



Chapter 3

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

3.1.2 Experimental Chemicals and Materials

Reactive black5 ($\text{C}_{26}\text{H}_{25}\text{N}_5\text{O}_{19}\text{S}_{6.4}\text{Na}$), reactive orange16 ($\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_{11}\text{S}_{3.2}\text{Na}$) and reactive blue2 ($\text{C}_{29}\text{H}_{20}\text{ClNa}_3\text{N}_7\text{O}_{11}\text{S}_3$) were purchased from Sigma-Aldrich Company. Ferrous Sulfate Hepta-hydrated ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 35% Hydrogen Peroxide (H_2O_2) were purchased from the Merck Company. All chemical substances are reagent grade. The carriers in the fluidized-bed reactor was silica oxide (SiO_2) has grain shape with 0.84 – 2.00 mm of particle diameter.

- Reactive black 5 (Fig 3.1)

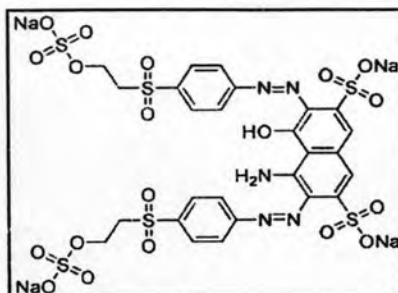


Figure 3.1 Structure of Reactive Black 5 (Sigma-Aldrich Co., 2006)

CI Name	: Reactive Black 5
Synonym	: Remazol Black B
Chemical Name	: 2,7-naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis ((4-((2(sulfoxy)ethyl) sulfonyl)phenyl)azo)-tetrasodium salt
Molecular Formula	: $C_{26}H_{25}N_5O_{19}S_{6.4}Na$
Molecular Weight	: 991.82 g/mol
Melting Point	: 300 °C
λ_{max}	: 597 nm

- Reactive orange 16 (Fig 3.2)

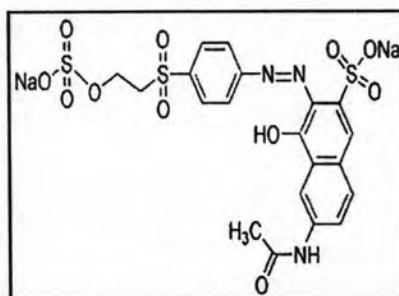


Figure 3.2 Structure of Reactive Orange 16 (Sigma-Aldrich Co., 2006)

CI Name	: Reactive Orange 16
Synonym	: Remazol Brilliant Orange 3R
Molecular Formula	: $C_{20}H_{19}N_3O_{11}S_{3.2}Na$
Molecular Weight	: 617.54 g/mol
Melting Point	: 300 °C
λ_{max}	: 388 nm, 494 nm (2nd)

- Reactive blue 2 (Fig 3.3)

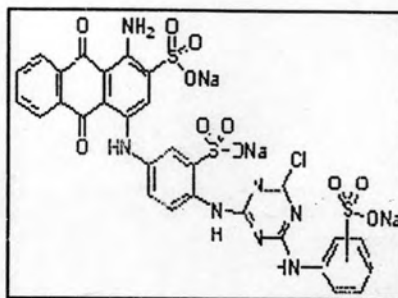


Figure 3.3 Structure of Reactive Blue 2 (Sigma-Aldrich Co., 2006)

CI Name	: Reactive Blue 2
Synonym	: Basilen blue E-3G
Chemical Name	: 1-Amino-4-[[4-[[4-chloro-6-[[3 (or 4)-sulfophenyl]amino]-1,3,5-triazin-2-yl]amino]-3-sulfophenyl]amino]-9,10-dihydro-9,10-dioxo-2-anthracenesulfonic acid
Molecular Formula	: $C_{29}H_{20}ClNa_3N_7O_{11}S_3$
Molecular Weight	: 840.10 g/mol
λ_{max}	: 615 nm

