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**ชื่อโครงการ** Decolorization of dye wastewater containing Reactive Red 239 by Fenton process

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### บทคัดย่อ

งานวิจัยชิ้นนี้มีวัตถุประสงค์เพื่อศึกษาหาสภาวะที่เหมาะสมต่อการลดความเข้มข้นของสีของสีของรีแอคทีฟเรด 239 (RR239) ในสารละลายน้ำโดยใช้กระบวนการเฟนตัน โดยมีปัจจัยที่มีอิทธิพลต่อความสามารถในการลดความเข้มข้นที่ต้องการศึกษา ได้แก่ ความเป็นกรด-ด่าง, ความเข้มข้นเริ่มต้นของเหล็กและความเข้มข้นเริ่มต้นของไฮโดรเจนเปอร์ออกไซด์ ผลการศึกษาพบว่า สภาวะที่เหมาะสมในการลดความเข้มข้น RR239 ที่มีความเข้มข้นเริ่มต้น 100 มิลลิกรัม/ลิตร ณ อุณหภูมิห้อง คือ ความเป็นกรด-ด่างเริ่มต้น เท่ากับ 3 ความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์และเหล็กเริ่มต้น เท่ากับ 2.7 และ 0.25 มิลลิโมลาร์ ตามลำดับ ภายใต้สภาวะที่เหมาะสมนี้ ประสิทธิภาพการลดความเข้มข้นของกระบวนการเฟนตัน สูงถึง 96.9% หลังจากทำปฏิกิริยา 30 นาที

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### **Abstract**

The main objective of this work was to study the decolorization of the azo dye Reactive Red 239 (RR239) in aqueous solution using Fenton process. Effects of various experimental parameters of the oxidation reaction of the dye were investigated. The parameters studied were the initial pH, the initial concentrations of ferrous ( $\text{Fe}^{2+}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The results showed that the optimal condition was experimentally determined and it was found to be initial pH was 3, initial  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentration were 2.7 mM and 0.25 mM, respectively, for initial dye concentration was 100 mg/L at temperature room. Under optimal conditions, 96.9% degradation efficiency of dye in aqueous solution was achieved after 30 min of reaction.

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## Chapter I

### Introduction

Water contaminating by industrial discharging of toxic chemicals has been a worldwide concern. Synthetic dyes are a major category of contaminants, which have been broadly employed in the textile industry (Benkhaya *et al.*, 2020; Lellis *et al.*, 2019). Approximately 80% of all reactive dyes are based on azo chromogen (Su *et al.*, 2011). Characteristics of azo dye such as Reactive Red 239 is consisted of nitrogen double bonds together with other chromophores to responsible for the color (Idel-aouad *et al.*, 2011). These dye-containing wastewater generally are constitute of high COD concentration, dark color, high concentration of organic substances along with strong acidity. The ratio of BOD to COD is generally very low and it can be harmful to aquatic ecosystems and potentially disturb aquatic biological processes because they hinder light penetration due to their ability to block and/or absorb sunlight (Berradi *et al.*, 2019; Tkaczyk *et al.*, 2020). Furthermore, synthetic dye-based materials can be highly toxic (Liang *et al.*, 2018), mutagenic (Brüschweiler & Merlot, 2017), allergenic (Brüschweiler & Merlot, 2017) and carcinogenic (Cox & White, 2019). These issues are further complicated by the high-water solubility of dyes, thus making synthetic dye materials a commonly encountered contaminants that can be toxic even at small concentrations (Liang *et al.*, 2018).

Traditionally, the treatment of solutions containing soluble dyes is performed by biochemical and coagulation processes. All these methods are either costly, inefficient or result in the production of secondary toxic waste products (Schrank *et al.*, 2007, Chanderia *et al.*, 2017). Recently, Advanced Oxidation Processes (AOPs) have been reported as efficient procedures for obtaining high oxidation yields from several kinds of organic compounds. These

methods are based on the generation of very reactive agents such as hydroxyl radicals ( $\cdot\text{OH}$ ) that are extremely reactive ( $E^0 = 2.80 \text{ V|SHE at pH 0}$ ) and strong oxidizing agent, capable of mineralizing organic pollutants. (El Malah *et al.*, 2021). AOPs may be classified broadly into three groups: photocatalytic process ( $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{UV}/\text{TiO}_2$ ,  $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$ ,  $\text{O}_3/\text{TiO}_2/\text{UV}$ ); the Fenton reaction-based processes ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ , Electro-Fenton), and ozone-based processes ( $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{Fe}^{2+}$ ,  $\text{O}_3/\text{metal oxide catalyst}$ ,  $\text{O}_3/\text{activated carbon}$ ,  $\text{O}_3/\text{ultrasound}$ ) (Yan *et al.*, 2021). Fenton process is a kind of AOPs that is widely used for wastewater treatment because it is very effective for the removal of many hazardous organic pollutants from water based on an electron transfer between  $\text{H}_2\text{O}_2$  and iron ( $\text{Fe}^{2+}$ ).  $\text{H}_2\text{O}_2$  acts as an oxidizing agent and  $\text{Fe}^{2+}$  as a catalytic agent to produce  $\cdot\text{OH}$ . The main advantage of this processes is the complete destruction of contaminants to harmless compounds (Rozendal *et al.*, 2009).

