



CHAPTER IV

RESULTS AND DISCUSSION

There are many parameters which affect contaminant removal in Fenton: air flow rate, the concentration of ferrous ion and hydrogen peroxide. Moreover, the mathematical model for Fenton was studied and proposed to compare the results obtained from the model and from experiment. The details of results and discussion are presented in this chapter.

4.1 Fenton Process

4.1.1 The Effect of Air

In this study, the wastewater was simulated by the addition of ethanol 1%wt and isopropanol 0.2%wt in the distilled water. At the higher air flow rates, TOC remaining is less than at lower air flow rate as shown in Figure 4.1. % TOC remaining for the air flow rate of 1, 2, and 3 mL/hr at four hours are 90.7%, 83.4%, and 71.9%, respectively. Since ethanol and isopropanol are volatile organic compounds, air passing through in the wastewater could cause vaporization, and thus %TOC remaining decreased.

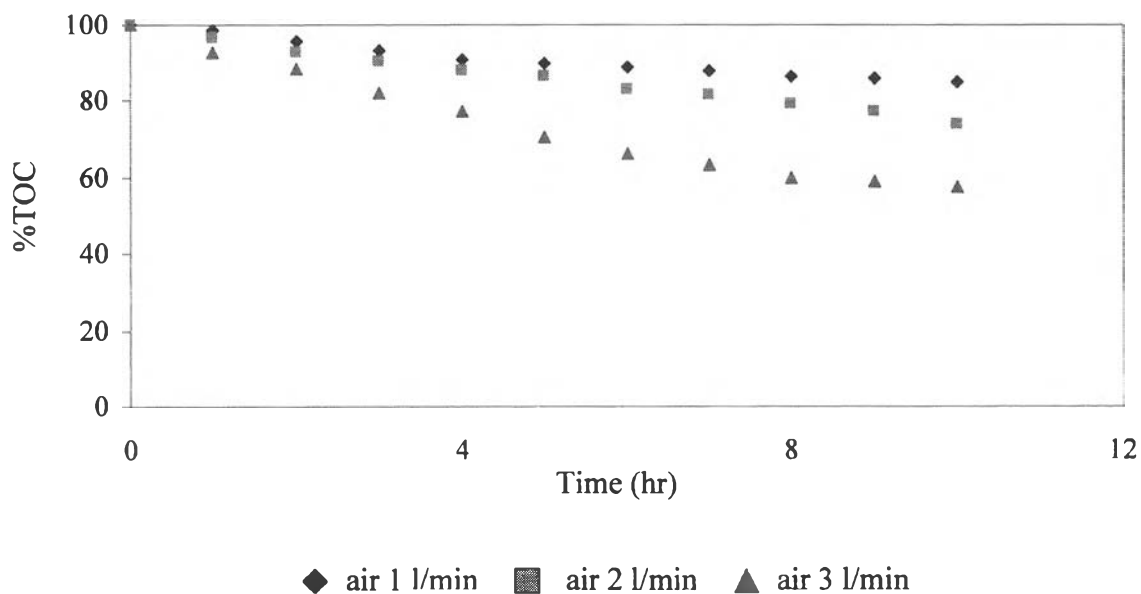


Figure 4.1 % TOC remaining along time-on-stream when the simulated wastewater was treated with air at different flow rates.

4.1.2 The Effect of Hydrogen Peroxide

When only hydrogen peroxide was added into the simulated wastewater at ambient temperature, TOC was reduced as shown in the Figure 4.2. %TOC remaining at ten hours for H_2O_2 at the flow rates of 15, 30, and 50 mL/hr are 84.8, 74.0, and 57.8, respectively. At higher H_2O_2 flow rate, %TOC decreased to a greater extent.