3.1.3 Fluidized-bed Reactor

A 1.35-litres fluidized-bed reactor (FBR) was operated in all experiments. Fluidized-bed reactor, the cylinder reactor consists of outlet, inlet and recirculating sections. The figure of fluidized-bed reactor is shown in Figure 3.1. The carriers was fluidized by adjustment the internal circulation at 50% bed expansion. (Chou et al., 2004)

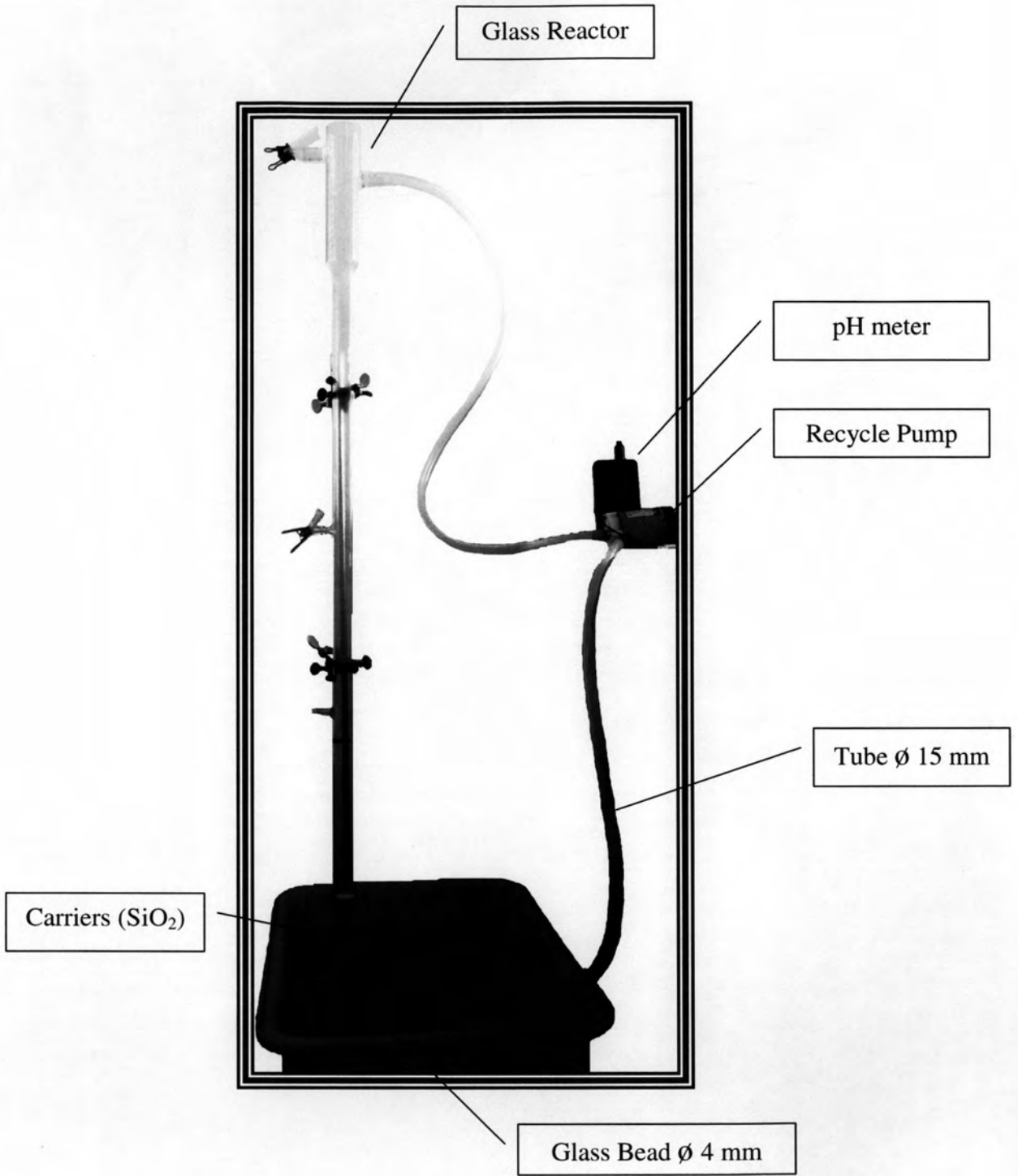


Figure 3.4 Fluidized-bed reactor (FBR) compartments (I)

