



CHAPTER III

METHODOLOGY

3.1 Materials and Chemicals

3.1.1 Chemicals

O-toluidine, Fenton's reagents ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2) and all other chemical substances were reagent grade (purity $\geq 99.5\%$, Merck Company). The carriers used in this study were silica dioxide (SiO_2), which has a grain-shape with diameter ranging between 0.42 and 0.59 mm. All solutions were prepared by de-ionized water from a Millipore system with a resistivity of $18.2 \text{ M}\Omega/\text{cm}$

3.1.2 Fluidized-bed Reactor

A 1.35 liter fluidized-bed reactor was used in all experiments performed. The reactor was a cylinder vessel, which consisted of inlet, outlet and recirculation compartments as shown in Figure 3.1. The carriers were fluidized at the optimum bed expansion by controlling the internal circulation rate.

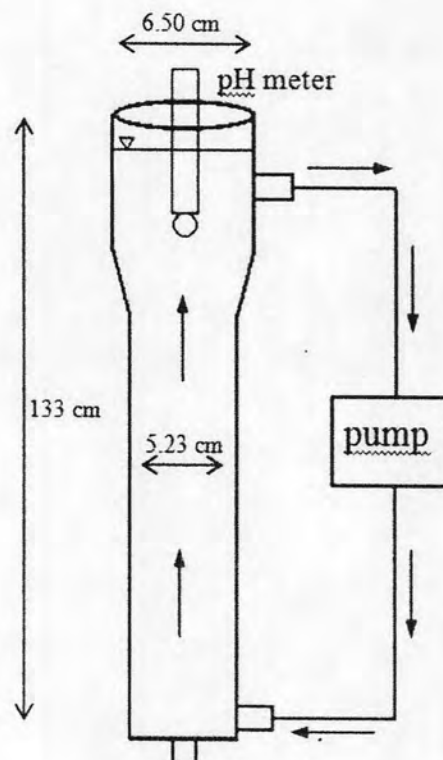


Figure 3.1 The fluidized-bed reactor

3.2 Experimental Procedures

3.2.1 Fluidized-bed Fenton Experiment

At the beginning, the synthetic *o*-toluidine wastewater was prepared by diluting the reagent grade *o*-toluidine with de-ionized water. The desired *o*-toluidine concentration was 1 mM. Next, the calculated amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the synthetic wastewater as the source of ferrous ions. The wastewater was filled into the reactor, followed by silica dioxide. After that, the recycle pump was turned on to mix the solution and suspend the silica dioxide. Next, the pH was adjusted to the desired value by 1:4 H_2SO_4 . When hydrogen peroxide was added, the reaction was simultaneously started. At selected time interval of 0, 1, 2, 5, 10, 20, 30, 60, 90 and 120 minutes, 4 mL of sample was taken from the reactor and was analyzed for residual hydrogen peroxide, ferrous ions, total iron, and *o*-toluidine. All these experimental steps are shown in Figure 3.2.

3.2.2 Design of Experiments

For the design of experiments, the "Design Expert" software (Version 7.0.0, Stat-Ease Inc., Minneapolis, USA) was used to calculate and evaluate the experiments and results. There were two designs used in this study, the two-level factorial design and the Box-Behnken design. The two-level factorial design was used first to determine significant factors principally affecting on the removal of *o*-toluidine by the fluidized-bed Fenton process. After that, the Box-Behnken design was used to determine the optimum condition.

Firstly, the variables were input into the software. These variables were chosen by considering the major factors that possibly affected the process. The highest and lowest levels of each variable were also input into the software. Another kind of inputs needed for the software is the response. The responses are the parameters that show the results of experiments. After all parameters were input into the software, the experiments then were designed. The number of experiments for the two-level factorial design of 4 variables was 16 runs (2^4). The data then were analyzed and evaluated after the design matrix was completed. By using this design, the insignificant factors would be excluded from further experiment.

After the insignificant factors were excluded by using the two-level factorial design, the same data were used further for determining the optimum condition. The Box-Behnken design was used in this step. The design included another input, which was the center level of each variable. Therefore, the design matrix obtained from the Box-Behnken design was similar to that in the two-level factorial design except the number and the level of variables. There were 17 runs of experiment for the Box-Behnken design. The optimum condition was obtained from this design.

