CHAPTER III

METHODOLOGY

3.1. Experimental Instruments and Chemicals

3.1.1. Experimental Instruments and Equipments

1. pH meter: SUNTEX TS-1 Digital pH/MV meter
2. UV-VIS Spectrophotometer: THERMO HELIONS ALPHA
3. Thermometer
4. Auto Pipette
5. Weighing Machine (4-Digits Balance)
6. Magnetic Stirrer
7. Magnetic Bar
8. Glassware
9. 1.35-litre cylinder fluidized-bed reactor with recycle pump
10. Glass Bead Ø 2, 6, and 7 mm
11. Clock Timer
12. Membrane Filter 0.45 and 0.2 μm
13. Syringe

3.1.2. Chemicals

1. 2,6-dimethylaniline (>98%) (Merck Co., Ltd.)
2. Ferrous sulfate heptahydrated (Merck Co., Ltd.)
3. Hydrogen peroxide (35%) (Merck Co., Ltd.)

3.1.3. Fluidized-bed Reactor

A 1.35-litre fluidized-bed reactor (FBR) will be used in all experiments. The fluidized-bed reactor is a cylinder vessel which consists of outlet, inlet and re-circulating sections as shown in Figure 3.1. The carrier is fluidized by adjustment the internal circulation at 50% bed expansion (Chou et al., 2004).

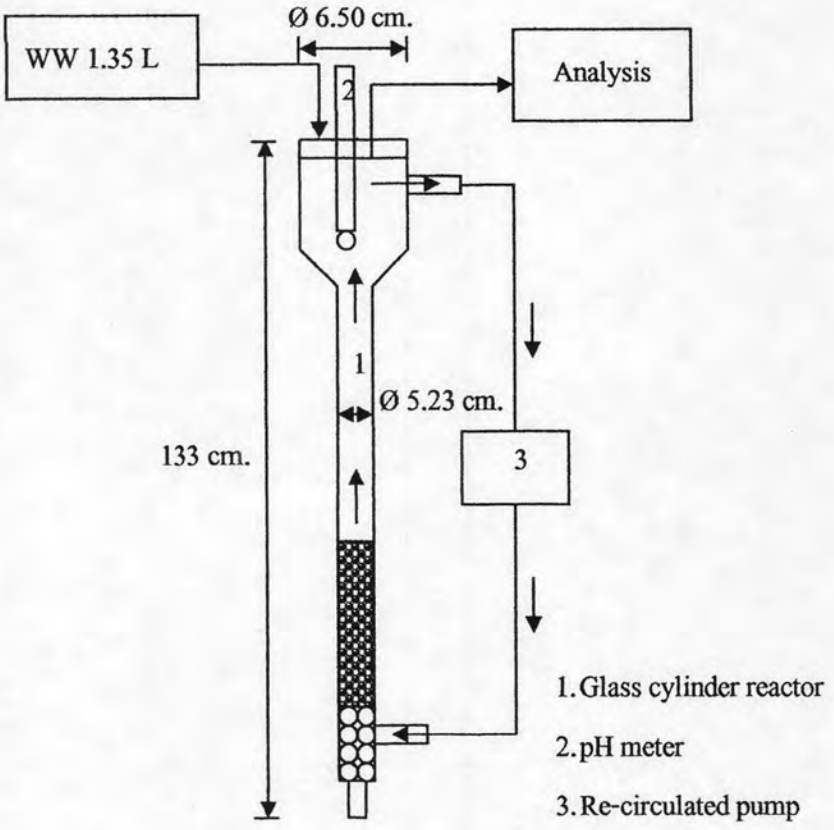

Figure 3.1 Fluidized-bed reactor (FBR) compartments

3.1.4. Preparation of synthesis 2,6-dimethylaniline wastewater

2,6-Dimethylaniline was dissolved in diethyl ether on a molar basis by shaking until it was dissolved. Completed preparations were placed in serum vials fitted with Teflon® stoppers and sealed. Appropriate amounts of 2,6-dimethylaniline were weighed and then mixed with enough diethyl ether to obtain the desired concentrations (Kornreich and Montgomery, 1990). Such as the preparation of synthesis 1 mM 2,6-dimethylaniline wastewater, mixing

2,6-dimethylaniline and diethyl ether solution with the ratio of 2,6-dimethylaniline to diethyl ether as 1:33 in a molar basis (Reilly, 1999). Then, fill tap water to the solution until 1 liter and store following the above mention.

