

Chapter III

Methodology

3.1 Experiment Instrument and Chemicals

3.1.1. Experiment Instrument and Equipment

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 Bars
8. COD Closed Reflux Heater Block
9. Glassware
10. 1.35-litres cylinder fluidized-bed reactor with recycle
11. Glassbed Bead diameter 4 mm
12. Clock Timer
13. Membrane Filter 0.45 μm
14. Syringe

3.1.2 Chemicals

Nitrobenzene was obtained from the Merck Company. Ferrous sulfate and hydrogen peroxide (purity, 35%) were manufactured by the Merck Company. Sodium chloride was obtained from the Showa Company. The rest of the reagents used were at least of reagent grade. Two types of metal oxide i.e. Al_2O_3 and SiO_2 , was used in this study. Al_2O_3 serving as the main carrier in the FBR has white color, circle shape with 2.50 mm of average particle diameter. SiO_2 has a grain shape with 0.84-2.00 mm.

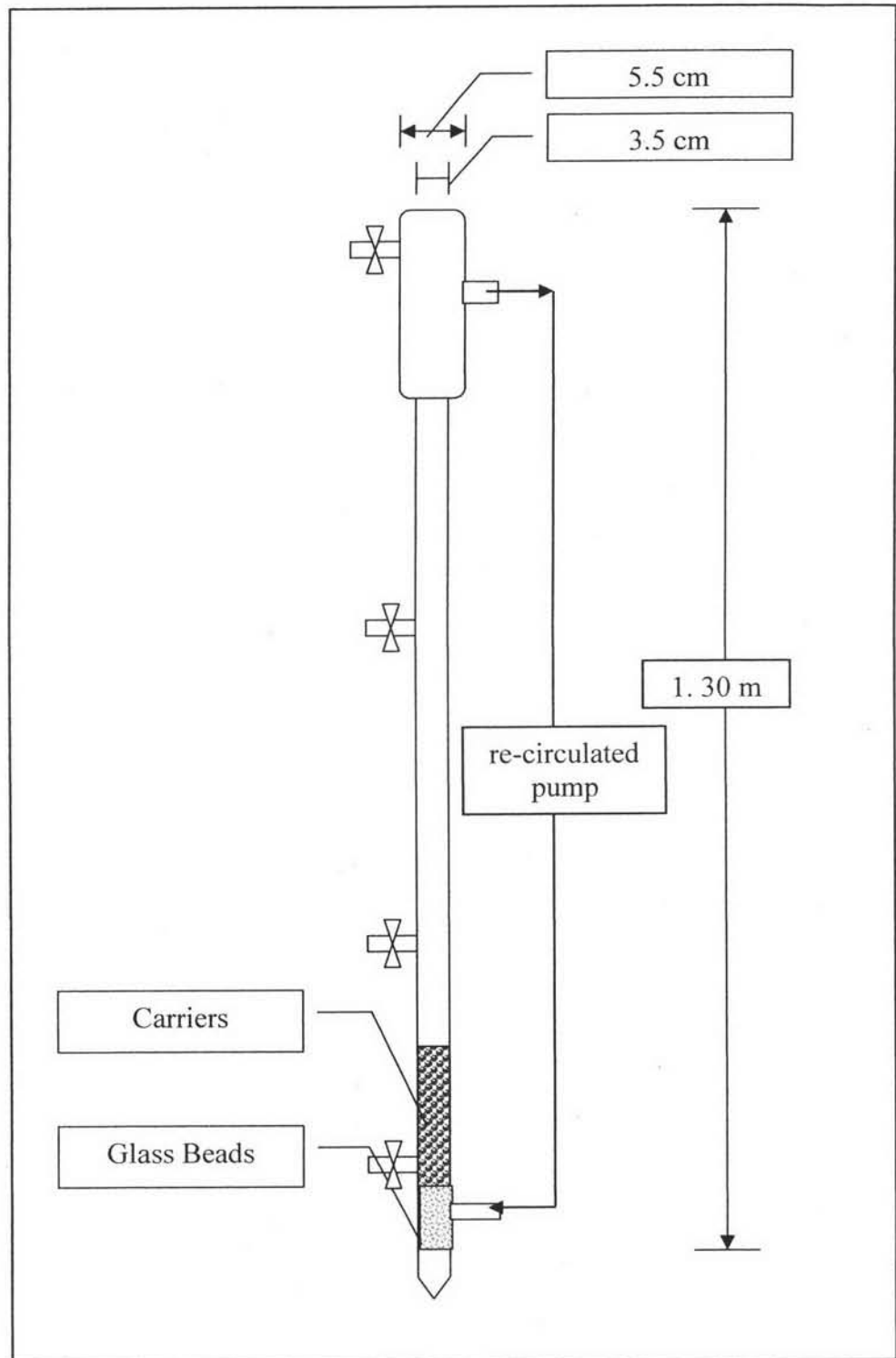


Figure 3.1 Fluidized-bed reactor (FBR) compartments.