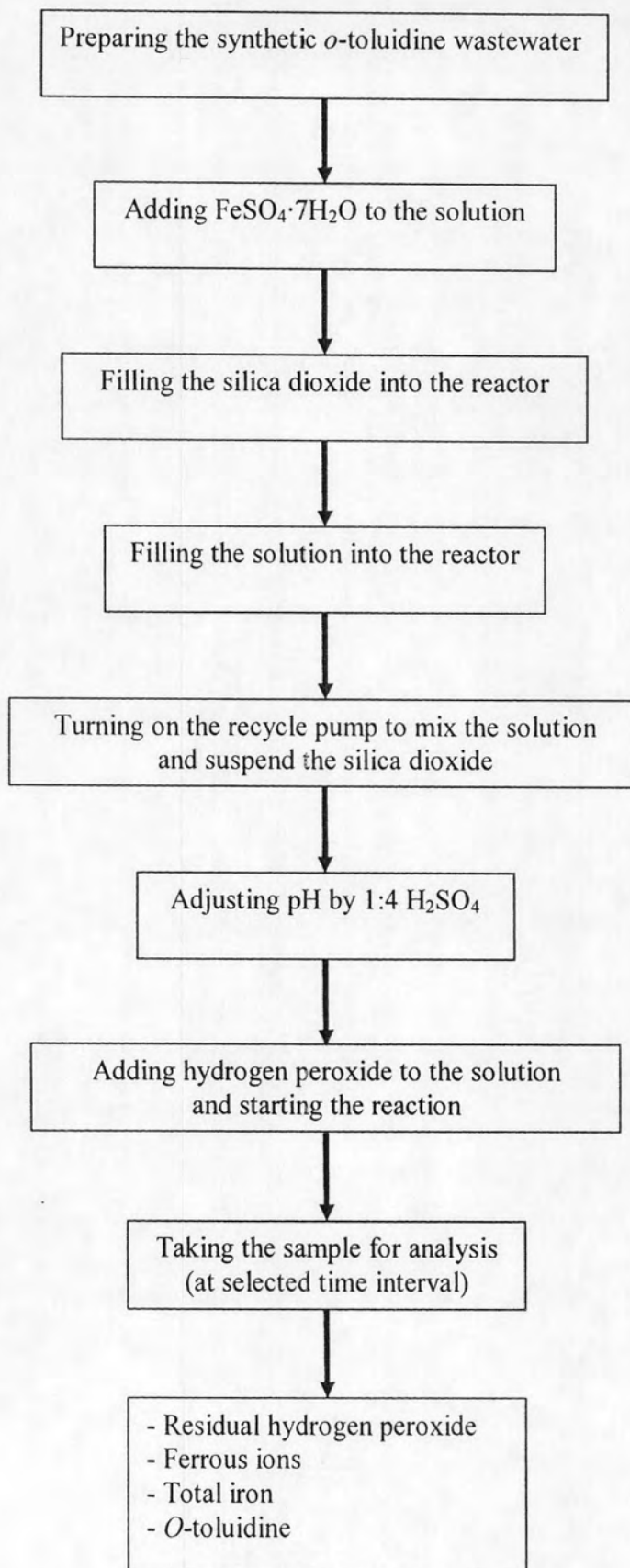


Figure 3.2 Experimental scheme for fluidized-bed Fenton process.

3.3 Experimental Scenarios

3.3.1 Control Experiments

Table 3.1 Effect of individual component

<i>O</i> -toluidine (mM)	pH	Carriers (g)	Control parameters
1	3	100	Adsorption
			Fe ²⁺
			H ₂ O ₂

3.3.2 Screening Tests

This part aimed to identify the primary factors affecting on the *o*-toluidine oxidation by fluidized-bed Fenton process. Four independent variables which have a possibility to affect the process performance were selected as shown in Table 3.2. Upper and lower values for each variable were also specified as shown in Table 3.2. From two-level factorial design, 16 experimental runs were generated as shown in Table 3.3. The responses or dependent variables were the removal of *o*-toluidine, of COD and total iron.

3.3.3 Optimization Experiments

This part aimed to identify the optimum condition for the *o*-toluidine oxidation by fluidized-bed Fenton process. Three independent variables, which have a possibility to affect the process performance, selected from previous section were shown in Table 3.4. Upper, center and lower values for each variable were also specified as shown in Table 3.4. From Box-Behnken design, 17 experimental runs were generated as shown in Table 3.5. The responses or dependent variables were the removal of *o*-toluidine, of COD and total iron.