During the Fenton reaction,  $\text{H}_2\text{O}_2$  rapidly decomposes into  $\cdot\text{OH}$ , which are highly reactive and can act as an oxidant in subsequent reactions. Fenton's reagent has the capacity to completely decolorize and partially mineralize textile industry dyes in short reaction time. There were several studies that have been reported on the treatment of swine effluent by Fenton process. Zhang *et al.* (2005) reported that Fenton's reagent can effectively degrade leachate organics. Fenton process was so fast that it was complete in 30 min. The oxidation of organic materials in the leachate was pH dependent and the optimal pH was 2.5. The favorable  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  molar ratio was 1.5, and organic removal increased as dosage increased at the favorable  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  molar ratio (Zhang *et al.*, 2005). Papadopoulos *et al.* (2008) also found that chemical oxidation of leachate (initial COD range of 6500–8900 mg/L) with Fenton's reagent (100 ml, 30%, w/w  $\text{H}_2\text{O}_2$  and 40 mg  $\text{Fe}^{2+}$  mg/L) after aerobic biological treatment and observed up to

33% COD reduction ( Papadopoulos *et al.*, 2008 ). Hui *et al.* (2009) reported the optimal conditions for the decolorization of Direct Blue 15 (DB15) were determined as pH = 4.0, initial H<sub>2</sub>O<sub>2</sub> concentration ([H<sub>2</sub>O<sub>2</sub>]) =  $2.8 \times 10^{-3}$  mol/L, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio = 100:1, H<sub>2</sub>O<sub>2</sub>/dye ratio = 60:1 and temperature = 30 °C. Under the optimal conditions,  $4.7 \times 10^{-5}$  mol/L of the DB15 aqueous solution can be completely decolorized by Fenton oxidation within 50 min reaction time and the decolorization kinetic rate constant  $k$  was determined as 0.1694 min<sup>-1</sup> (Hui *et al.*, 2009). Moreover, Bouasla *et al.* (2010) reported that efficiency of degradation methyl violet 6B obtained after 60 min of reaction, was about 97.6%. The optimal parameters were: initial pH = 3; [H<sub>2</sub>O<sub>2</sub>] = 2.1 mM; initial Fe<sup>2+</sup> concentration ([Fe<sup>2+</sup>]) = 0.06 mM; for a initial concentration of dye ([dye]) = 0.06 mM; temperature = 30 °C. (Bouasla *et al.*, 2010).

Due to several studies that mentioned above, Fenton process is an interesting method to apply for decolorization of azo dye in wastewater at different conditions. Reactive Red 239 (RR239) is used in the textile industry for dyeing of cotton and polyester fabrics. There were several studies that have been reported on the treatment of RR239 by several methods. Banaei *et al.* (2018) recently reported that RR239 could be decolorized by using batch adsorption procedure that synthesized from 2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde-modified magnetic chitosan nanoparticles (Fe<sub>3</sub>O<sub>4</sub> @CS-BAL). The experimental results showed that the Fe<sub>3</sub>O<sub>4</sub>@CS-BAL could be remove more than 99% of investigated dye within the first 2 min of contact time (Banaei *et al.*, 2018). Although Liu & Chiou (2005) reported the optimal decolorization efficiency of RR239 by UV/TiO<sub>2</sub> photocatalytic process coupled with response surface methodology and the results showed that under the optimum condition, the maximal decolorization efficiency of 99.82% was achieved (Liu & Chiou, 2005), the decolorization of RR239 wastewater by Fenton oxidation has not been reported (Günes *et al.*, 2012). Therefore,

the aim of the present study is to investigate the feasibility of the decolorization of RR239 in aqueous solution by using the Fenton oxidation process.

## **1.2 Objectives**

To investigate the optimal condition for decolorization of dye wastewater containing Reactive Red 239 by Fenton process.

## Chapter II

### Literature Review

#### 2.1 Dye wastewater

Nowadays, the water resource is getting worse due to the arbitrary releasing of effluent from chemical enterprises. Various organic dyes commonly exist in the industrial effluent as the dominant pollutants. These organic dyes, being toxic and carcinogenic, are hard to be self-decomposed in nature due to their high chemical stability. Some reactive dyes were toxic, carcinogenic, mutagenic and obviously colored even at low concentration, threatening ecology and public health.(Lellis *et al.*, 2019) More than 10,000 different textile dyes are currently in use, and the estimated annual production of dyes is close to 800,000 tons (Ayadi *et al.*, 2016). These organic chemicals are usually classified as azo, anthraquinone, vat, phtalocyanine, indigo, polymethylene, carbonium and nitro dyes.(Lucas *et al.*, 2007)

#### 2.2 Azo dye

Amongst the 10,000 different types of dyes and pigments, azo dyes constitute over 50% of all textile dyes used in the industry (Liu & Chiou, 2005). Azo dyes are characterized by nitrogen-to-nitrogen double bonds ( $\text{—N}=\text{N—}$ ), superior fastness to the applied fabric and high photolytic stability. Due to the stability of modern dyes and the large degree of aromatics present in dye molecules, conventional biological treatment methods are ineffective for decoloring such wastewaters. The intermediates generated from the degradation of azo dye are toxic, carcinogenic, and mutagenic (Gu *et al.*, 2021), which can be harmful to both nature and human health. Till date, azo dye wastewater has been considered to be one of the most difficult types of dye wastewater to treat (Krishnamoorthy *et al.*, 2018).

Reactive Red 239 (RR239) is one of azo dye which is a well known mono-azo dye and has been widely used in the dyeing process of textiles industry. (Liu and Chiou, 2005) In addition, the properties of RR239 was show in Table 2.1

Table 2.1 Properties of Reactive Red 239

Generic name	Reactive Red 239
Abbreviation	RR239
Molecular formation	$C_{31}H_{24}ClN_7O_{19}S_6$
Molecular mass (g/mol)	1,026.4
$\lambda_{max}$ (nm)	542
IUPAC Name	5-[[6-chloro-4-[4-(2-sulfooxyethylsulfonyl)anilino]-1H-1,3,5-triazin-2-ylidene]amino]-3-[(1,5-disulfonaphthalen-2-yl)diazenyl]-4-hydroxynaphthalene-2,7-disulfonic acid
Molecular structure	

### 2.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are powerful methods that were traditionally used for treatment of hazardous materials. (M' Arimi *et al.*, 2020) This process are methods of treating

substrates by oxidation with radicals produced from the reactions as the driving force. The generation and utilization of hydroxyl radicals for oxidation is the common feature in all AOPs.