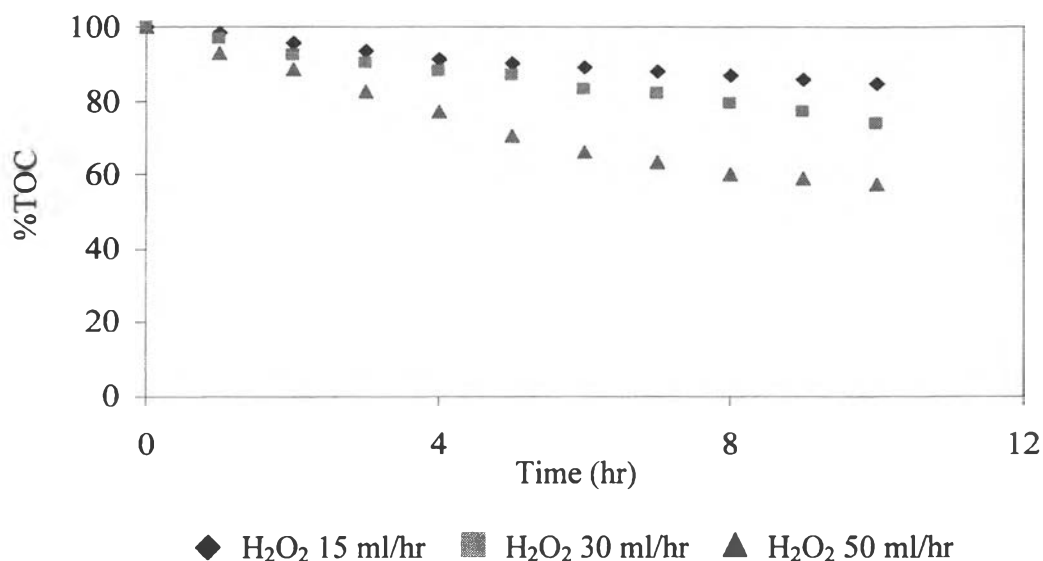


Figure 4.2 % TOC remaining along time-on-stream when the simulated wastewater was treated with hydrogen peroxide with different H₂O₂ flow rates.

4.1.3 The Effect of Air and Hydrogen Peroxide

When the air and hydrogen peroxide were added into the simulated wastewater at ambient temperature, TOC was reduced as shown in Figure 4.3. %TOC remaining at eight hours for H₂O₂ at the flow rates of 15, 30, and 50 ml/hr are 60.8%, 54.3%, and 47.0%, respectively. At the higher H₂O₂ flow rate, %TOC remaining did not decrease significantly. Hydrogen peroxide was converted to hydroxyl radicals which can reduce contaminants in the wastewater. As hydrogen peroxide flow rate increased, %TOC remaining decreased due to oxidation reaction and dilution. The results clearly showed that air and hydrogen peroxide affected the %TOC remaining. The higher air and hydrogen peroxide flow rates, the lower %TOC was obtained.

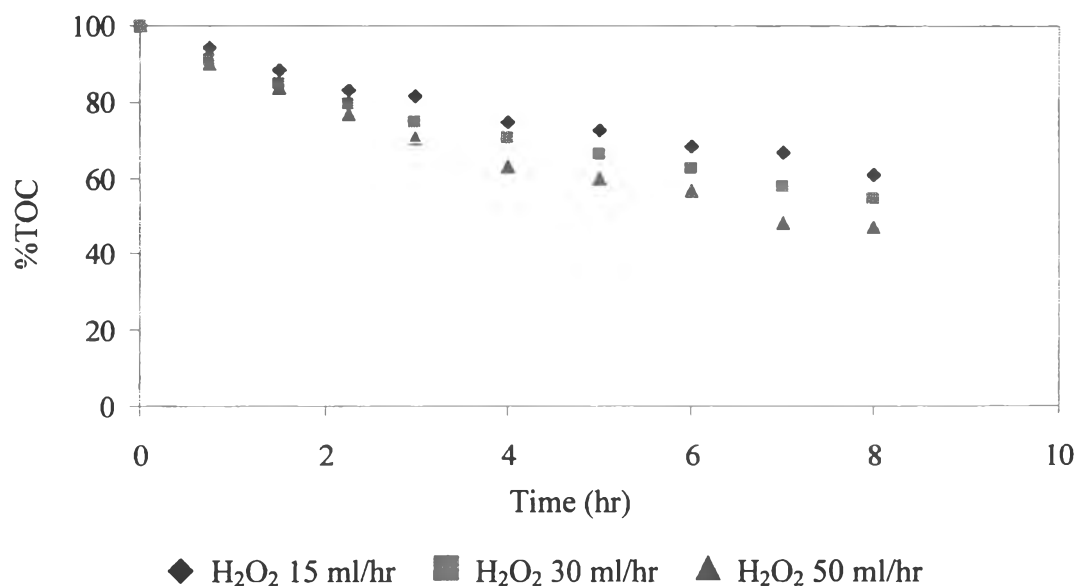


Figure 4.3 % TOC remaining along time-on-stream when the simulated wastewater was treated with air and hydrogen peroxide with different H₂O₂ flow rates (air flow rate 2 l/min).