3.2. Scope of overall experiment

Figure 3.2 is illustrated the scope of overall experiment that used to determine the oxidation of 2,6-dimethylaniline.

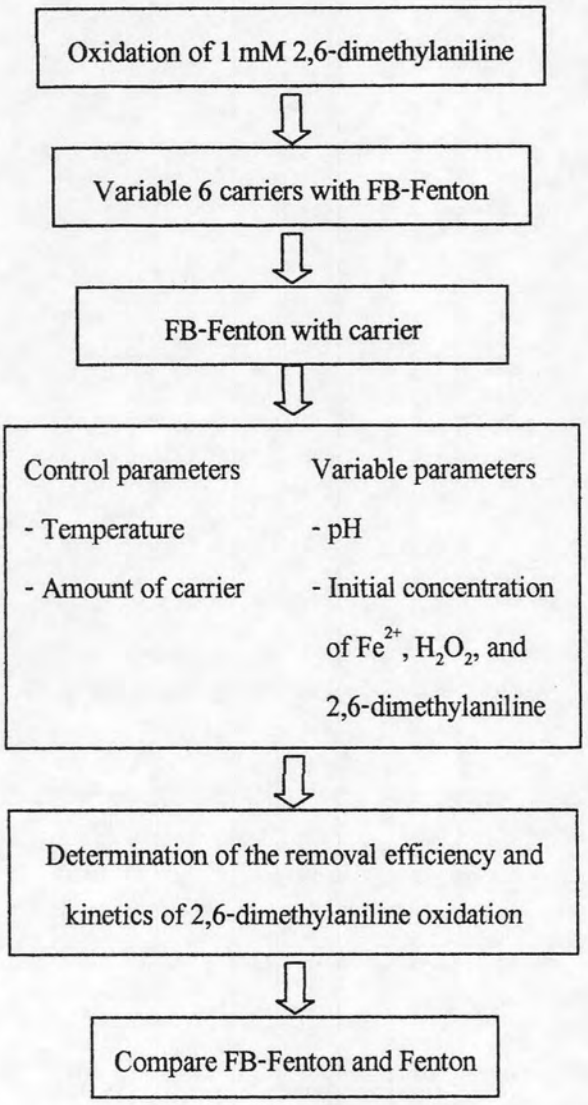

Figure 3.2 Scope of overall experiment

3.3. Experimental Procedures

3.3.1. Fluidized-bed Fenton Experiment

At the beginning, the synthesis wastewater containing 2,6-dimethylaniline was poured into fluidized-bed reactor. Next, the recycle pump was turned on to mix the solution at 50% bed expansions. After that, adjusted to pH 3.5 by 6N NaOH or 1:4 H_2SO_4 to prevent $Fe(OH)_3$ precipitation (Chou et al., 1999). Pre-calculated ferrous sulfate heptahydrated was put at the 5^{th} minute after the recycle pump had been switched on. The solution was rechecked and adjusted to initial pH again before adding hydrogen peroxide solution and the reaction was simultaneously started. At selected time interval of 0, 2, 5, 10, 20, 40 60, 90, 120, and 150 minutes, 5 ml aliquot was taken from the fluidized-bed reactor and analyzed immediately for residual hydrogen peroxide, 2,6-dimethylaniline, ferrous ion, total iron. All experimental activities are as shown in Figure 3.3.

In this study separated in 4 parts, the first part is the comparison of carrier for determining the optimum carrier to use in next parts by varying 6 types of carrier with the condition from Ting et al. (2008) who determined the optimum condition of 2,6-dimethylaniline degradation in electro-Fenton process, which was 1 mM of 2,6-dimethylaniline degraded by 20 mM of hydrogen peroxide and 1 mM of ferrous ion concentration at pH 2 in 300 minutes. There are black gravel, white gravel, brown gravel, colour gravel, alumina dioxide (Al_2O_3) and silica dioxide (SiO_2).