AOPs are classified into different types, including photocatalytic oxidation, Fenton or Fenton-like processes (Gode *et al.*, 2019), electrochemical oxidation (Nie *et al.*, 2016), and persulfate-based AOPs (Han *et al.*, 2020). Traditionally, AOPs have been applied in the treatment of water and wastewater (M'Arimi *et al.*, 2020) because these method have many advantages. For example, the reagents were cheap, high efficiency to degrade pollutants and environmental friendly. AOPs are based on the intrinsic ability of  $\cdot\text{OH}$  with redox potential of 2.8 V (Moradi *et al.*, 2020a) generated in the case of the Fenton processes, by specific chemical reactions in aqueous solution, to promote rapid and non-selective oxidation of organic molecules, thereby promoting their degradation.  $\cdot\text{OH}$  are powerful oxidation agents that have an oxidation potential only lower than fluorine and higher than ozone as shown in Table 2.2

Table 2.2 Electro-chemical oxidation potential of some oxidizing agents

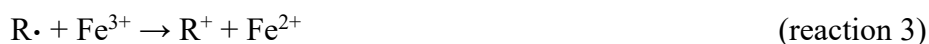
Oxidation species	Oxidizing potential (V)
$\text{F}_2$	3.03
$\cdot\text{OH}$	2.08
$\cdot\text{O}$	2.42
$\text{O}_3$	2.07
$\text{H}_2\text{O}_2$	1.78
$\cdot\text{O}_2\text{H}$	1.70
$\text{Cl}_2$	1.36

## 2.4 Fenton Process

Fenton process is a preferred option among AOPs due to their cost effectiveness and higher reaction efficiencies (Wang *et al.*, 2018), involving  $\text{H}_2\text{O}_2$  and an iron source, which are responsible for the peroxide activation (reaction 1) at low pH (2–4), needing no energy input for these purpose and occurring at room temperature and pressure (Domingues *et al.*, 2021).



Then,  $\cdot\text{OH}$  are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of these compounds by H-abstraction and addition to C–C unsaturated bonds (Lucas & Peres, 2006). The reactions are as follows :



Reactions 5-7 shown other rate-limiting steps for  $\text{Fe}^{2+}$  regeneration and hydroxyl radical production. Over dose of ferrous ions could scavenge the produced radical species.(Cai *et al.*, 2021) Then, the radical species could react with ferric ions ( $\text{Fe}^{3+}$ ) for additional ferrous ion regeneration as showed in reaction 7.



Reactions 8-10 summarize the other radical scavenging effect that could occur during the Fenton reaction (Mahtab *et al.*, 2021). The scavenging nature of  $\text{H}_2\text{O}_2$  towards  $\cdot\text{OH}$  when it is



present in higher concentration. This reaction produces  $\cdot\text{O}_2\text{H}$  which are significantly less reactive than  $\cdot\text{OH}$  (reaction 8-9). The produced  $\cdot\text{O}_2\text{H}$  reacts rapidly with the  $\cdot\text{OH}$  (Dükkanci et al., 2014).



In addition, the whole Fenton process involves a complex reaction mechanism as presented in the following reactions. Summarized from literature reviews. (Lucas & Peres, 2006; Khan *et al.*, 2015; Cai *et al.*, 2021)

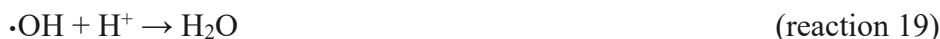


Due to the cost of hydrogen peroxide and ferrous ion, it necessary to find the optimum dosage of each parameter to manage the cost of wastewater treatment by Fenton oxidation process. (Vallejo *et al.*, 2014)

#### 2.4.1 Effect of the initial pH on Fenton process

Solution pH is an important factor in Fenton process. The optimal pH values obtained are within the range commonly found for the Fenton's process, which usually falls in acidic values of

pH between 3 and 4 (Sun *et al.*, 2009). Then, the decolorization efficiency decreases as the pH decreases due to the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  is seriously affected causing the reduction in  $\cdot\text{OH}$  production. Inhibition of radical  $\cdot\text{OH}$  formation at pH below 3 seems also to be because the small amount of soluble iron ( $\text{Fe}^{3+}$ ), responsible for the continuity of the oxidation process, occurring in the formation of  $\text{Fe}(\text{OH})^{2+}$  and  $\text{Fe}(\text{OH})_2^+$  (Sun *et al.*, 2007). The low decolorization at pH 1 and 2 is also due to the hydroxyl radical scavenging of  $\text{H}^+$  ions (Lucas & Peres, 2006) as showed in reaction 18 and 19.



Moreover, at higher pH, tends to decrease the color removal efficiency primarily because of the formation of  $\text{Fe}^{3+}$  complexes which precipitate between the pH range of 6–10. Another reason might be scavenging of  $\cdot\text{OH}$  radicals by alkalinity ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) and decomposition of  $\text{H}_2\text{O}_2$  (Mahtab *et al.*, 2021).

#### 2.4.2 Effect of the initial $\text{H}_2\text{O}_2$ concentration on Fenton process

$\text{H}_2\text{O}_2$  is one of the most important chemical oxidation reagents, widely using in various environmental and biological processes. The activation of  $\text{H}_2\text{O}_2$  can generate reactive oxygen species of  $\cdot\text{OH}$  in Fenton process.  $\cdot\text{OH}$  are generally dominant oxidants for degradation of the pollutants (Chu *et al.*, 2020). Due to the high redox potential of  $\cdot\text{OH}$ , it can decolorize azo dyes via electron transfer, hydrogen abstraction and addition to the azo bond ( $-\text{N}=\text{N}-$ ) (Zhang *et al.*, 2018). Additionally, it has been found that the oxidative decolorization of azo dyes by  $\cdot\text{OH}$  depends on their chemical structures. Sun *et al.* (2009) had reported that the decolorization of OG was initiated by the breakdown of  $-\text{N}=\text{N}-$  bond because of the attack by  $\cdot\text{OH}$  that generated

in Fenton system. Özcan *et al.* (2009) reported that the decolorization of AO7 can be attributed to the cleavage of  $-N=N-$  bond by  $\bullet OH$  in the electro-Fenton technology. Moreover, in the study reported by Lucas *et al.*, the decolorization of RB5 in the process of the activation of  $H_2O_2$  by Fenton and photo-Fenton systems was also supposed to be the breakdown of  $-N=N-$  bond by the generated  $\bullet OH$  (Lucas *et al.*, 2006). Consequently, in the present work, it can be concluded that  $\bullet OH$  is sensitive for the cleavage of  $-N=N-$  bond, which is also mainly responsible for the decolorization of dye wastewater in Fenton system.