4.1.4 Fenton Process (Batch)

For Fenton experiments, hydrogen peroxide and ferrous sulfate were added in the system. Ferrous sulfate was varied from 0 to 0.015 g. The initial concentration of hydrogen peroxide was 1 molar after being added. The temperature was 25°C. From Figure 4.4, % TOC remaining reduced dramatically because of adding hydrogen peroxide at first time and oxidation reaction. After that, %TOC decreased slightly and became constant. % TOC remaining for 0.0075, 0.015 g FeSO₄ at six hours are 86.64%, 87.17%, respectively. When ferrous sulfate created ferrous ion which reacted with hydrogen peroxide, hydroxyl radical was created. % TOC remaining decreased slightly when ferrous sulfate increased. Any increase in ferrous sulfate beyond this, % TOC remaining will not decrease due to precipitation.

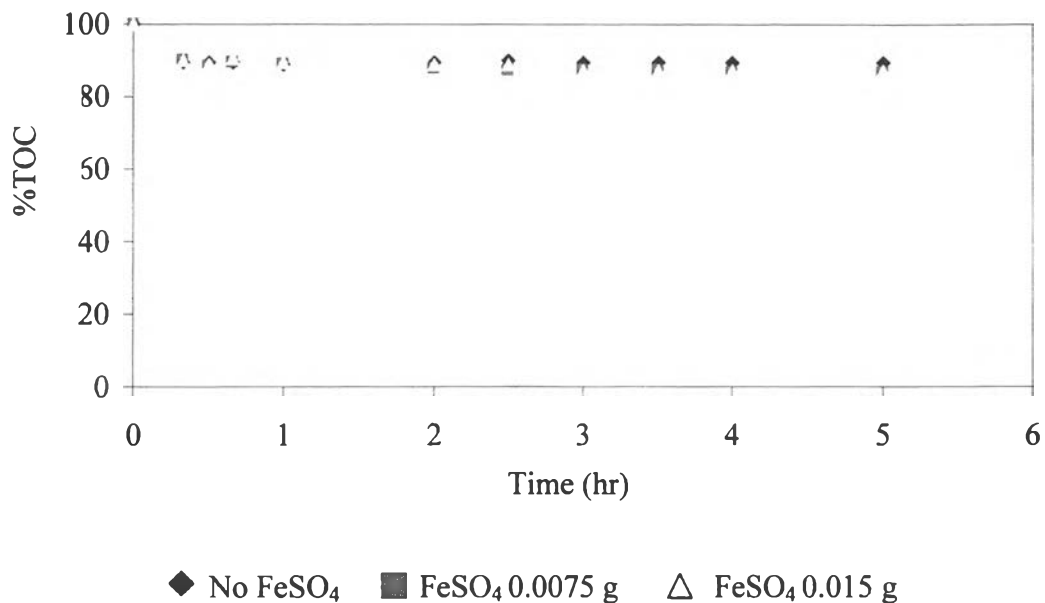


Figure 4.4 % TOC remaining along time-on-stream when the simulated wastewater was treated using Fenton process (batch) with different ferrous sulfate amounts

4.1.5 Fenton Process (Semi-Batch)

For Fenton process, hydrogen peroxide and ferrous sulfate were added in the system. H_2O_2 flow rate was fixed at 30 ml/hr. Ferrous sulfate was varied from 0 to 0.015 g. The temperature was set at 25°C. From Figure 4.5, %TOC remaining reduces. % TOC remaining when using 0, 0.003, 0.0075, 0.0113, 0.015 g of FeSO_4 at eight hours are 69.3%, 66.3%, 61.1%, 64.4%, and 69.2%, respectively. When FeSO_4 was added, %TOC remaining decreased more than the system without FeSO_4 . Moreover, when higher amounts of FeSO_4 were added, ferrous ions possibly reacted with hydroxyl radical, leading to precipitation. This was the reason why % TOC remaining of FeSO_4 0.0075 g was less than the other.