The second part is the control experiment as the basic experiment for investigating pure 2,6-dimethylaniline degradation efficiency of each reagent that we are interested. There are free ferrous with carrier, free hydrogen peroxide with carrier, free ferrous and hydrogen peroxide with carrier as adsorption and free carrier as Fenton process.

The third part is the variable experiment of pH value to find out the optimum pH for this experiment from 1, 2, 3 and 4 and includes kinetic experiment and the optimum values from each reagent by varying concentrations of ferrous ion, hydrogen peroxide and 2,6-dimethylaniline. To determine the effect of hydrogen peroxide concentration on the degradation of aniline, hydrogen peroxide concentrations are varied as 2.5, 5, 10, 15 and 20 mM. The concentration of ferrous ion is following the ratio between hydrogen peroxide and ferrous ion as

1:0.2, 1:0.5 and 1:1. Then, 2,6-dimethylaniline concentrations are varied as 0.5, 1 and 5 mM for getting slope from linear equation to calculate the kinetic equation.

And the last one, when this study gets the optimum value and concentration from each part, the comparison of 2,6-dimethylaniline oxidation efficiency between fluidized-bed Fenton and Fenton processes is examined. The mainly condition in this study from pre-test experiment; 1 mM of 2,6-dimethylaniline, 15 mM of hydrogen peroxide, 5 mM of ferrous ion and 74.07 g/L of the carrier (Hseuh et al., 2006a) and initial pH 3 in 150 minutes. All is operated in fluidized-bed reactor (FBR).

3.4. Experimental Scenarios

A) Comparison of different carriers in 2,6-dimethylaniline oxidation on fluidized-bed Fenton process

This is the first part to determine the optimum carriers to use in this experiment from 6 types of carrier by operating in fluidized-bed reactor to oxidize 2,6-dimethylaniline as conditions recommended by Ting et al. (2008) as shown in Table 3.1.

Table 3.1 Comparison of different carriers

2,6-dimethylaniline (mM)	pH	Fe^{2+} (mM)	H_2O_2 (mM)	Carrier in fluidized-bed reactor (74.07 g/l)
1	2.0±0.2	1	20	Al_2O_3 SiO_2 Black Gravel White Gravel Brown Gravel Colour Gravel

