



CHAPTER III EXPERIMENTAL

The experimental apparatus was constructed to study the Fenton process for the wastewater treatment. The operating temperature for Fenton was 25°C. This section composes of the details of materials, experimental apparatus, and experiment. Moreover, the concentration of each component had been predicted from the mathematical model which was compared with the experiments.

3.1 Materials

3.1.1 Experimental Chemicals

- Hydrogen peroxide of 30% v/v purity was obtained from Carlo Elba Reagent
- Ferrous sulfate was obtained from Labscan
- Ethanol was obtained from Carlo Elba Reagent Co.,Ltd.
- Isopropanol was obtained from Carlo Elba Reagent Co.,Ltd.

3.1.2 Reactant Gases

Air zero grade was obtained from Parex co.,Ltd.

3.2 Experimental Apparatus

The equipment set was designed which mainly composed of four-neck round bottle flask, liquid pump, and rotameter shown in Figure 3.1. 500 ml of simulated wastewater was composed of 1% wt ethanol and 0.2 %wt isopropanol in a four-neck round bottle flask. H₂O₂ 30% v/v was introduced to the flask using a microtube pump with controlled flow rates. Air flow rate was controlled by a rotameter. There were various parameters: hydrogen peroxide flow rate (30-70 ml/hr), air flow rate (1-2.35 l/min), and ferrous sulfate (0-0.015 g). The suitable pH was 3.0. Samples were collected to examine COD/TOC value and the concentration of each component.

Hydrogen peroxide was used as an oxidant. Hydrogen peroxide was converted to hydroxyl radicals (OH^\bullet) which can destroy organic compounds to other. The flow rate of hydrogen peroxide was controlled by microtube pump, Tokyo Rikakikai co., EYELA with a range between 0-200 ml/hr.

Air zero was used to remove some volatile organic compounds. The flow rate was measured by using a rotameter with a range between 0 to 6 l/min.

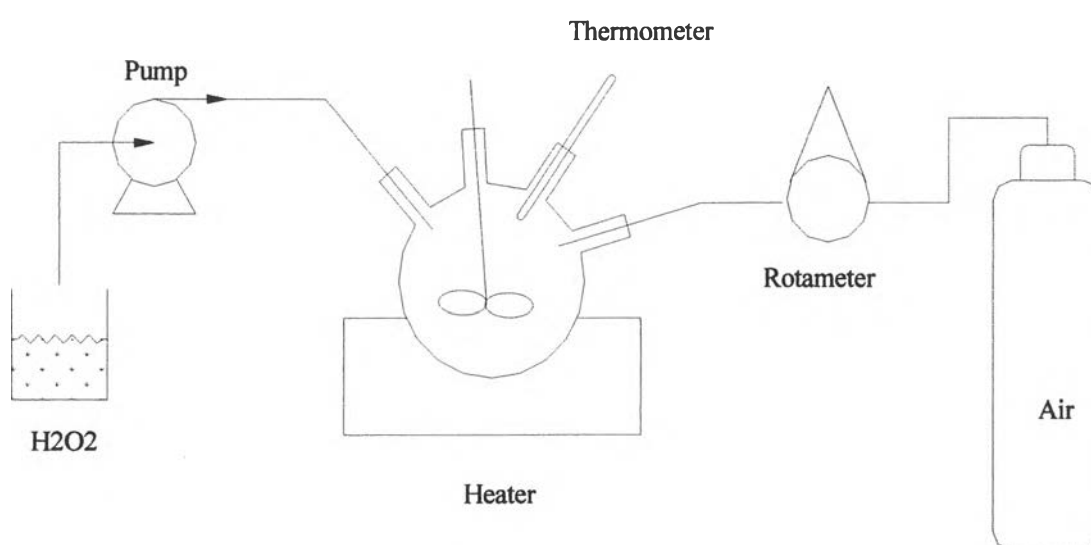


Figure 3.1 Design and Experimental Setup

3.2.1 Wastewater Preparation

The simulated wastewater was prepared by addition of 1% wt ethanol and 0.2 %wt isopropanol into 500 ml distilled water.