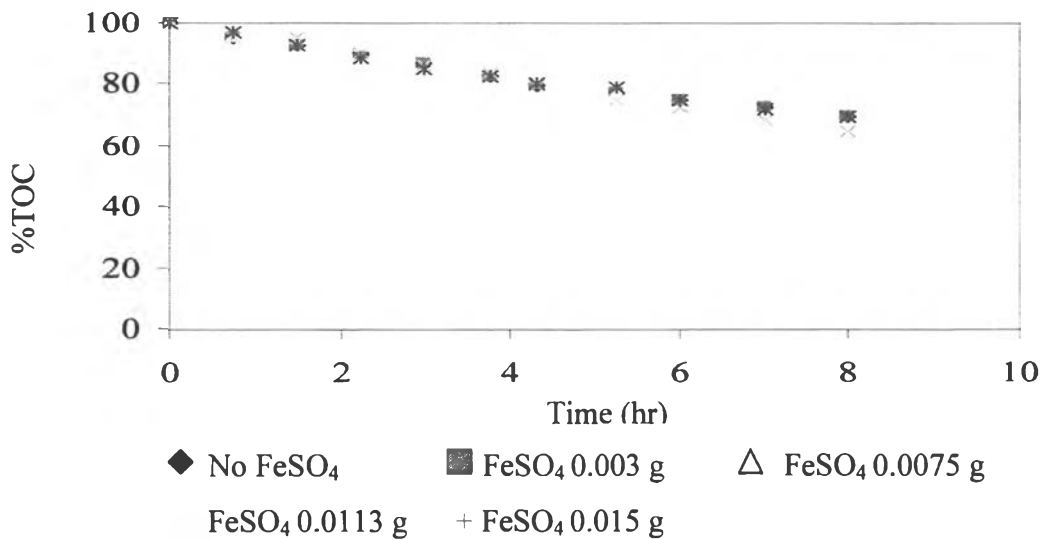


Figure 4.5 % TOC remaining along time-on-stream when the simulated wastewater was treated using Fenton process (semi-batch) with different ferrous sulfate amounts.

The concentration of ethanol and isopropanol decreased along time-on-stream as shown in Figures 4.6 and 4.7. When 0.0075 g of ferrous sulfate was added into the simulated wastewater, the concentrations of isopropanol were lowest at all times when compared among the systems with different amounts of ferrous sulfate. Adding more ferrous sulfate did not improve the removal efficiency, on the other hand, it decreased the efficiency of the process.

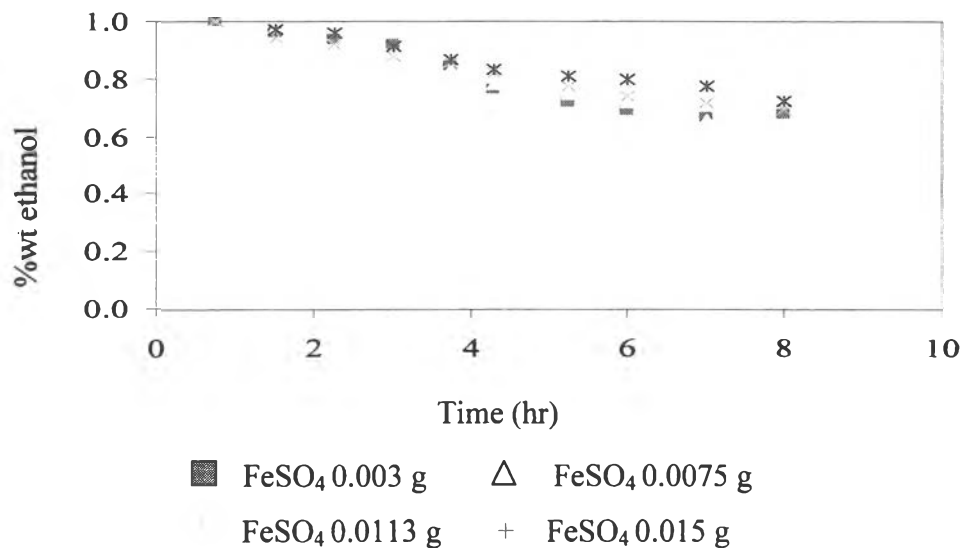


Figure 4.6 The concentration of ethanol along time-on-stream when the simulated wastewater was treated using Fenton process (semi-batch) with different ferrous sulfate amounts.