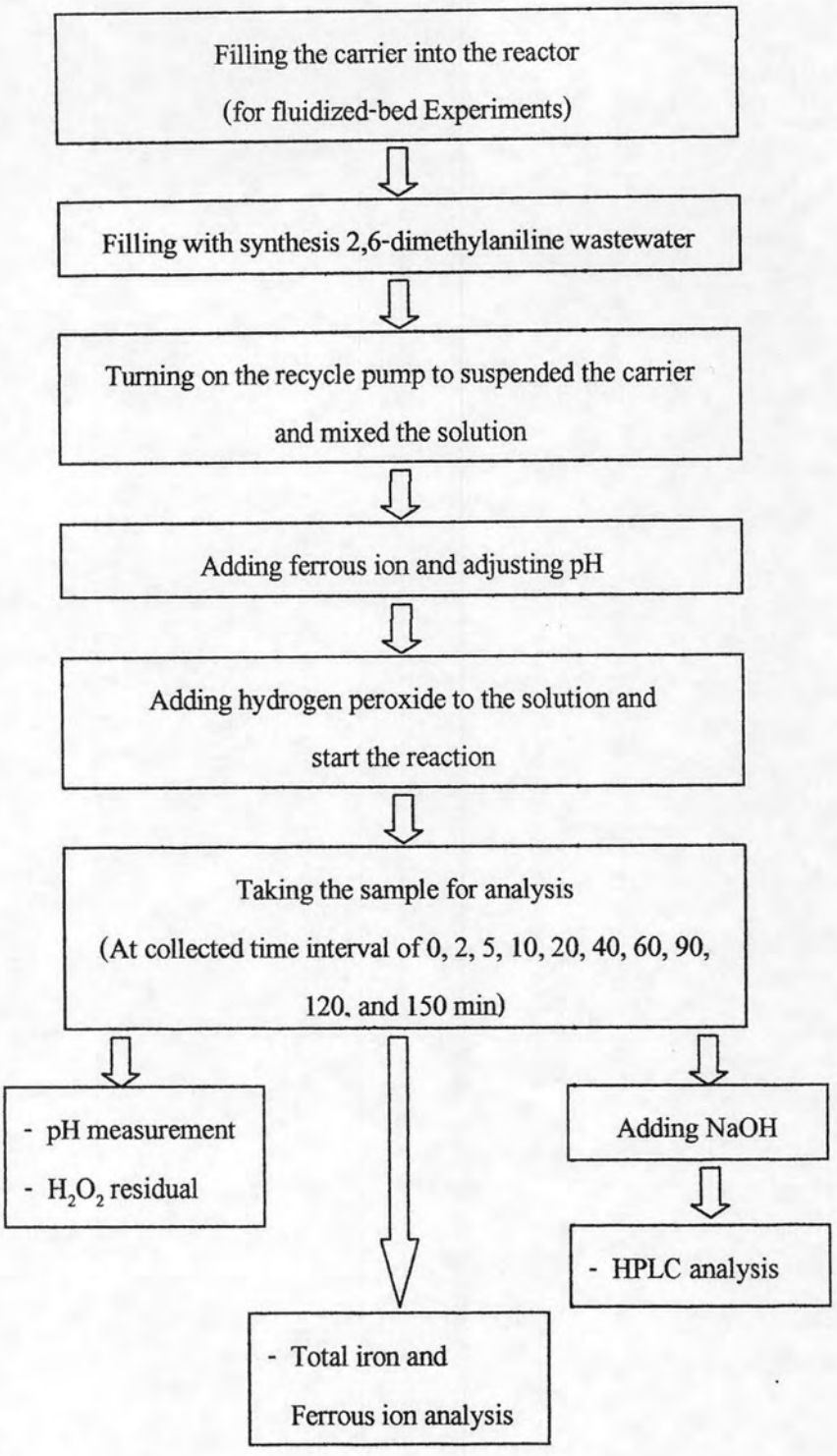

Figure 3.3 Experimental procedure charts for Fenton and fluidized-bed Fenton Processes

B) Control experiments of 2,6-dimethylaniline oxidation on fluidized-bed Fenton process

This part is the control experiments to investigate the effects of carrier, ferrous ion, and hydrogen peroxide on the oxidation of 2,6-dimethylaniline in fluidized-bed reactor with the condition as shown in Table 3.2.

Table 3.2 Control experiments

2,6-dimethylaniline (mM)	pH	Carrier in fluidized-bed reactor (g/l)	Control parameter
1	3.0±0.2	74.07	With Fe^{2+}
			With H_2O_2
			Adsorption (no Fe^{2+} and H_2O_2)
		0	Fenton (no carriers)

C) Oxidation of 2,6-dimethylaniline in fluidized-bed Fenton process

To study the mechanical, investigate the kinetics and determine the optimum condition of this process, this part consisting of variable effect of pH, Fe^{2+}, H_2O_2 and 2,6-dimethylaniline is important to examine.

C-1) Effect of initial pH

The variable values of pH determines the initial pH from pH 1 to 4 as shown in Table 3.3. From previous experiment, the optimum pH of fluidized-bed Fenton process is 3 (Chou et al., 1999) but Ting et al. (2008) investigated that pH 2 is the optimum pH for 2,6-dimethylaniline in electro-Fenton process. For examining the optimum pH for this study, the part has to investigate.

Table 3.3 The variable values of initial pH on 2,6-dimethylaniline oxidation in FB-Fenton

2,6-dimethylaniline (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	Carrier in fluidized-bed reactor (g/l)	pH
1	5	15	74.07	1.0±0.2
				2.0±0.2
				3.0±0.2
				4.0±0.2

C-2) Effects of initial hydrogen peroxide concentration

Hydrogen peroxide is the oxidizing agent in Fenton process. If hydrogen peroxide is more than ferrous ion, the reaction of target compound degradation is oxidation. Anyway, if it absences hydrogen peroxide, most compound will be occurred as coagulation. For determining the optimum hydrogen peroxide concentration as shown in Table 3.4.