3.1.3 Fluidized-bed Reactor

A 1.35-litres fluidized-bed reactor (FBR) was operated in all experiments performed. The FBR is a glass cylinder vessel which consists of outlet, inlet and recalculate sections as shown in the Figure 3.1.

3.2 Experiment Procedures

3.2.1 Point of zero chare of metal oxide

De-ionized water having very low ionic strength is used to make suspensions. The use of aqueous solutions containing monovalent ions is worthwhile; provides that added ions are not specifically adsorbed on the surface oxide. It is important to select the electrolyte nature as a function of the studied oxide. In this research, the solution containing 0.01 M of aniline and 0.025 M of Na_2SO_4 which stand for the experimental solutions was used to determine the pzc and compared to that of pure water.

Predetermine amounts of metal oxide particles were put into the flasks provides that added ions are not specifically adsorbed on the surface oxide. It is important to select the electrolyte nature as a function of the studied oxide. In this research, the solution containing 0.01 M of aniline and 0.025 M of Na_2SO_4 which stand for the experimental solutions was used to determine the pzc and compared to that of pure water containing either DI water or experiment solution to yield 0, 0.2, 0.4, 0.6, 1.2, 2.4, 5, 10, 20, 30, 40, 50 g/l. Both DI water or experiment solutions were used after bubbling with nitrogen gas. The flasks of metal oxide/water were purged with nitrogen gas, sealed, and placed on a shaker for 24 hours, which was found to be sufficient to allow the mixture to reach equilibrium. Then, pH of the mixture was measured. The experimental procedure chart is mentioned in Figure 3.2.

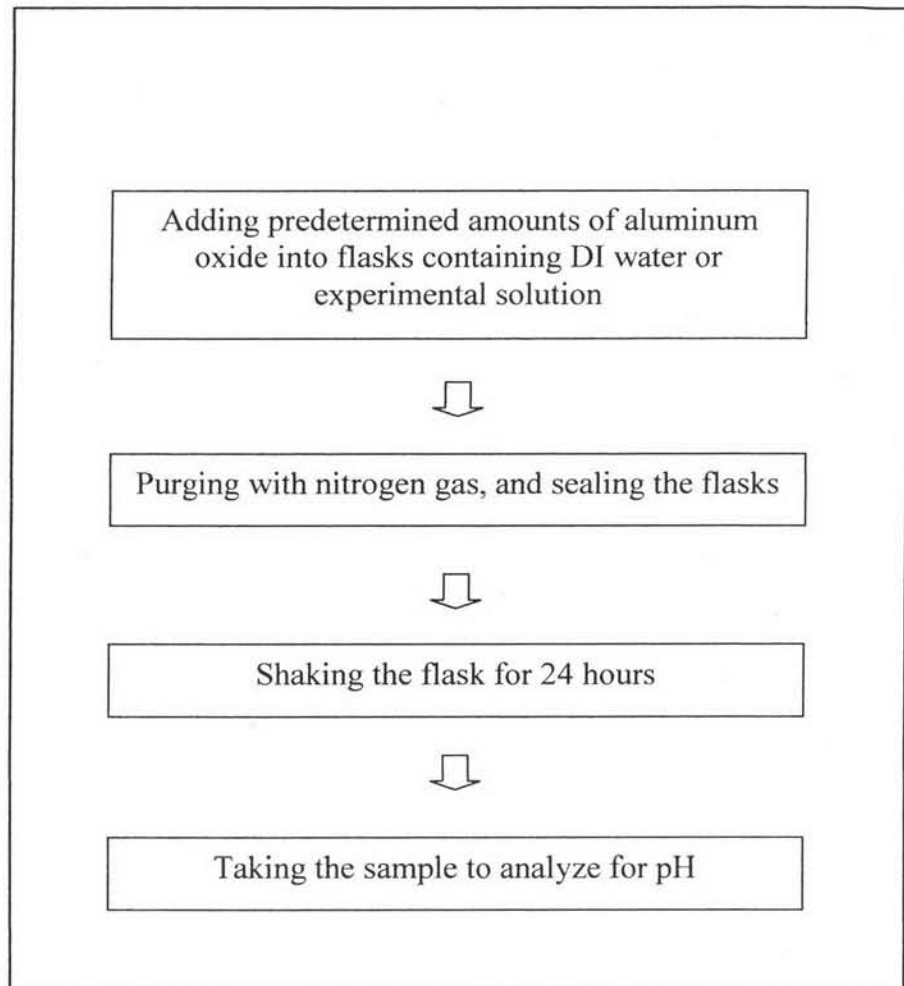


Figure 3.2 Experimental procedure chart of point of zero charge.