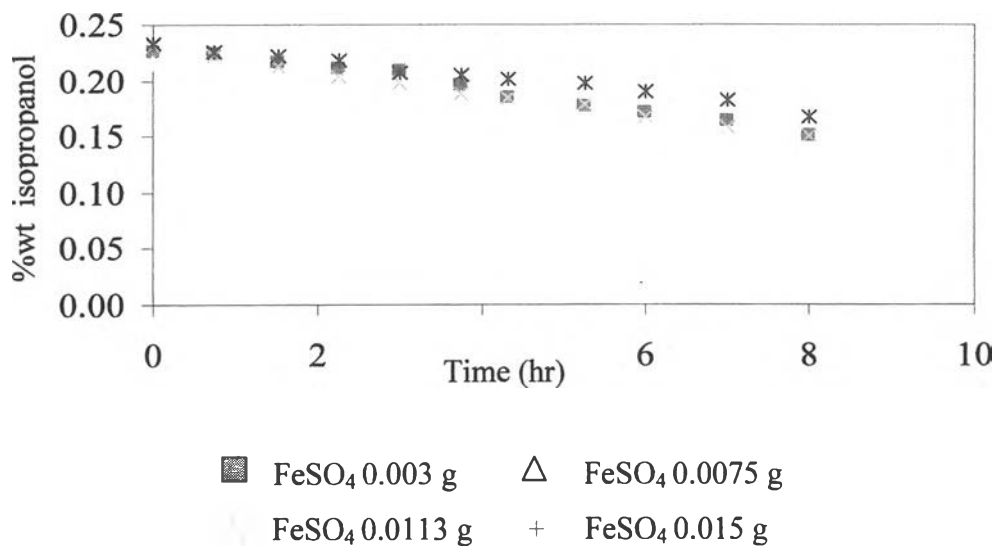


Figure 4.7 The concentration of isopropanol along time-on-stream when the simulated wastewater was treated using Fenton process (semi-batch) with different ferrous sulfate amounts.

4.1.6 Fenton/Air (Semi-Batch)

When air with the flow rate of 2 l/min and 30% v/v hydrogen peroxide with the flow rate of 30 ml/hr were fed in the Fenton system at the ambient temperature, %TOC remaining reduced dramatically and became constant after five hours as shown in Figure 4.8. From Figures 4.5 and 4.8, %TOC remaining of Fenton/Air reduced more than when only Fenton process was employed. Addition of air increased %TOC removal efficiency. With 0.003 g ferrous sulfate, %TOC remaining was the lowest. If ferrous sulfate was added more than 0.003 g, %TOC remaining at eight hours would be higher. Percent ethanol and isopropanol remaining in Figures 4.9 and 4.10 decreased along with time similar to %TOC removal.

