Hydrogen peroxide (H_2O_2, 30% w/w, Merck), ferrous sulfate ($FeSO_4.7H_2O$, Qrec), sulfuric acid (H_2SO_4, Qrec), sodium hydroxide (NaOH, Merck) were used for Fenton experiment. All chemicals used were analytical grade without any further purification. Deionized water was used throughout this study.

2.2 Experimental procedures

The experiments were conducted in a one-liter batch reactor with a magnetic stirrer. The reactor was filled with 50 mg/L of synthetic RB5 wastewater. The initial pH of the solution using a SUNTEX pH meter was adjusted to the desired value by using H_2SO_4 and NaOH. After pH adjustment, $FeSO_4$ at predetermined amount was added as a source of Fe^{2+}. The Fenton reaction was then started by adding H_2O_2 into the reactor. At the time point of 0,
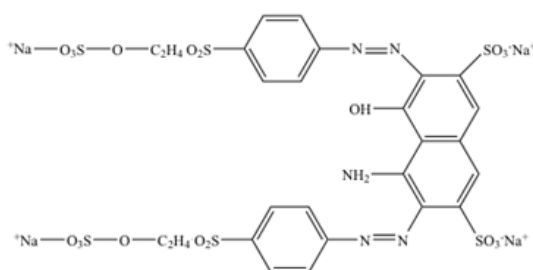

Figure 1. Chemical structure of Reactive Black 5

1, 2, 5, 10, 20, and 30 minutes, 1 ml of sample was taken from the reactor and was immediately injected into 4 ml of 0.01 N NaOH to stop the Fenton reaction.

2.3 Analytical methods

The dye concentration was measured through the absorbance of the sample (λ_{max}= 600) by a spectrophotometer. The standard curve of RB5 was conducted to determine the concentration. The decolorization efficiency (DE) was then defined by the following expression:

$$DE\ (\%) = \frac{(1- C_0)}{C_t} \times 100$$

Where C_0 and C_t are the concentrations at time 0 and t, respectively.

The Fe^{2+} concentration was determined by the phenanthroline method (APHA, 1992). The sample of 1mL was filtrated by using 0.45 µm of cellulose acetate membrane (Verticlean) to remove the precipitates formed. The permeate sample was added with 1,10-phenenthroline agent. Then, the DI water is added to make up the volume to 50 ml before analyzing by the Genesis 20UV-VIS spectrophotometer (λ_{max}= 510 nm). The DI water mixed with sample without phenanthroline is used as a blank for every sample. The concentration was interpolated from a standard curve.

The H_2O_2 concentration was determined by potassium titanium (IV) oxalate agent following the potassium titanium (IV) oxalate method (Eisenberg, 1943; Liu *et al.*, 2007; Sellers, 1980). Then, the sample was analyzed by the Genesis 20UV-VIS spectrophotometer (λ_{max}= 400 nm).

3. Results and Discussion

3.1 Effect of Fe^{2+} concentration

Fenton process showed the feasibility to RB5 decolorization in all of the Fe^{2+} concentrations applied in this study. The decolorization efficiencies of RB5 were not significant difference (61.14-66.54%) after 30 min when the Fe^{2+} concentrations 0.1-

0.5 mM as illustrated in Figure 2a. The RB5 was decolorized due to the the fact that Fe^{2+} plays a very important role in initiating the decomposition of H_2O_2 to generate the •OH in the Fenton process as presented in reactions 1 and 2. According to reaction (1), more Fe^{2+} in the system can react with H_2O_2 and generate more •OH (Andreozzi *et al.*, 1994; Ertugay and Acar, 2013), which then degrades RB5 as in reaction (2) (Ertugay and Acar, 2013).

$$Fe^{2+} + H_2O_2 \ \rightarrow \ Fe^{3+} + \bullet OH \quad (1)$$
$$\bullet OH + organic \rightarrow \ products \qquad (2)$$
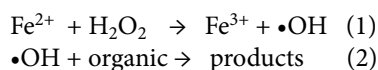
However, adverse effects were observed when excess dose of Fe^{2+}. Increasing the Fe^{2+} concentration from 0.5 mM to 1.0 mM, the decolorization of RB5 was decreased from 66.43% to 61.14% due to the •OH scavenging effect of Fe^{2+} which consumed the •OH as shown in the reaction 3 (Behnajady *et al.*, 2007; (Babuponnusami and Muthukumar, 2014).

$$Fe^{2+} + \bullet OH \ \rightarrow \ Fe^{3+} + \ OH- \quad (3)$$
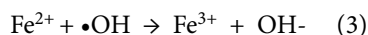
The quick decolorization of RB5 within 5 minutes could be explained from the high generation rate of •OH (Lu *et al.*, 2005). The increase in the RB5 decolorization, the initial rate decolorization can be explained by the rate constant of reaction (1) being 63 $M^{-1}s^{-1}$, while that for reaction (3) is only 0.01 $M^{-1}s^{-1}$ (Kang *et al.*, 2002). This means that ferrous ions are consumed faster than they are produced. Accordingly, increase in the initial Fe^{2+} concentration promoted the hydroxyl radical generation through the reaction (1) and enhanced the RB5 decolorization. In this process, $Fe^{2\pm}$ in RB5 wastewater is present during all the oxidation time illustrated in Figure 2b.