However, an unnecessarily high concentration of  $\bullet OH$  (if  $H_2O_2$  is added in excess) can cause unproductive reactions (reaction 8-9) downgrading process performance (Tokumura *et al.*, 2011).

#### **2.4.3. Effect of the initial $Fe^{2+}$ concentration on Fenton process**

The role of the catalyst ( $Fe^{2+}$ ) is indeed important to start the Fenton process (Mahtab *et al.*, 2021). The concentration of these ions is crucial in any Fenton system. Kang *et al.* (2002) have observed that OM oxidization may be limited due to the rapid consumption of  $Fe^{2+}$  during the initial phase of the reaction. Usually, by increasing the dosage of  $Fe^{2+}$ , the degradation efficiency of the pollutants increases. However, the excessive  $Fe^{2+}$  not only increases the operational costs and iron sludge production but also enhances the scavenging effect of  $\bullet OH$  by  $Fe^{2+}$  as shown in reaction 5 (Mahtab *et al.*, 2021). Several studies have been reported in favor of a low dosage of  $Fe^{2+}$  (Zhang *et al.*, 2019; Ferrentino *et al.*, 2020). Furthermore, by applying a low dosage of  $Fe^{2+}$  the residual iron will be lesser in the effluent hence no further treatment is required. Hence, the suitable dosage of  $Fe^{2+}$  is a must for the high treatment efficiency, low

treatment cost, and less sludge production for the overall improvement of the process (Mahtab *et al.*, 2021).

## Chapter III

### Methodology

#### 3.1 Chemicals and Materials

The Reactive Red 239 was kindly supported by Dystar Thai Ltd. Fenton's reagents were ferrous sulfate acid ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Qrec) and 30% (w/w) hydrogen peroxide ( $\text{H}_2\text{O}_2$ , Merck). The pH of the solution was adjusted with sodium hydroxide (NaOH, Merck) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , Qrec). DI water was used as solvent for chemical preparation. Potassium titanium oxalate ( $\text{C}_2\text{K}_2\text{O}_{12}\text{Ti}$ , Sigma Aldrich) was used to analysis  $\text{H}_2\text{O}_2$  concentration. 1,10-phenanthroline monohydrate ( $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ , Merck), ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , Merck) and hydrochloric acid (HCl, Qrec) were used to analyzed  $\text{Fe}^{2+}$  concentration.

#### 3.2 Experimental design

A 1000 ml of RR239 wastewater was added to the 1000 ml capacity beaker for Fenton experiment. The dye solution was completely mixed by magnetic stirrer (Sturt) under room temperature and controlled pH by pH meter (UB-10) as depicted in Figures 3.1.

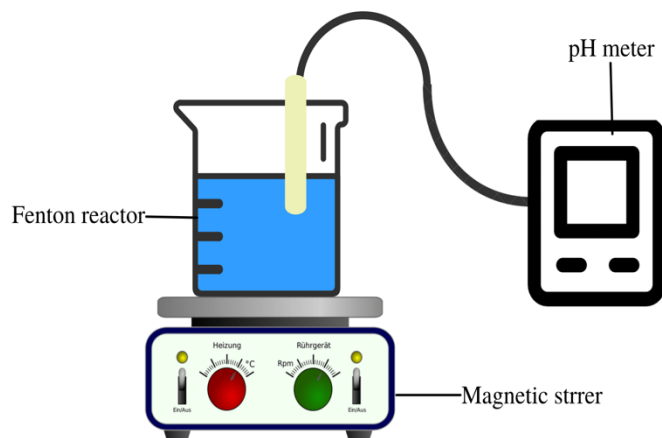


Figure 3.1 Fenton reactor

### 3.3 Experimental procedures

Synthetic RR239 dye wastewater was prepared by dissolved 0.1 g of RR239 with 1,000 ml of deionization water (DI) into the 1L capacity beaker and the mixed by magnetic stirrer under room temperature. The initial pH of the solution was measured by a pH meter. NaOH and H<sub>2</sub>SO<sub>4</sub> were used to adjust the initial to pH 3,4 and 5. After the pH reading stabilized, the ferrous was added. Then, the sample was taken at 0 min. The reaction was started after the addition of H<sub>2</sub>O<sub>2</sub> into RR239 solution. The sample was taken out of beaker at 1,2,5,10,20 and 30 minutes to analyze the RR239 concentration Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> remaining. The conditions investigated in this study are given in Table 3.1. 1 ml of sample was taken and stopped reaction in 4 ml of 0.1 N NaOH to analyze RR239. 1 ml of sample was taken and analyzed H<sub>2</sub>O<sub>2</sub> by the titanium oxalate method with a maximum wavelength 400 nm and 1 ml of sample was taken and filtrated through 0.45 μm syringe membrane filter to determine Fe<sup>2+</sup> concentration using a 1,10-phenanthroline colorimetric method as presented in Figure 3.2.

### 3.4 Analytical methods

#### 3.4.1 Dye concentration

1 ml of Dye sample was taken out of beaker then, mixed with 0.1 N NaOH for stoped the reaction. Dye concentrations were analyzed by visible spectrophotometer (Specter sc brand). The maximum absorbance wavelength ( $\lambda_{\max}$ ) of RR239 is 542. (Banaei *et al.*, 2018; dos Santos *et al.*, 2018). Therefore, the concentration of azo dyes in water was determined by the absorption intensity at  $\lambda_{\max}$ . Standard curve was plotted by using standard dyes with known concentration to determine the dye concentration. The decolorization efficiency (%) of dye contaminated was defined as follow equation :

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (\text{equation 3.1})$$

where  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium concentrations of dyes.