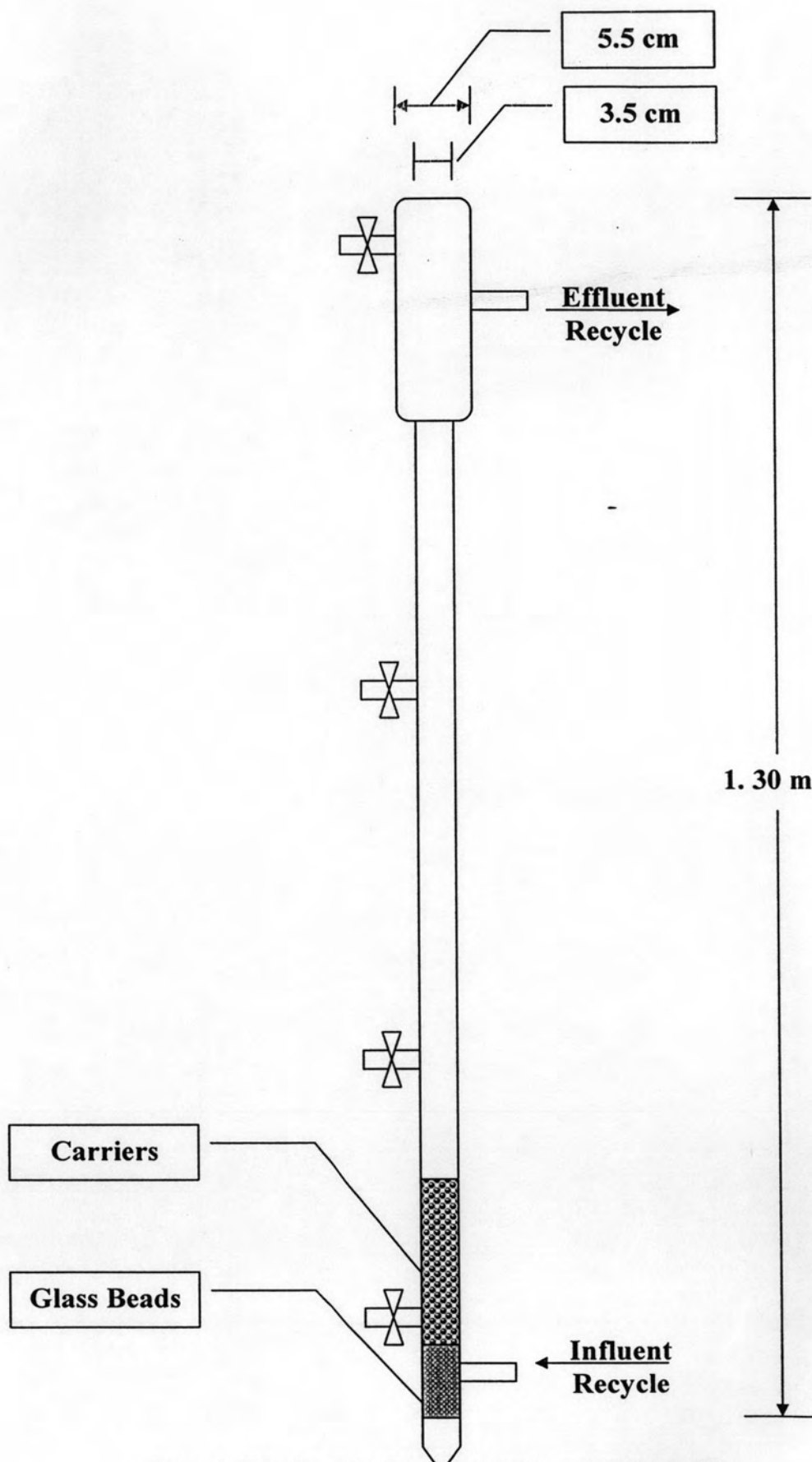


Figure 3.5 Fluidized-bed reactor (FBR) compartments (II)