3.2.2 Fenton Process

Four parameters were varied: temperature, hydrogen peroxide flow rate (30-70 ml/hr), air flow rate (1-3 l/min), and ferrous sulfate (0-0.015 g) in order to examine optimum conditions for the operation. Firstly, the simulated wastewater was added into a four-neck round bottle. The pH of wastewater was adjusted to 3.0 by using 1M nitric acid. Ferrous sulfate was added into the simulated wastewater. Air and 30% v/v hydrogen peroxide was added into the simulated wastewater, and

the experiment was begun. Samples were taken and measured for COD/TOC and concentration of each component.

3.3 Analytical Part

3.3.1 Total Organic Carbon (TOC)

TOC was used to determine the quantity of organically bound carbon. TOC methods utilized heat and oxygen, ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide(CO₂). The CO₂ can be measured directly by nondispersive infrared analyzer, or it can be reduced to methane and measured with a flame ionization detector. TOC was measured by Shimadzu TOC-5000A.

3.3.2 Chemical Oxygen Demand (COD)

COD was used as a measurement of the oxygen equivalent of the organic matter content of a sample that was susceptible to oxidation by a strong chemical oxidant. COD was measured by PC compact from Lovibond and Tintometer. It was composed of the reactor and photometer.

3.2.3 Gas Chromatography (GC)

Gas chromatography is a chromatographic technique that can be used to separate volatile organic compounds. A gas chromatograph consists of a flowing mobile phase, an injection port, a separation column containing the stationary phase, and a detector. The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column. Gas Chromatography Hewlett Packard Series II 5990 was used to measure the concentration of each component in the wastewater.

3.4 Modeling

Advanced Oxidation Process (AOP) in this work combined Fenton process and air evaporation. A mathematical model was composed of two parts: evaporation and chemical oxidation. In order to solve ordinary differential equations (ODE), the Euler method was used to solve these two equations using computer program writing in Fortran language.

3.4.1 Evaporation

The change in concentration with time for each principle organic contaminant was estimated by

$$\frac{-d[CC_i]}{dt} = \left(\frac{Q}{22.4}\right)\left(\frac{M_i}{m_w}\right)(y_i) \quad (3.1)$$

where Q = air flow rate (STP), L/min,
 y_i = mole fraction of component i in the vapor phase,
 M_i = molecular weight of component i , grams/mol
 m_w = mass of water, grams, and
 $[CC_i]$ = concentration of organic component i in the liquid phase, mole/l.

It was assumed that deaeration of dissolved organics was not a part contributed to the total volumetric flow rate of the stripping air. Furthermore, assuming that equilibrium existed in the reaction vessel between the vapor and liquid phases of the organic contaminants, the mole fraction in the vapor phase of each contaminant was found to be related to its mole fraction in the liquid phase by the well established relationship.

$$y_i = \frac{P_i^{vap} x_i \gamma_i}{P} \quad (3.2)$$

where P_i^{vap} = vapor pressure of component i , atm,
 x_i = mole fraction of component i in the liquid phase,
 γ_i = activity coefficient of component i , and

P = total pressure, atm.

Equation (3.2) accounts for the non-idealities in the liquid phase through the use of activity coefficient. The vapor phase non-idealities were not considered in this model. It was further assumed that isothermal and isobaric condition existed in this reactor for entire treatment period. The liquid phase mole fraction was related to the concentration in the liquid phase as

$$x_i = \frac{M_w[CC_i]}{M_i} \quad (3.3)$$

where M_w = molecular weight of water

Using Equation (3.2) and (3.3), Equation (3.1) was modified as

$$\frac{-d[CC_i]}{dt} = \left(\frac{Q}{22.4}\right)\left(\frac{M_w}{m_w}\right)\left(\frac{P_i^{vap}}{P}\right)[CC_i]\gamma_i \quad (3.4)$$

The vapor pressure in Equation (3.4) was estimated by the Antoine equation:

$$\ln(P_i^{vap}) = A_i - \frac{B_i}{T + C_i} \quad (3.5)$$

In Equation (3.5), A_i , B_i , C_i are the Antoine constants, and T is the absolute temperature in kelvins. The Antoine equation takes into account the temperature dependence of equilibrium, while the activity coefficient depend on both the temperature as well as the composition of the wastewater.