*Table 3.1 the condition investigated in this study*

Run no.	pH	[H <sub>2</sub> O <sub>2</sub> ] (mM)	[Fe <sup>2+</sup> ] (mM)	[RR239] (mg/L)	[RR239] (mM)
1	3	2.7	0.25	100	0.097
2	4	1.4	0.25	100	0.097
3	4	2.7	0.25	100	0.097
4	4	5	0.25	100	0.097
5	4	5	0.065	100	0.097
6	4	5	0.13	100	0.097
7	4	5	0.25	100	0.097
8	4	5	0.5	100	0.097
9	5	2.7	0.25	100	0.097

### 3.4.2 Ferrous (Fe<sup>2+</sup>) concentration

The concentration of ferrous ions (Fe<sup>2+</sup>) was analyzed by phenanthroline method using a visible spectrophotometer with maximum absorbance wavelength 510 nm (Zhang *et al.*, 2018). Preparation of standard curve by using standard ferrous solution with known concentration to determine the Fe<sup>2+</sup> concentration.

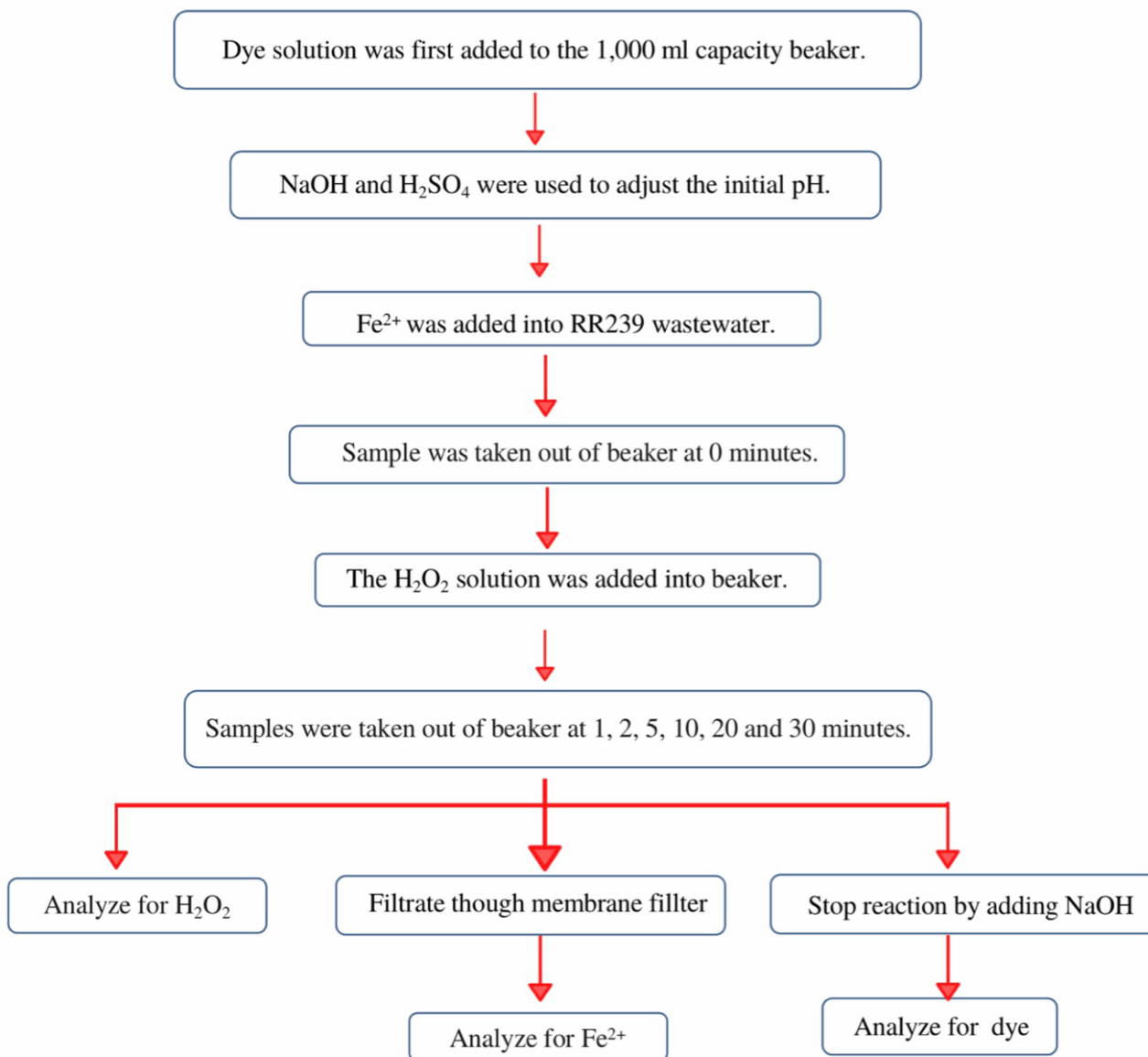


Figure 3.2 The step experiment of Fenton process for treatment of dye wastewater.

### 3.4.3 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentration

The H<sub>2</sub>O<sub>2</sub> concentration was analyzed using potassium titanium oxalate as reactants and using visible spectrophotometer at wavelength 400 nm. Preparation of standard curve by using standard H<sub>2</sub>O<sub>2</sub> with known concentration to determine the hydrogen peroxide concentration.



## Chapter IV

### Results and Discussion

#### 4.1 Effect of the initial pH

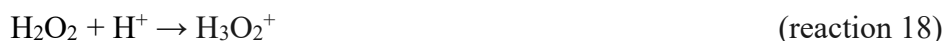
The pH of the solution is an important factor for wastewater treatment by Fenton process (Sun *et al.*, 2009). In order to find the optimal pH of reaction mixture for the degradation of RR239 in Fenton oxidation, a series of experiments were conducted at different pH values of 3, 4 and 5 at 0.25 of Fe<sup>2+</sup> and 2.7 mM of H<sub>2</sub>O<sub>2</sub> at room temperature for 30 min. The results are illustrated in Figure 4.1a. The results indicated that extent of decolorization decreases with increase in pH after pH 3 (96.9%) which was higher than those at pH 4 and pH 5 with 94.6% and 92.2%, respectively, after 30 min.

As showed in Figure 4.1a, at 0-2 min, the RR239 was decolorized very fast by Fenton process because Fe<sup>2+</sup> reacts with H<sub>2</sub>O<sub>2</sub> quickly to produced  $\cdot\text{OH}$ . Then, the produced  $\cdot\text{OH}$  will attack organic molecules (RH) through proton abstraction and produce highly reactive organic radicals (R $\cdot$ ) (Walling and Kato, 1971), which could be further oxidized to CO<sub>2</sub>.