This was likely because of the remaining of Fe^{2+} after Fenton oxidation. At 0.1 mM Fe^{2+} concentration, Fe^{2+} was consumed slowly because the rate of decolorizaton was slow that presented the lowest Fe^{2+} remaining in the system. On the other hand, 0.25 and 0.5 mM Fe^{2+} concentrations were reacted quickly due to the higher removal rate of RB5. Consequently,
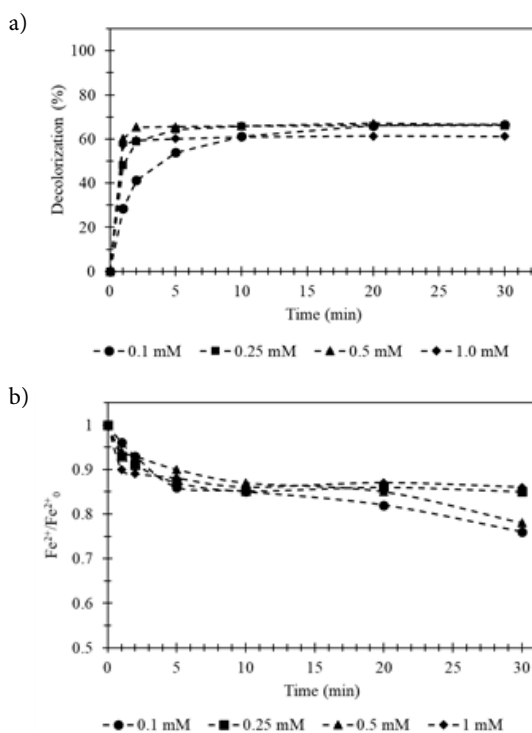
a)

b)

Figure 2. a) Effect of initial Fe^{2+} concentration on the decolorization of RB5 at 100 mg/l of RB5, 5 mM of H_2O_2 and pH 3, b) Trend of Fe^{2+} presence in the experiments

Table 1. Initial rate constant and efficiency of RB5 decolorization when the increasing initial Fe^{2+} concentration; [RB5] = 100 mg/l, [H_2O_2] = 5 mM, pH = 3

Fe^{2+} (mM)	Initial degradation rate (mM/min)	RB5 decolorization (%)
0.1	0.0037	66.54
0.25	0.0080	65.98
0.5	0.0098	66.43
1.0	0.0086	61.14

0.5 mM of Fe^{2+} concentration was sufficient in most cases because at exceeding Fe^{2+} (1.0 mM of Fe^{2+}), not only it has a higher cost of reagent but also the higher disposal costs for adding the subsequent treatment needed to remove the residual iron concentration.

Moreover, the initial rate of RB5 decolorization at different Fe^{2+} concentration also showed that the highest rate of 0.0098 mM/min was achieved as shown in Table 1. At the Fe^{2+} concentrations 0.1 mM to 1.0 mM, the initial rates were 0.0037, 0.0080, 0.0098,

and 0.0086 mM/min, respectively. Therefore, an initial Fe^{2+} concentration of 0.5 mM was applied to study further because the highest RB5 decolorization and initial rate decolorizaiton were achieved.

3.2 Effect of initial H_2O_2 concentraiton

Hydrogen peroxide plays an important role of an oxidizing agent in the Fenton process. As shown in the Figure 3, increasing initial concentration of H_2O_2 from 2.5 mM to 20 mM could promote the decolorization of RB5. The RB5 decolorization was 34.75% when the H_2O_2
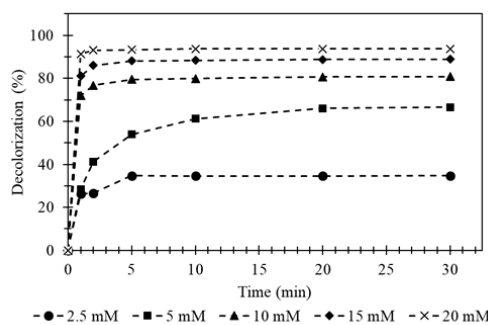
Figure 3. Effect of initial H_2O_2 concentration on the decolorization of RB5 at 100 mg/l of RB5, 0.5 mM of Fe^{2+} and pH 3

Table 2. Initial rate constant and efficiency of RB5 decolorization when the increasing initial H_2O_2 concentration; [RB5] = 100 mg/l, [Fe^{2+}] = 0.5 mM, pH = 3

H_2O_2 (mM)	Initial degradation rate (mM/min)	RB5 decolorization (%)
2.5	0.0023	34.75
5	0.0098	66.43
10	0.0193	80.86
15	0.0363	88.95
20	0.0754	93.67

was 2.5 mM. When using the an initial H_2O_2 concentraiton of 15 mM to 20 mM, the RB5 decolorization was achieved higher than 90%, as shown in Figure 3.