3.2.2 Fluidized-bed Fenton Experiment

Nitrobenzene stock solution was prepared with pure water at room temperature and was poured into a circulating fluidized-bed reactor. Then, they were diluted with pure water obtained from a Milli-Q/RO system (Millipore) which had a resistivity greater than 18 M Ω /cm. Next, the recycle pump was turned on to mix the solution at the desired bed expansions. After that, the desire pH was adjusted by 1:4 H₂SO₄ which took approximately 10 minutes before the pH reading was stable.

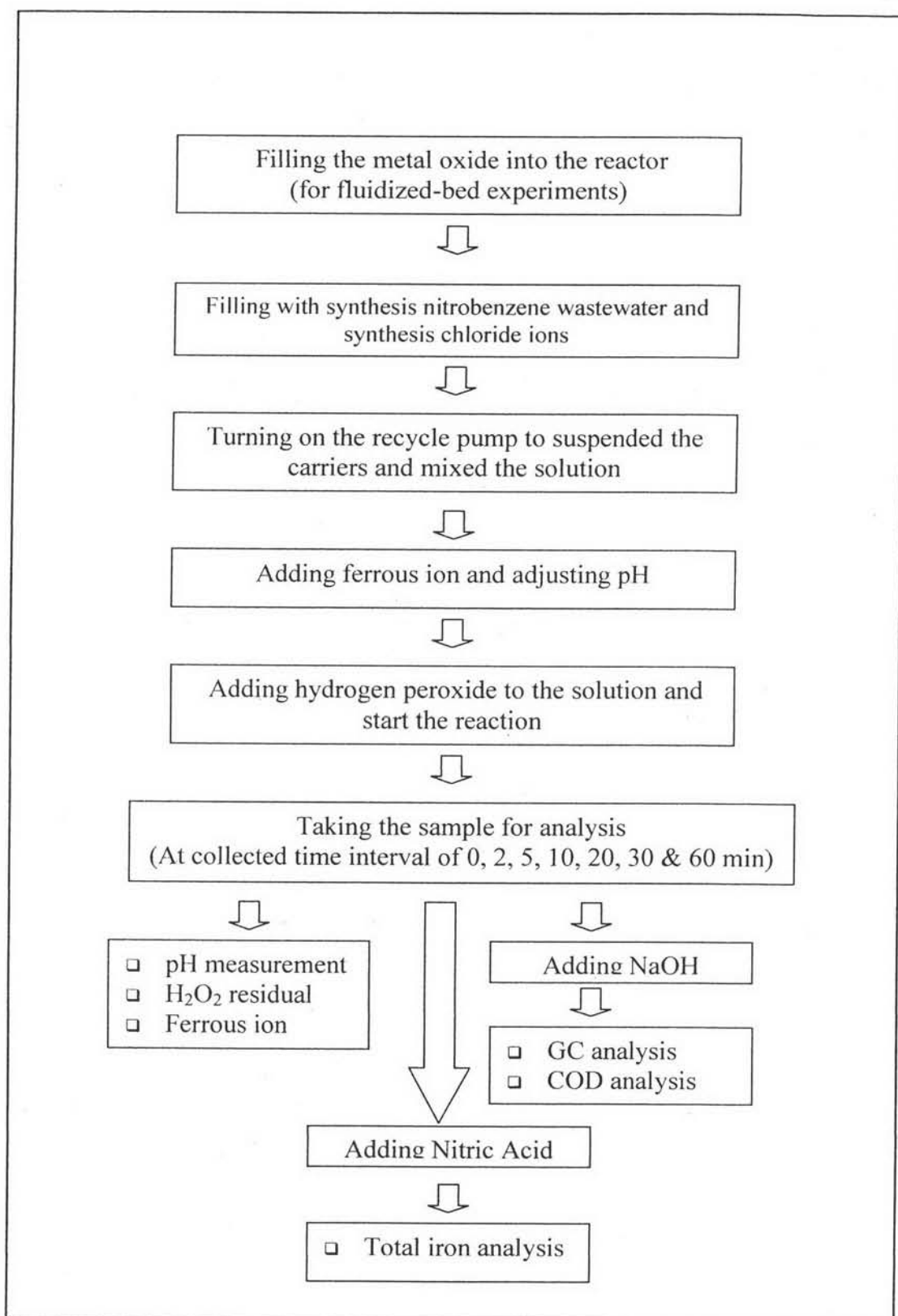


Figure 3.3 Experiment for Fenton and fluidized-bed Fenton process

Pre-calculated ferrous solution was added at the 5th minute after the recycle pump had been switched on. The solution was rechecked again before adding H₂O₂ solution and the reaction was simultaneously started. At selected time interval of 0, 2, 5, 10, 20, 30 and 60 minutes, sample was taken from the FBR and analyzed immediately. All experimental activities are as shown in Figure 3.3.