The degradation efficiencies were 75.5%, 81.5% and 75.2 at pH 3,4 and 5 respectively, after the 2 min and then slowed down as the time goes on. This is due to the fact that with constant H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentration more H<sub>2</sub>O<sub>2</sub> was consumed in the first 2 min because of a higher RR239 concentration. After 2 min, the amount of RR239 was smaller and the degradation of RR239 slowed down significantly.

Many studies have revealed that the optimal solution pH values for Fenton process at range 3–4 (Gomathi Devi *et al.*, 2009). Bai *et al* (2017) reported that at lower pH (below 3), the reaction according to reaction 18 and 19 could be slow down that rate of reaction because  $\cdot\text{OH}$  was scavenged by Hydronium ion and proton ( $\text{H}^+$ ) in solution could be react with  $\text{H}_2\text{O}_2$  to formed oxonium ( $\text{H}_3\text{O}_2^+$ ) which cannot react with  $\text{Fe}^{2+}$  to produce  $\cdot\text{OH}$  and reduced efficiency of  $\text{H}_2\text{O}_2$  (Vallejo *et al.*, 2014).



Moreover Figure 4.1b shows that when pH was increased from 3 to 5, RR239 decolonization efficiency was decreased from 96.9% to 92.2%. This was because of the decomposition of  $\text{H}_2\text{O}_2$  and became to oxygen and the formation of ferric hydroxide complexes such as  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_4^-$  leading to a reduction of  $\cdot\text{OH}$  (Cuiping *et al.*, 2012).

The measured final pH values after 30 min of process were 2.51 for an initial pH of 3.00, 3.44 for an initial pH of 4.00 and 2.91 for an initial pH of 5.00. The change in solution pH was because of the acidity of the intermediates produced during the degradation of RR239 by Fenton process (Sun *et al.*, 2007). Thus, the optimum pH for degraded RR239 was obtained at pH 3. The decolorization efficiency was reached to 96.9%.

a)

b)

*Figure 4.1 Effect of initial pH on the decolorization of RR239 by Fenton process under  
[RR239] = 100 mg/L; [Fe<sup>2+</sup>] = 0.25 mM; [H<sub>2</sub>O<sub>2</sub>] = 2.7 mM*

*a) RR239 decolonization duration time 30 min*

*b) RR239 decolonization at 30 min*

a)

b)

*Figure 4.2 The remaining of Fenton's reagents on the degradation of RR239 by Fenton  
[RR239] = 100 mg/L; [Fe<sup>2+</sup>] = 0.25 mM; [H<sub>2</sub>O<sub>2</sub>] = 2.7 mM; duration Time 30 min*

*a) The remaining of H<sub>2</sub>O<sub>2</sub> dosage*

*b) The remaining of Fe<sup>2+</sup> dosage*

## 4.2 Effect of the initial H<sub>2</sub>O<sub>2</sub> concentration

H<sub>2</sub>O<sub>2</sub> was also an important role of an oxidizing agent in Fenton oxidation process (Sun *et al.*, 2007). The selection of an optimal hydrogen peroxide concentration for treatment RR239 by Fenton oxidation is important because the cost of H<sub>2</sub>O<sub>2</sub>. Therefore, the effect of initial H<sub>2</sub>O<sub>2</sub> concentration was studied varied from 1.4 mM to 5 mM with fixed Fe<sup>2+</sup> concentration at 0.25 mM and pH 4 for 30 minutes. The results found that the decolorization of RR239 at 5.0 mM was highest (96.8%), while those of 2.7 mM and 1.4 mM were 94.6% and 86.1%, respectively, after 30 min. Hence, the optimum concentration of H<sub>2</sub>O<sub>2</sub> was considered to be 5.0 mM.

As illustrated in Figure 4.2a, the efficiency of Fenton process was increased from 86.1% to 96.8% with the increase in initial H<sub>2</sub>O<sub>2</sub> concentration from 1.4 mM to 5.0 mM after 30 min. This is because of the increase of initial H<sub>2</sub>O<sub>2</sub> concentration allowing an enhancement in the quantum yield of active •OH. Then, •OH will attack the unsaturated dye molecules and the azo bond in the chromogen, thus decolorizing the wastewater (Huang *et al.*, 1999,). However, there are several studies reported that there is a higher concentration of H<sub>2</sub>O<sub>2</sub> in the Fenton process, the scavenging of •OH by excessive H<sub>2</sub>O<sub>2</sub> (reactions 8-9) became more significant. •OH reacted with H<sub>2</sub>O<sub>2</sub> to produce •O<sub>2</sub>H. Additionally, •O<sub>2</sub>H was less oxidative potential than •OH and cause the degradation efficiency and rate of pollutants to decrease. Moreover, at higher concentration of H<sub>2</sub>O<sub>2</sub>, the concentration of H<sub>2</sub>O<sub>2</sub> was still remained in the system as shown in Figure 4.5.



Thus, it is important to control the initial H<sub>2</sub>O<sub>2</sub> concentration because H<sub>2</sub>O<sub>2</sub> is highly related to the generation of •OH (Wang *et al.*, 2021) and •OH is the key species attacking organic molecules in an efficient but non-selective manner. The amount of hydrogen peroxide should be

enough for the treatment RR239 wastewater, but a high concentration would be decreased the efficiency of the degradation and would increase the cost of the wastewater treatment. According to the results above, the optimal  $\text{H}_2\text{O}_2$  concentration for the most effective degradation of 5.0 mM that could decolonized by 96.8%

a)

b)

c)

*Figure 4.3 Under the condition  $[RR239] = 100 \text{ mg/L}$ ;  $[Fe^{2+}] = 0.25 \text{ mM}$ ;  $pH = 4$ ; duration time 30 min*

*a) Effect of initial  $H_2O_2$  concentration on the degradation of RR239 by Fenton*

*b) The remaining of  $H_2O_2$  dosage*

*c) The remaining of  $Fe^{2+}$  dosage*

### 4.3 Effect of the initial Fe<sup>2+</sup> concentration

To elucidate the role of initial concentration of Fe<sup>2+</sup> on the degradation of RR239 by Fenton oxidation process, a series of experiments were conducted with different initial Fe<sup>2+</sup> concentration from 0.065mM to 0.5 mM with fixed H<sub>2</sub>O<sub>2</sub> concentration at 5 mM at pH 3 for 30 min. The results indicate that the extent of degradation increases with the increase in initial Fe<sup>2+</sup> concentration as illustrated in Figure 4.4a. At initial Fe<sup>2+</sup> concentration was 0.25, the decolorization efficiency was 96.5% which was higher than that at initial Fe<sup>2+</sup> concentration 0.50, 0.13 and 0.065 with 86.1% , 91.8% and 62.6%, respectively, after 30 min.