Temperature and pressure were assumed to be fixed values in the model. Activity coefficient of the individual contaminant was also a constant value due to low concentration of contaminant.

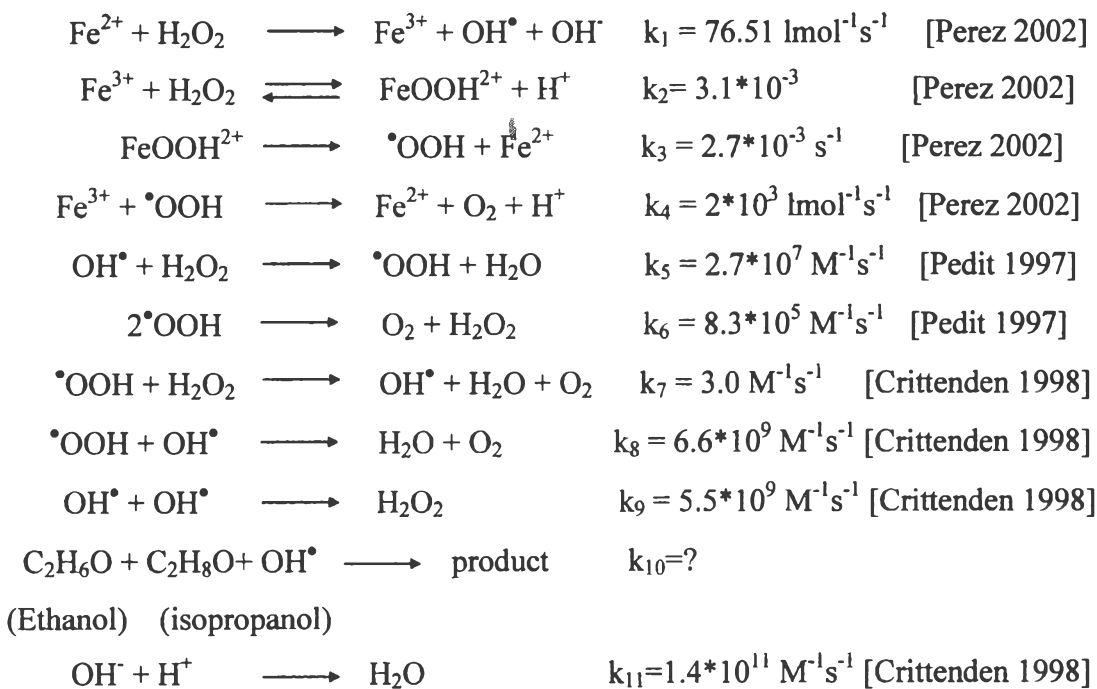
3.4.2 Chemical Oxidation

The oxidation of organic components by the oxidizing species was showed in Equation (3.6) with respect to the organic components, hydroxyl radicals, and the orders of reaction.

$$\frac{-d[CC_i]}{dt} = k[\text{ethanol}]^\alpha [\text{isopropanol}]^\beta [\text{OH}^\bullet]^{\gamma} \quad (3.6)$$

where $[CC_i]$ = concentration of organic species, mol/L,
 k = reaction rate constant, L/mol/min
 $[\text{OH}^\bullet]$ = concentration of hydroxyl radical, mol/L

The hydroxyl radical was calculated from the mechanism:



Based on the above mechanism, the overall elementary kinetic rate expressions can be written. These species include: Fe^{2+} , Fe^{3+} , OH^\bullet , FeOOH^{2+} , H^+ , OH^- , $\bullet\text{OOH}$, H_2O_2 , ethanol, and isopropanol.

$$\begin{aligned} d[\text{Fe}^{2+}]/dt &= -k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] + k_3[\text{FeOOH}^{2+}] + k_4[\text{Fe}^{3+}][\bullet\text{OOH}^\bullet] \\ d[\text{Fe}^{3+}]/dt &= k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_2\{[\text{FeOOH}^{2+}][\text{H}^+] - [\text{Fe}^{3+}][\text{H}_2\text{O}_2]\} \\ &\quad + k_4[\text{Fe}^{3+}][\bullet\text{OOH}^\bullet] \\ d[\text{OH}^\bullet]/dt &= k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_5[\text{OH}^\bullet][\text{H}_2\text{O}_2] + k_7[\bullet\text{OOH}^\bullet][\text{H}_2\text{O}_2] \end{aligned}$$

$$\begin{aligned}
& -k_9[\text{OH}^\bullet]^2 - k_{10}[\text{ethanaol}][\text{isopropanol}][\text{OH}^\bullet] \\
d[\text{FeOOH}^{2+}]/dt &= k_2\{[\text{FeOOH}^{2+}][\text{H}^+] - [\text{Fe}^{3+}][\text{H}_2\text{O}_2]\} - k_3[\text{FeOOH}^{2+}] \\
d[\text{H}^+]/dt &= k_2\{[\text{FeOOH}^{2+}][\text{H}^+] - [\text{Fe}^{3+}][\text{H}_2\text{O}_2]\} + k_4[\text{Fe}^{3+}][\text{OOH}^\bullet] \\
& - k_{11}[\text{H}^+][\text{OH}^-] \\
d[\text{OOH}^\bullet]/dt &= k_3[\text{FeOOH}^{2+}] - k_4[\text{Fe}^{3+}][\text{OOH}^\bullet] + k_5[\text{OH}^\bullet][\text{H}_2\text{O}_2] \\
& - k_6[\text{OOH}^\bullet]^2 - k_7[\text{OOH}^\bullet][\text{H}_2\text{O}_2] - k_8[\text{OOH}^\bullet][\text{OH}^\bullet] \\
d[\text{OH}^-]/dt &= k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_{11}[\text{H}^+][\text{OH}^-] \\
d[\text{H}_2\text{O}_2]/dt &= -k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_2\{[\text{FeOOH}^{2+}][\text{H}^+] - [\text{Fe}^{3+}][\text{H}_2\text{O}_2]\} \\
& - k_5[\text{OH}^\bullet][\text{H}_2\text{O}_2] + k_6[\text{OOH}^\bullet]^2 - k_7[\text{OOH}^\bullet][\text{H}_2\text{O}_2] \\
& + k_9[\text{OH}^\bullet]^2 - k_{10}[\text{ethanaol}][\text{isopropanol}][\text{OH}^\bullet] \\
& + v_0\{[\text{H}_2\text{O}_2]_0 - [\text{H}_2\text{O}_2]\}/V \\
d[\text{ethanaol}]/dt &= k_{10}[\text{ethanaol}][\text{isopropanol}][\text{OH}^\bullet] - v_0[\text{ethanaol}]/V \\
d[\text{isopropanol}]/dt &= k_{10}[\text{ethanaol}][\text{isopropanol}][\text{OH}^\bullet] - v_0[\text{isopropanol}]/V
\end{aligned}$$

where v_0 = initial volume of hydrogen peroxide, mL/min, and

V = volume of water, mL

Hydrogen peroxide was fed into the system at a constant flow rate, and this system was semi-batch.

For data collecting, samples were collected to examine the concentration of each component and COD/TOC. The concentration of hydroxyl radical was calculated from the mechanism. The values of k , α , and β were examined. FORTRAN program was written to solve the model equations. The graphs between the concentration of each component and time were plotted to compare the model and experimental data.