3.2.3. Fenton experiment

In this experiment, the procedures are all the same as previous section for fluidized-bed Fenton process, except for there is no metal oxide inside the reactor. Analysis parameters are also similar to those shown in Figure 3.3.

3.2.4. Reusability of Aluminum oxide

All procedures were carried out as the fluidized-bed Fenton experiment, only that, the aluminum oxide particles were reused again in every experimental cycle required.

3.3 Experimental Scenarios

The mainly conditions; 0.01 M of nitrobenzene, 0.05 M of hydrogen peroxide and 100 g of metal oxide in FBR was referred from the investigation of oxidation of nitrobenzene in fluidized-bed Fenton as the previous study of Sakulkitimasak (2004).

Scenario A

Point of zero charge of metal oxide with the mass titration technique as shown in Table 3.1.

Table 3.1 Details for scenario A

Material	Reaction time (hr)	Metal oxide (grams/100ml)	Media	Typical sample
Erlenmeyer flask	24	0, 0.2, 0.4, 0.6, 1.2, 2.4, 5, 10, 20 30, 40	SiO ₂ (0.84-2.00mm)	DI water
			Al ₂ O ₃ (2.50 mm, average size)	0.01M of nitrobenzene and 0.025 M of Na ₂ SO ₄

Scenario B

Determination of effect of aluminium oxide, silica oxide, Fe^{2+} and H_2O_2 on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.2 (control experiment, adsorption).

Table 3.2 Details for scenario B

Nitrobenzene (M)	pH	Metal oxide (grams)	Media type	Control parameter
0.01	2.80	100	SiO_2 (0.84-2.00mm)	Adsorption
				0.05M of H_2O_2
		0	Al_2O_3 (2.50mm, average size)	0.001M of Fe^{2+}

Scenario C

The comparison of different carriers between aluminium oxide (Al_2O_3) and silica oxide (SiO_2) on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.3.

Table 3.3 Effect of media type on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	H_2O_2 (M)	Fe^{2+} (M)	pH	Media	Cl^- (M)
0.01	0.05	0.001	2.80	SiO_2 (0.84-2.00mm)	0
					1.5×10^{-3}
				Al_2O_3 (2.50mm, average size)	2.0×10^{-2}
					2.0×10^{-1}

Scenario D

Determination of effect of pH on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.4.

Table 3.4 Effect of pH on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	Cl ⁻ (M)
0.01	2.5X10 ⁻⁴	0.05	2.0, 2.8, 3.5, 4.0, 5.0, 6.0	100	0
					1.5X10 ⁻³
					2.0X10 ⁻²
					2.0X10 ⁻¹

Scenario E

Determination of effect of media size on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.5.

Table 3.5 Effect of media size on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	H ₂ O ₂ (M)	Fe ²⁺ (M)	pH	Media
0.01	0.05	0.001	2.80	Al ₂ O ₃ (2.50mm, average size)
				Al ₂ O ₃ (3.50mm, average size)

Scenario F

Determination of effect of chloride ions and comparison between FBR and traditional Fenton process on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.6.

Table 3.6 Effect of chloride ions on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	Cl ⁻ (M)
0.01	1.0X10 ⁻³	0.05	2.80	100	0
					1.5X10 ⁻³
				0	2.0X10 ⁻²
					2.0X10 ⁻¹

Scenario G

Determination of effect of ferrous on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.7.

Table 3.7 Effect of ferrous on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	Cl ⁻ (M)
0.01	1.0X10 ⁻³	0.05	2.80	100	0
	0.5X10 ⁻³				1.5X10 ⁻³
	3.75X10 ⁻⁴				2.0X10 ⁻²
	2.5X10 ⁻⁴				2.0X10 ⁻¹

Scenario H

It is important to mention that the kinetic determination for Fluidized-bed Fenton Process in this section was performed based on the optimum pH, nitrobenzene and aluminium oxide at 2.8, 0.01 M and 100 g/l respectively as shown in Table 3.8-3.10.