According to the result, the decolorization of RR239 was increased from 62.6% to 96.5% with increase in the Fe<sup>2+</sup> dosage from 0.065 mM to 0.25 mM. This is because more •OH radicals are produced with the increase of Fe<sup>2+</sup> according to reaction 1. However, when the initial Fe<sup>2+</sup> increased from 0.25 mM to 0.50 mM, the decolorization efficiency was obviously decreased from 96.5% to 62.6%. These results were expected and have been verified by other researchers as well. Kang *et al.* (2002) have observed that dye oxidization may be limited due to the rapid consumption of Fe<sup>2+</sup> during the initial phase of the reaction. In contrast, if the concentration of Fe<sup>2+</sup> is increased beyond an optimum level •OH scavenging (reaction 8) occurs, which may decrease the color removal efficiency (Kang *et al.*, 2002). Moreover, •OH can react with Fe<sup>2+</sup> to generate Fe<sup>3+</sup> which affect the reduction of degradation and production of Fe(OH)<sub>3</sub> sludge. In addition, Fe<sup>3+</sup> could react with H<sub>2</sub>O<sub>2</sub> to form •O<sub>2</sub>H (reactions 5-7) which is significantly less oxidizing agent than radical •OH (Wang *et al.*, 2021). An excessive dosage of iron also increases the total dissolved solids (TDS) of effluent and therefore might require further treatment (Sun *et al.*, 2009).



According to the results above, the optimal  $\text{Fe}^{2+}$  concentration for the most effective degradation of 0.25 mM that could decolonized by 96.5%

In fact, it is important to detect the optimum molar ratio of  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ , because the ratio can directly affect the production of  $\cdot\text{OH}$  in Fenton's reaction. According to the literature, there is still no agreement on the optimum molar ratio of  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  for the treatment of various wastewater by Fenton oxidation process (Peng sun *et al.*, 2009). Different optimum molar ratio of  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  has been proposed for the degradation of different pollutants in aqueous solution covering the range of 1:1 to 400:1 (Souna *et al.*, 2006). In this study, a suitable molar ratio of  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  for the decolorization of RR239 was experimentally detected as 10.8:1.



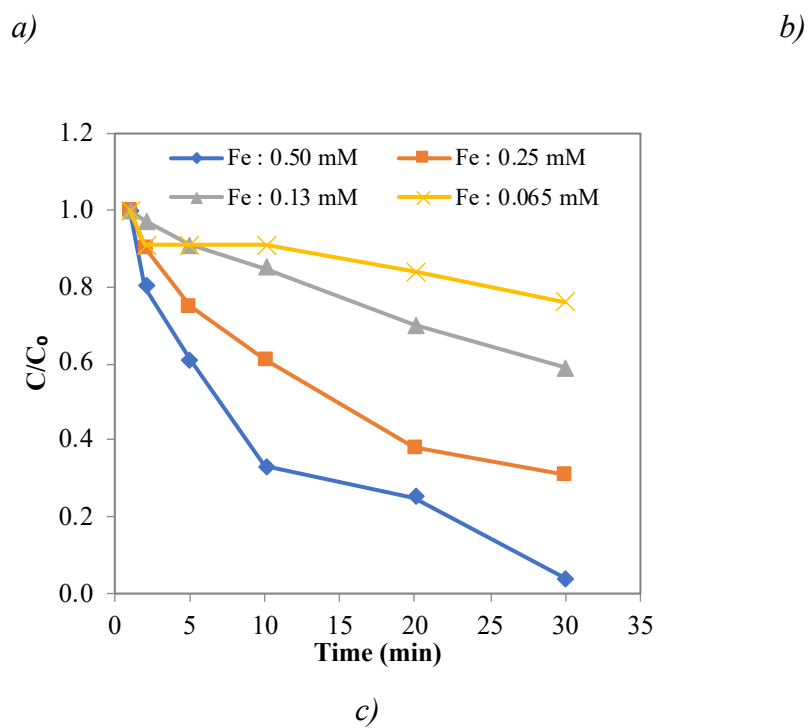


Figure 4.4 Under the conditions :  $[RR239] = 100 \text{ mg/L}$ ;  $[H_2O_2] = 5 \text{ mM}$ ;  $pH = 4$ ; duration Time 30 min

- a) Effect of initial  $Fe^{2+}$  concentration on the degradation of RR239 by Fenton  
 b) The remaining of  $Fe^{2+}$  dosage  
 c) The remaining of  $H_2O_2$  dosage

#### 4.4 Pathway of Reactive Red 239 degradation

There were several studies that have been reported on Fenton process products of different dyes: Reactive Red 2 (Zhang *et al.*, 2014), Reactive Red 195 (Zhang *et al.*, 2015), and Reactive Red X-3B (Shen *et al.*, 2017). The phthalic acid, catechol and phenol were found in the final steps of the degradation pathways of azo dyes (Shen *et al.*, 2017; Zhang *et al.*, 2015). This was because  $\cdot\text{OH}$  was produced by the reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ . RR239 degradation by  $\cdot\text{OH}$  occurs through the cleavage of  $-\text{N}=\text{N}-$  and  $-\text{C}-\text{N}-$  bonds in two ways. Finally, the cleavage of the azo bond generated the naphthalene compounds which were further oxidized to phthalic acid, whereas the cleavage of the carbon-nitrogen bond led to triazine and aromatic sulfonated compounds. Triazine was released by oxidation of the C-S bond of  $\cdot\text{OH}$  that converted molecule to an easily oxidizing phenolic compound and the sulfonated compound was converted to phenol and catechol. Secondly, the sulfonated compound was oxidized to aniline, and further to phenol and catechol. Finally, the intermediates were slowly converted to  $\text{CO}_2$  and water by  $\cdot\text{OH}$  in the Fenton process, namely mineralization process (Banaei *et al.*, 2018).