3.2 Experimental Scenarios

3.2.1 Experimental Procedures

In this experiment, the silica oxide particles were added initially into the reactor and followed by synthetic dyeing wastewater and wastewater from textile factory. Then, the recycle pump was turned on to suspended the silica oxide and mix the solution. pH was adjusted to 3.0 ± 0.2 (Hsueh et al., 2005) by an addition of H_2SO_4 which took approximately 10 minutes before the pH reading was stable. Ferrous solution was added at the 5th minute after the recycle pump had been turned on. The solution pH was rechecked again prior to the addition of H_2O_2 solution and the reaction was simultaneously started. At selected time interval of 0, 2, 5, 10, 25, 50 and 100 minutes, some samples was withdrawn from the reactor and analyzed immediately for residual H_2O_2 , color, COD and ferrous ion. All experimental activities can be summarized as shown in Figure 4.3.

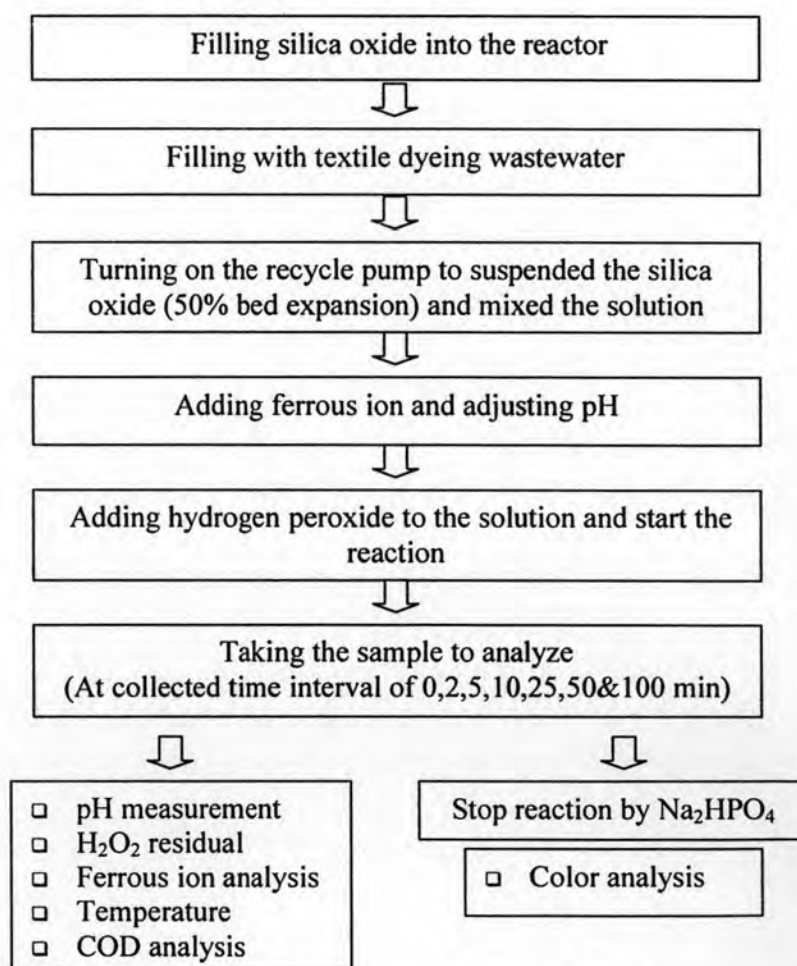


Figure 3.6 Experimental activity chart for fluidized-bed Fenton process