Determination of effect of ferrous on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.8.

Table 3.8 Effect of ferrous at 0.2M of chloride ions on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	Cl ⁻ (M)
0.01	1.0X10 ⁻³	0.05	2.80	100	2.0X10 ⁻¹
	0.5X10 ⁻³				
	3.75X10 ⁻⁴				
	2.5X10 ⁻⁴				

Determination of effect of hydrogen peroxide on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.9.

Table 3.9 Effect of hydrogen peroxide on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	H ₂ O ₂ (M)	Fe ²⁺ (M)	pH	Aluminium oxide (grams)	Cl ⁻ (M)
0.01	1.0X10 ⁻¹	2.5X10 ⁻⁴	2.80	100	2.0X10 ⁻¹
	7.5X10 ⁻²				
	5.0X10 ⁻²				
	2.5X10 ⁻²				

Determination of effect of chloride ions on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.10.

Table 3.10 Effect of chloride ions on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Cl ⁻ (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)
0.01	0	2.5X10 ⁻⁴	0.05	2.80	100
	1.5X10 ⁻³				
	2.0X10 ⁻²				
	2.0X10 ⁻¹				

Scenario I

Determination of effect of carriers on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.11-3.13.

Determination of effect of initial amount of aluminium oxide media on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.11.

Table 3.11 Effect of initial amount of aluminium oxide media on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	H ₂ O ₂ (M)	Fe ²⁺ (M)	pH	Metal oxide (grams)
0.01	0.05	0.001	2.80	0
				25
				50
				75
				100

Determination of effect of initial reusability of aluminium oxide media on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.12.

Table 3.12 Effect of reusability of aluminium oxide media on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	H ₂ O ₂ (M)	Fe ²⁺ (M)	pH	Usable cycle
0.01	0.05	0.001	2.80	1
				2
				3
				4
				5

Determination of effect of iron recovery of aluminium oxide media on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.13.

Table 3.13 Iron recovery of aluminium oxide media on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	Aluminium oxide (grams)	H ₂ O ₂ (M)	pH	Method
0.01	1.0X10 ⁻³	100	0.05	2.80	Total Iron by ICP
	0.5X10 ⁻³				
	2.5X10 ⁻⁴				

Scenario J

Determination of effect of inorganic ions on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.14-3.15.

Determination of effect of dyhydrogen phosphate on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.14.

Table 3.14 Effect of dyhydrogen phosphate on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	H ₂ PO ₄ ⁻ (M)
0.01	1.0X10 ⁻³	0.05	2.80	100	0
					1.5X10 ⁻³
					2.0X10 ⁻²
					2.0X10 ⁻¹

Determination of effect of nitrate on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.15.

Table 3.15 Effect of nitrate on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	NO ₃ ⁻ (M)
0.01	1.0X10 ⁻³	0.05	2.80	100	0
					1.5X10 ⁻³
					2.0X10 ⁻²
					2.0X10 ⁻¹

Scenario K

Determination of effect of ferrous by COD analysis on the oxidation of nitrobenzene in fluidized-bed reactor with the condition as shown in Table 3.16.

Table 3.16 Effect of ferrous by COD analysis on the oxidation of nitrobenzene in FBR.

Nitrobenzene (M)	Fe ²⁺ (M)	H ₂ O ₂ (M)	pH	Aluminium oxide (grams)	Method
0.01	1.0X10 ⁻³	0.05	2.80	100	COD
	0.5X10 ⁻³				
	2.5X10 ⁻⁴				

3.4 Analytical Methods

3.4.1. Measurement of Nitrobenzene

Before the measurement, liquid samples were first filtered through 0.45 µm syring microfilters to separate precipitated iron from the solutions. Then, residual nitrobenzene was analyzed using a HP4890 gas chromatograph equipped with a flame ionization detector and an HP-5 column (0.53 mm in inside diameter, 15 m long). The samples were injected into an aqueous phase. The column temperature was initially set at 85 °C for 3 min, then increased by 65 °C per min to 200 °C and maintained at

this isothermal temperature for the final 5 min. Injector and detector temperatures were set at 250 °C and 250 °C, respectively.

3.4.2 Analysis of hydrogen peroxide concentration

The samples were analyzed by standard iodometric method in Appendix L.

3.4.3 Analysis of ferrous concentration

The samples were analyzed by phenanthroline method in Appendix B. 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.

3.4.4 Analysis of total 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 ICP from Perkin Elmer precisely company.

3.4.5 Other measurements

The pH measurement was carried out by a SUNTEX TS-1 Digital pH/MV meter. COD was measured by closed reflex titrimetric method.