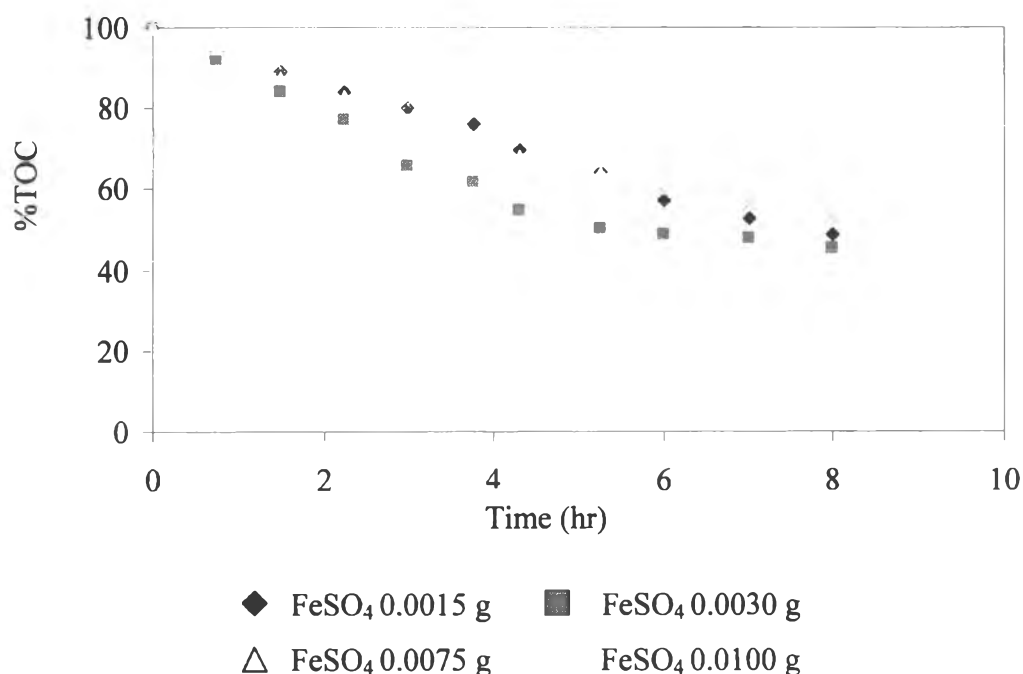


Figure 4.8 % TOC remaining along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different ferrous sulfate amounts.

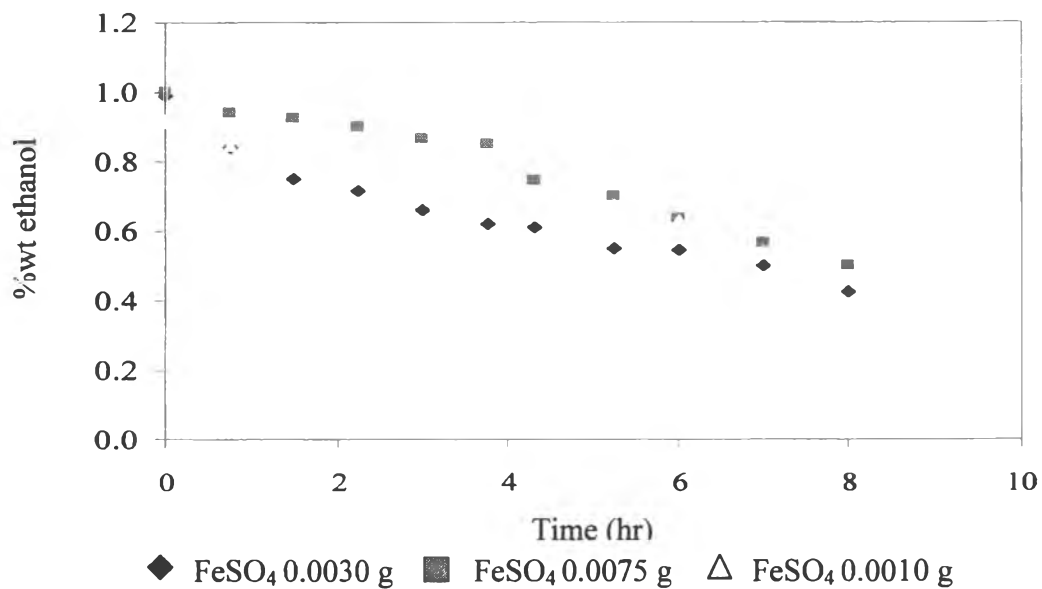


Figure 4.9 The concentration of ethanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different ferrous sulfate amounts.