## Chapter V

### Conclusions

The decolorization of a solution containing RR239 by Fenton oxidation process has been taken into account in this study. The experimental results showed that the initial pH, the initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  had great influence on the degradation of RR239 by the process of Fenton. The results also showed that the decolorization efficiency was decreased when pH was increased. Additionally, the results also presented that dye decolorization efficiencies were increased when the initial of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations were increased.  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  are essential to generate  $\cdot\text{OH}$ . However, at very high concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  and  $\cdot\text{OH}$ , the decolorization efficiency could be reduced because of scavenging effect. Therefore, the optimal condition for decolorization of 100 mg/L RR239 by the process of Fenton are pH at 3 and initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentration are 2.7 mM and 0.25 mM, respectively, under room temperature. At this condition, the decolorization rate can reach 96.9% in 30 min.

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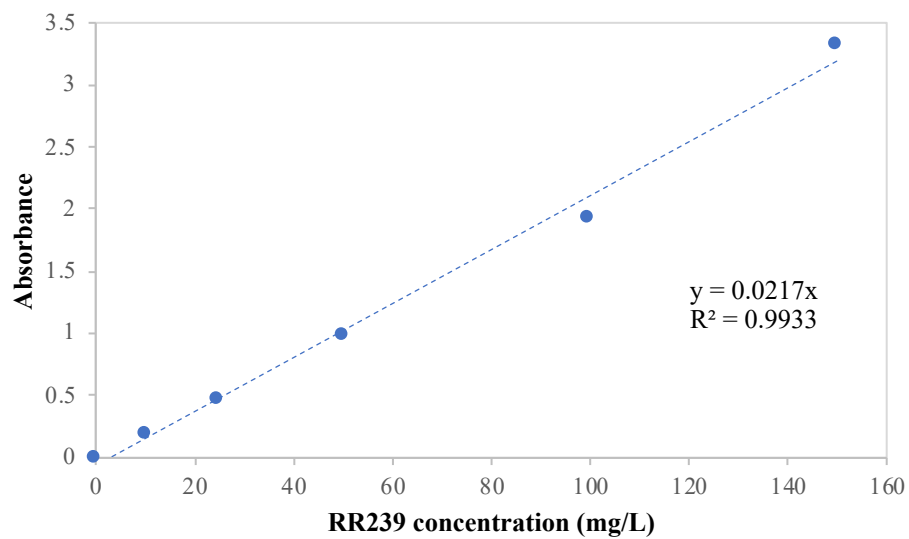
# Appendices



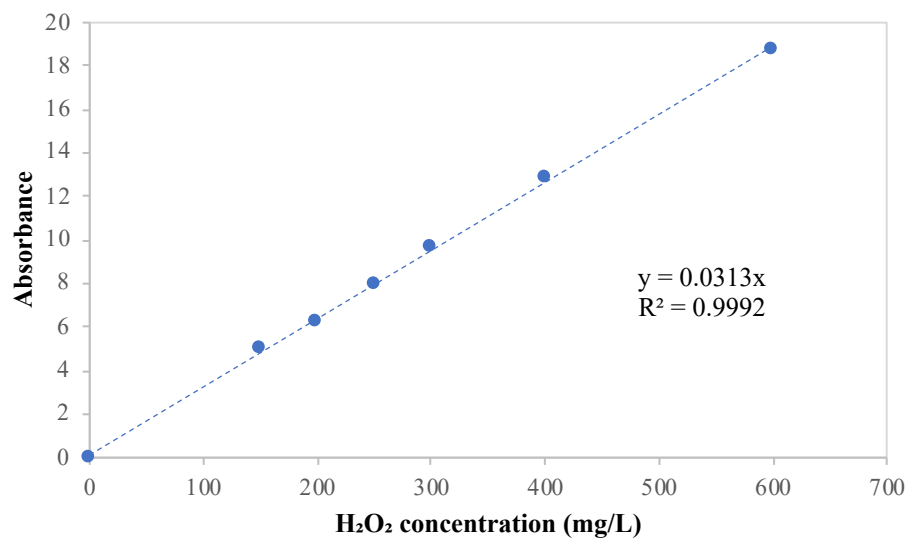
## Appendix A

### Standard curve

#### 1. Standard curve for RR239 concentration



#### 2. Standard curve for H<sub>2</sub>O<sub>2</sub> concentration



### 3. Standard curve for $\text{Fe}^{2+}$ concentration

## Appendix B

### Preparation of Reagents

#### 1. Measurement of $\text{Fe}^{2+}$ concentration

##### 1.1 1,10-phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2$ )

Dissolve 1 g of 1,10-phenanthroline monohydrate in 100 ml of DI water.

##### 1.2 Hydroxylamine hydrochloride ( $\text{H}_2\text{NOH} \cdot \text{HCl}$ )

Dissolve 10 g of hydroxylamine hydrochloride in 100 mL of DI water.

##### 1.3 Ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) buffer solution

Dissolve 250g of ammonium acetate in 150 ml of DI water in 1000 ml beaker glass. Then, add 700 ml conc glacial acetic acid in to the beaker. The solution was completely mixed by magnetic stirrer.

##### 1.4 Iron (II) standard solution

Dissolve 0.702 g of ferrous ammonium sulfate, hexahydrate in DI water. Dilute to 1 L in volumetric flask. This solution is 100 mg/L of  $\text{Fe}^{2+}$  (same as 100 ppm).

#### 2. Measurement of $\text{H}_2\text{O}_2$ concentration

##### 1.1 Potassium titanium oxalate solution

Dissolve 25 g of potassium titanium oxalate in 400 ml of DI water. Then, add 2.5 ml of sulfuric acid into the solution. Dilute to 1 L in volumetric flask.

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