Table 3.4 The variable values of initial H_2O_2 concentration on 2,6-dimethylaniline oxidation in FB-Fenton

2,6-dimethylaniline (mM)	Fe^{2+} (mM)	pH	Carrier in fluidized-bed reactor (g/l)	H_2O_2 (mM)
1	5	Optimum value from C-1	74.07	2.5
				5
				10
				15
				20

C-3) Effects of initial ferrous ion concentration

Ferrous ion is the catalytic reagent in Fenton process for being faster oxidation and in fluidized-bed Fenton, ferrous ion can regenerate because of crystallization on carriers if it has the optimum ferrous ion concentration. For determining the optimum ferrous ion concentration as shown in Table 3.5.

Table 3.5 The variable values of initial Fe^{2+} concentration on 2,6-dimethylaniline oxidation in FB-Fenton

2,6-dimethylaniline (mM)	H_2O_2 (mM)	pH	Carrier in fluidized-bed reactor (g/l)	$H_2O_2 : Fe^{2+}$
1	Optimum value from C-2	Optimum value from C-1	74.07	1:0.2
				1:0.5
				1:1

C-4) Effects of initial concentration of 2,6-dimethylaniline

This part is for completely investigating the kinetics of 2,6-dimethylaniline oxidation on fluidized-bed Fenton process with the optimum condition as shown in Table 3.6.

Table 3.6 The variable values of initial 2,6-dimethylaniline concentration on 2,6-dimethylaniline oxidation in FB-Fenton

Fe^{2+} (mM)	H_2O_2 (mM)	pH	Carrier in fluidized-bed reactor (g/l)	2,6-dimethylaniline (mM)
Optimum value from C-2	Optimum value from C-3	Optimum value from C-1	74.07	0.5
				1
				5

D) Comparison 2,6-dimethylaniline removal between fluidized-bed Fenton and Fenton processes

To compare the 2,6-dimethylaniline removal efficiency in Fenton, and fluidized-bed Fenton processes with the conditions as shown in Table 3.7.

Table 3.7 Comparison 2,6-dimethylaniline removal between FB-Fenton and Fenton processes

2,6-dimethylaniline (mM)	pH	Fe^{2+} (mM)	H_2O_2 (mM)	Carrier in fluidized-bed reactor (g/l)
1	Optimum value from C-1	Optimum value from C-2	Optimum value from C-3	0
				74.07

3.5. Analytical Methods

3.5.1. Measurement of 2,6-dimethylaniline

First of all, the liquid samples were filtered through 0.20 μm syringe microfilters to separate precipitated iron from the solutions. Next, the analysis of residual sample was determined by using a high performance liquid chromatography (HPLC) with mobile phase as 29% Acetonitrile and 71% DI water. The column was operated between 18 and 22°C. The pump was SpectraSYSTEM model SN4000 with the operating flow rate were 1.5 ml/min through Asahipak ODP-506D column (150mm x 6mm x 5μm). The 254 nm outputs from UV1000 detector were measured. 2μL of sample was injected. The pH was monitored using a SUNTEX pH/mV/TEMP. model SP-701.

3.5.2. Analysis of total iron and soluble iron concentration

The samples were digested by nitric acid and diluted 8 times by RO water. Then, the samples were filtered with 0.45 μm microfilters to separate small particles from the solutions. Next, the total iron concentration was analyzed using a HITACHI Z6100 polarized Zeeman atomic absorption spectrophotometer.

3.5.3. Analysis of ferrous ion concentration

The samples were analyzed by phenanthroline method in Appendix A. the RO water was added to making up to volume to 50 ml. The RO water mixed with the sample but no phenanthroline was used as a blank for every sample.

3.5.4. Analysis of hydrogen peroxide

The concentration of hydrogen peroxide was determined by standard iodometric method where potassium iodide with $Na_2S_2O_3$ solution was used as a titrant as described in Appendix B.

3.5.5. Other measurements

The composition of carrier is determined by using Ceramic or agate mortar to crack the carriers and give the sample to analyze by X-ray Diffraction in Cheng Kong University, Tainan, Taiwan. The pH measurement is carried out by a SUNTEX TS-1 Digital pH/MV meter and analyzed COD by closed reflux titrimetric method in Appendix C.