3.2.2 Experimental Scenarios

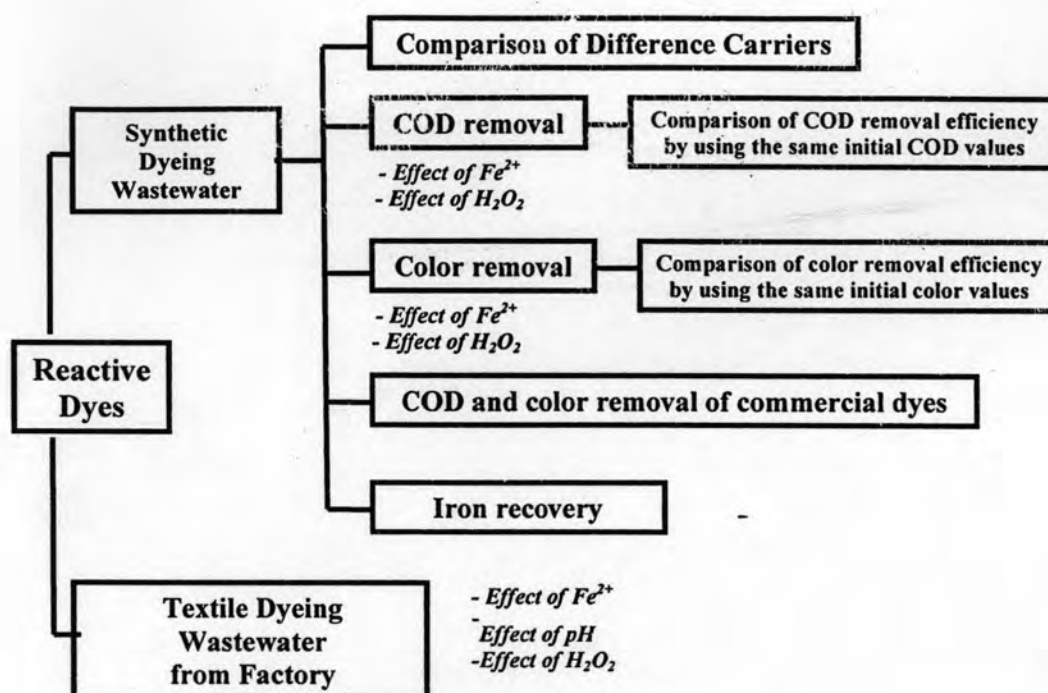


Figure 3.7 Schematic Diagram of Research Work

3.2.2.1 Synthetic Dyeing Wastewater

The reactive dyes, reactive black 5, reactive orange 16 and reactive blue 2 were used in this research.

The degradation of reactive dyes 0.1 mM (Hsueh et al., 2005) was carried out in lab scale fluidized-bed reactor of 1.35 liters. The fluidized-bed reactor consists of outlet, inlet and recirculation compartment. Experiments were conducted at room temperature. The carriers used in this study is sand (SiO₂), the diameter range is 0.84 to 2.00 mm. The carriers 74.07 g/l were packed in the FBR. Dyes stock solution, FeSO₄ and H₂O₂ were added into the reactor, and adjusted pH with H₂SO₄ and NaOH solution. The reaction was initiated by adding H₂O₂. Samples of the reaction were withdrawn at regular intervals; the reaction was then blocked by adding Na₂HPO₄ 0.01 M (Liou et al., 2004). Taking samples was withdrawn from the reactor and analyzed immediately for residual H₂O₂, color and COD.