Similar result with Hassan and Hameed (2011) that the decolorization of RB4 increased from 80% to 96% with increase of H_2O_2 dosage from 4 mM to 8 mM. The RB5 decolorization efficiency of almost 100% was observed when 20 mM of H_2O_2 was used. This was due to the presence of excess H_2O_2 available for the production of hydroxyl radicals. The results were similar with the removal of Bisphenol A by microwaveenhanced Mn-Fenton process. The results found that the exceeded H_2O_2 present as a scavenger of •OH. As a result, there were insufficient •OH generated to degrade bisphenol A and had a negative effect on the degradation of bisphenol A (Li *et al.*, 2016). Therefore, it can be state that the RB5 decolorization increased with increase the concentration of H_2O_2.

Moreover, the initial rate of RB5 decolorization at different H_2O_2 concentration also showed that the highest rate of 0.0754 mM/

min was achieved as shown in Table 2.

At the H_2O_2 concentrations 2.5 mM to 15 mM, the initial degradation rates were 0.0023, 0.0098, 0.0193, and 0.0363 mM/min, respectively.

3.3 Effect of initial pH on RB5 removal

The removal of RB5 decreased with increasing the pH from 3 to 5 as shown in Figure 4. When the pH was 2, the RB5 decolorizatiojn efficiency was 59.84%. The decolorizationof RB5 increased as pH increased to 3. In contrast, the RB5 decolorizations were decreased from 66.43%, 60.00% and 55.95% when pH increased from 3 to 5. At higher initial pH, the iron is precipitated as iron hydroxide during the Fenton reaction, leading to the inhibition of the reaction between Fe^{2+} and H_2O_2. Nurbus and Kutukcuoglu (2015) reported that the Acid Red 88 removal decreased from 99.4% to 79% in 60 minutes when pH was increased from 2 to 4. The highest removal of RB5 was achieved after 30 min of reaction time at pH 3. The results were similar with the treatment of cosmetic
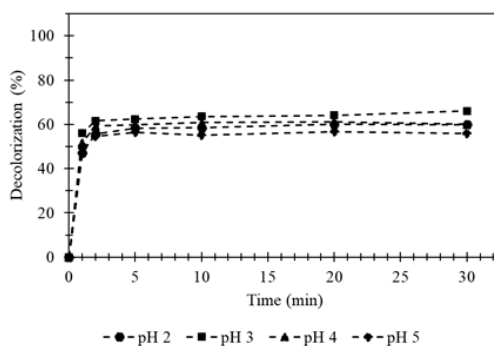
Figure 4. Effect of initial pH on the removal of RB5 using 50 mg/l of RB5, 5 mM of H_2O_2, and 0.1 mM of Fe^{2+}

Table 3. Initial rate constant and efficiency of RB5 decolorization at different initial pH; [RB5] = 100 mg/l, $[Fe^{2+}]$ = 0.5 mM, $[H_2O_2]$ = 5 mM

pH	Initial degradation rate (mM/min)	RB5 decolorization (%)
2	0.0074	59.84
3	0.0098	66.43
4	0.0090	60.00
5	0.0075	55.95

wastewaters by Fenton oxidation (Bautista *et al.*, 2007) which it achieved 60% TOC removal at pH 3.0. In addition, 58.1% COD removal and 78.3% decolorization were obtained at pH 3 in the decolorization of municipal landfill leachate by Fenton process (Mohajeri *et al.*, 2010).

Moreover, the initial RB5 decolorization at different initial pHs also showed that at the optimum pH (pH 3) the highest initial rate of 0.0098 mM/min was achieved shown in Table 3. At pHs 2 to 5, the initial rates were 0.0074, 0.0098, 0.0090, and 0.0075 mM/min, respectively.

4. Conclusions

The Fenton process was an effective method for RB5 removal. The results revealed pH value and initial concentrations of Fe^{2+} and H_2O_2 are the important parameters to the decolorization of RB5. Increasing the concentration of Fenton's reagents can increase the RB5 decolorization by Fenton process. In contrast, the RB5 decolorization of RB5 was decreased when increasing the pH

from 3 to 5. The optimum condition for the decolorization of dye wastewater containing RB5 was determined as follows: pH 3, 5 mM of H_2O_2, and 0.5 mM of Fe^{2+}. At this condition, the complete delorization of RB5 by Fenton process was achieved under 30 minutes.

Acknowledgements

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