Table 3.2 Variable levels for two-level factorial design

Variable	Symbol	Variable level	
		Low	High
		-1	+1
pH	A	2	4
Fe ²⁺ (mM)	B	0.1	1
H ₂ O ₂ (mM)	C	1	17
Amount of carriers (g)	D	50	300

Table 3.3 Design matrix for the two-level factorial design of fluidized-bed Fenton process (*o*-toluidine concentration = 1 mM)

Run number	pH	Fe ²⁺ (mM)	H ₂ O ₂ (mM)	Carriers (g)
1	-1	-1	-1	-1
2	-1	-1	-1	+1
3	+1	-1	-1	-1
4	+1	-1	-1	+1
5	-1	+1	-1	-1
6	-1	+1	-1	+1
7	+1	+1	-1	-1
8	+1	+1	-1	+1
9	-1	-1	+1	-1
10	-1	-1	+1	+1
11	+1	-1	+1	-1
12	+1	-1	+1	+1
13	-1	+1	+1	-1
14	-1	+1	+1	+1
15	+1	+1	+1	-1
16	+1	+1	+1	+1

Table 3.4 Variables levels for Box-Behnken design

Variable	Symbol	Variable level		
		Low	Center	High
		- 1	0	+1
pH	A	2	3	4
Fe ²⁺ (mM)	B	0.1	0.55	1
H ₂ O ₂ (mM)	C	1	9	17

Table 3.5 Design matrix for the Box-Behnken design of fluidized-bed Fenton process (*o*-toluidine concentration = 1 mM, carriers = 100 g)

Run number	pH	Fe ²⁺ (mM)	H ₂ O ₂ (mM)
1	-1	-1	0
2	+1	-1	0
3	-1	+1	0
4	+1	+1	0
5	-1	0	-1
6	+1	0	-1
7	-1	0	+1
8	+1	0	+1
9	0	-1	-1
10	0	+1	-1
11	0	-1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0

3.3.4 Kinetic Study

In this part, the kinetics of *o*-toluidine oxidation by hydroxyl radicals in the fluidized-bed Fenton process was investigated. Three independent variables were studied including *o*-toluidine, Fe²⁺, and H₂O₂ concentrations. The studied ranges for each variable were shown in Tables 3.6 to 3.7.

Table 3.6 Effect of *o*-toluidine concentration on *o*-toluidine oxidation

Fe ²⁺ (mM)	H ₂ O ₂ (mM)	pH	Carriers (g)	<i>O</i> -toluidine (mM)
1	3	3	100	0.5
				1
				2
				5

Table 3.7 Effect of Fe²⁺ on *o*-toluidine oxidation

<i>O</i> -toluidine (mM)	pH	Carriers (g)	H ₂ O ₂ (mM)	Fe ²⁺ (mM)
1	3	100	17	0.1
				0.5
				1
				2

Table 3.8 Effect of H₂O₂ on *o*-toluidine oxidation

<i>O</i> -toluidine (mM)	pH	Carriers (g)	Fe ²⁺ (mM)	H ₂ O ₂ (mM)
1	3	100	1	1
				9
				17
				34

3.4 Analytical Methods

3.4.1 Measurement of *o*-toluidine

Firstly, the sample was filtered through cellulose acetate membrane with 0.2 μm pore size to separate precipitated iron from the solution. Next, the analysis of residual *o*-toluidine was performed by high performance liquid chromatography (HPLC) with 20 μL of injecting sample. The mobile phase was 60% acetonitrile with 40% DI water (v/v). The column was operated between 18 and 22 $^{\circ}\text{C}$. The pump was SpectraSYSTEM model SN4000 with the operating flow rate of 1 ml/min through Asahipak ODP-506D column (150 mm \times 6 mm \times 5 μm). The 254 nm outputs from UV1000 detector were measured.

3.4.2 Measurement of ferrous

The ferrous ions in the samples was analyzed by the phenanthroline method as describe by Standard Methods (American Public Health Association [APHA], 1992). DI water was used to adjust the volume to 50 mL. A blank was prepared by mixing DI and acid for every sample.

3.4.3 Measurement of hydrogen peroxide

Hydrogen peroxide was determined by a spectrophotometric method using potassium titanium (IV) oxalate as described in Appendix A. The absorbance of samples was measured by the the Spectronic™ GENESYS™ 20 spectrophotometer.

3.4.4 Measurement of total iron

Sample was digested by nitric acid and diluted by DI water (10 times dilution). The total iron concentration was analyzed by using PerkinElmer Atomic Absorption Spectrometer (AAS) model AAnalyst 200 with hollow cathode lamps Fe at 248.33 nm with Slit of 1.8/1.35 and used acetylene gas as the carrier.