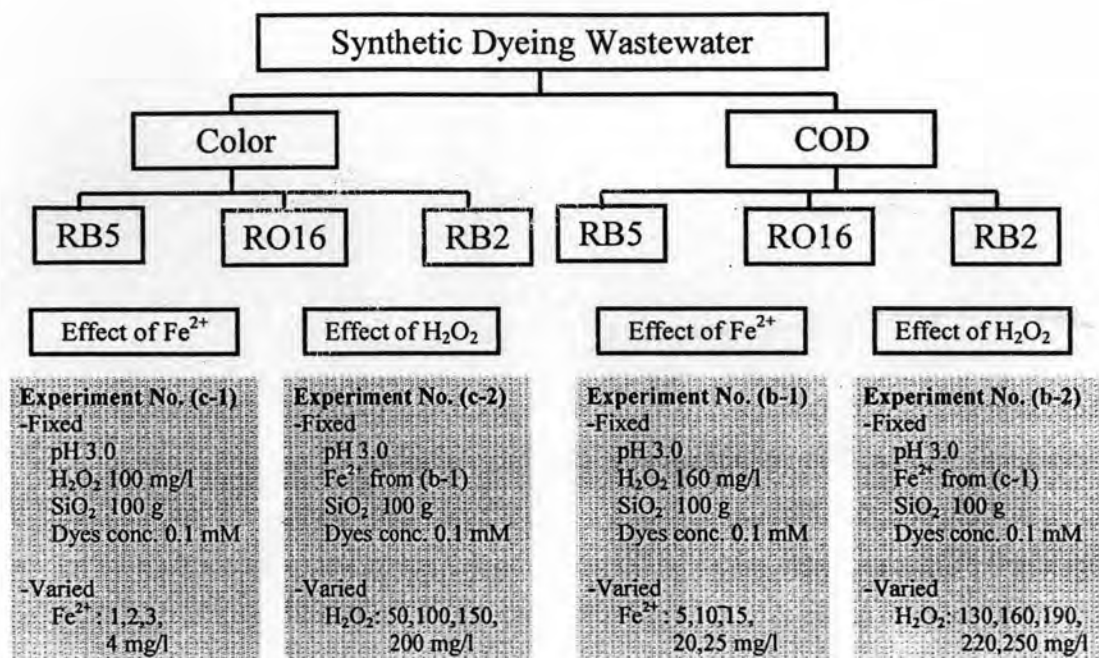


Figure 3.8 Schematic Diagram of synthetic dyes wastewater

The experiment was In this experiment, Concentration of 0.1mM dyes will be used because it corresponded to the level of pollution found in strongly colored polluted waters located close to textile manufacturing sites (Hsueh et al., 2005). The optimum pH for Fenton reactions for treating azo dyes in the study of Hsueh et al. (2005) are about pH 3.0. So, pH in this experiment was fixed at 3.0. First, the amount of SiO₂ will be fixed 74.07 g/l because if the amount of the carriers is too much, effect of adsorption will be obvious.

a) Comparison of different carriers

a-1) Synthetic dyeing wastewater (Control Experiment) in fluidized-bed reactor with the condition as shown in the table.

Synthetic Dye 0.1 mM	pH	Silica oxide (74.07 g/l)		Control parameter
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	3.0±0.2	SiO ₂	Al ₂ O ₃	Adsorption

a-2) Comparison of different carriers with the condition.

Synthetic Dye 0.1 mM	pH	Silica oxide (74.07 g/l)		Fe ²⁺ (mg/l)	H ₂ O ₂ (mg/l)
Reactive Black 5	3.0±0.2	SiO ₂	Al ₂ O ₃	20	160
Reactive Orange 16				10	
Reactive Blue 2				15	

b) Investigation of COD removal efficiency for synthetic dyeing wastewater

b-1) Investigation of COD removal efficiency with vary the initial concentrations of Fe^{2+}

The optimal H_2O_2 dosage to COD removal is calculated based on the disproportion of H_2O_2 to provide 0.5 mole O_2 per mole H_2O_2 .

COD removal : H_2O_2 = 1 : 2.1 (weight concentration) (Chou et al., 2003)

COD of synthetic dyeing wastewater is about 80 mg/l. So, concentration of H_2O_2 by calculation is about 160 mg/l. And Concentration of Fe^{2+} varied from 5 to 25 mg/l due to the study of Powell et al., cited in Viphanphong, W. (1997) investigated the removal of color and TOC from segregated dye using ozone and Fenton's reagent suggested that the ratio of H_2O_2 and Fe^{2+} should be 10:1.

Synthetic Dye 0.1 mM	H_2O_2 (mg/l)	Silica oxide (g/l)	pH	Fe^{2+} (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	160	74.07	3.0±0.2	5
				10
				15
				20
				25

b-2) Investigation of COD removal efficiency with vary the initial concentrations of H_2O_2

Synthetic Dye 0.1 mM	Fe^{2+} (mg/l)	Silica oxide (g/l)	pH	H_2O_2 (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	Optimum from (b-1)	74.07	3.0±0.2	130
				160
				190
				220
				250

b-3) Comparison of COD removal efficiency by using the same initial COD values

COD of dyes 60 mg/l	H_2O_2 (mg/l)	Silica oxide (g/l)	pH	Fe^{2+} (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	160	74.07	3.0±0.2	20

c) Investigation of color removal efficiency for synthetic dyeing wastewater

c-1) Investigation of color removal efficiency with vary the initial concentrations of Fe^{2+}

In this experiment, Concentration of Fe^{2+} will be used from 1 mg/l until the color removal will be less than 400 ADMI units which it is discharge standard of Taiwan. Because the study of Hsueh et al. (2005), the experiment conditions: H_2O_2 dose of 100 mg/l, Fe^{3+} dosage varied from 0 to 10 mg/l, there is almost no difference between 1 and 10 mg/l of Fe^{3+} for the dye decolorization during a 1h reaction time. Additionally, the results show that dye decolorization can occur at very low iron concentrations (1 mg/l) in both Fenton-like and Fenton reactions.

Synthetic Dye 0.1 mM	H_2O_2 (mg/l)	Silica oxide (g/l)	pH	Fe^{2+} (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	100	74.07	3.0±0.2	1
				2
				3
				4
				5

c-2) Investigation of color removal efficiency with vary the initial concentrations of H_2O_2

Concentration of H_2O_2 will be varied until the color removal efficiency until a critical H_2O_2 concentration is achieved. Because when a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect. (Hsueh et al., 2005)

Synthetic Dye 0.1 mM	Fe^{2+} (mg/l)	Silica oxide (g/l)	pH	H_2O_2 (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	Optimum from (c-1)	74.07	3.0±0.2	50
				100
				150
				200

c-3) Comparison of color removal efficiency by using the same initial color values

color of dyes 6500 ADMI units	H_2O_2 (mg/l)	Silica oxide (g/l)	pH	Fe^{2+} (mg/l)
Reactive Black 5 Reactive Orange 16 Reactive Blue 2	100	74.07	3.0±0.2	2

d) COD and color removals of synthetic commercial dyeing wastewater

Dyes 100 mg/l	H ₂ O ₂ (mg/l)	Silica oxide (g/l)	pH	Fe ²⁺ (mg/l)
Black B Blue ER-A Orange BR2	160	74.07	3.0±0.2	20

e) Iron recovery

Synthetic Dye 0.1 mM	H ₂ O ₂ (mg/l)	Silica oxide (g/l)	pH	Fe ²⁺ (mg/l)
Reactive Black 5	160	74.07	3.0±0.2	20
				50
				75
				100

3.2.2.2 Industrial Wastewater**f) Investigation of COD and color removal efficiency with vary the initial concentrations of Fe²⁺**

Target	Silica oxide (g/l)	pH	[COD]:[Fe ²⁺]:[H ₂ O ₂]
Industrial Wastewater	74.07	3.0±0.2	1 : 0.32 : 3.17
			1 : 0.63 : 3.17
			1 : 0.95 : 3.17
			1 : 1.27 : 3.17
			1 : 1.59 : 3.17

g) Investigation of COD and color removal efficiency with vary the initial pH

Target	[COD]:[Fe ²⁺]:[H ₂ O ₂]	Silica oxide (g/l)	pH
Wastewater from textile factory	Optimum from (f)	74.07	2.0±0.2
			3.0±0.2
			4.0±0.2
			5.0±0.2

h) Investigation of COD and color removal efficiency with vary the initial concentrations of H₂O₂

Target	Silica oxide (g/l)	pH	[COD]:[Fe ²⁺]:[H ₂ O ₂]
Wastewater from textile factory	74.07	Optimum from (g)	1 : 0.95 : 3.17
			1 : 0.95 : 4.76
			1 : 0.95 : 6.35
			1 : 0.95 : 7.94

3.3 Analytical Method

Parameter	Analytical Method	Standard Method
Color	Colorimetric (ADMI units)	2120E
COD	Closed Reflux Titrametric Method	5220C
Ferrous ion	Phenanthroline Method	3500
Hydrogen Peroxide	Standard Iodometric Method	4500