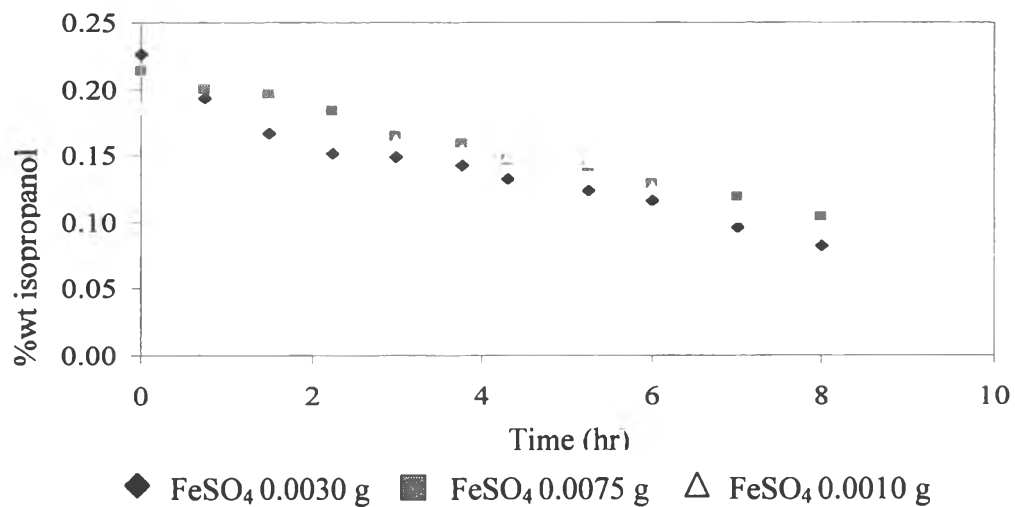


Figure 4.10 The concentration of isopropanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different ferrous sulfate amounts.

For Fenton/Air process, after the experiment began, COD increased as shown in Table 4.1. COD at the beginning was about 27 g/l. At different ferrous sulfate amounts, COD at 4 hours was not much different. COD increased along time-on-stream when the simulated wastewater was treated with Fenton/Air because there were by-product occurred from the oxidation reactions when high amounts of oxygen were co-fed.

Table 4.1 COD of the simulated wastewater treated using Fenton/Air (semi-batch) process with different ferrous sulfate amount after four hours

Time(hr)	COD(g/l)		
	FeSO ₄ 0.003 g	FeSO ₄ 0.0075 g	FeSO ₄ 0.01 g
0	27.3	27.36	27.3
4	45.48	43.2	47.04

When varied H₂O₂ flow rate, were fed in the Fenton system, and 0.003 g ferrous sulfate was added at the ambient temperature, %TOC remaining reduced along time on stream as shown in Figure 4.11. With H₂O₂ at flow rate of 50 ml/hr, %ethanol and isoproanol remaining were the lowest as shown in Figures 4.12 and 4.13. When H₂O₂ flow rate increased from 30 to 50 ml/hr, % ethanol and isoproanol remaining was not much different. COD still increased along time as shown in Table 4.2. With 50 ml/hr of H₂O₂ flow rate, COD was higher than the others.

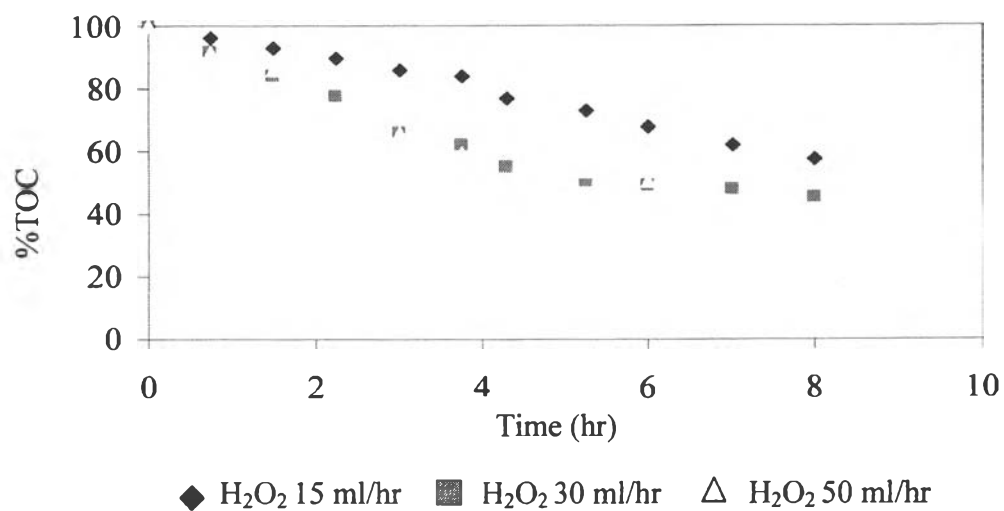


Figure 4.11 % TOC remaining along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different hydrogen peroxide flow rates.

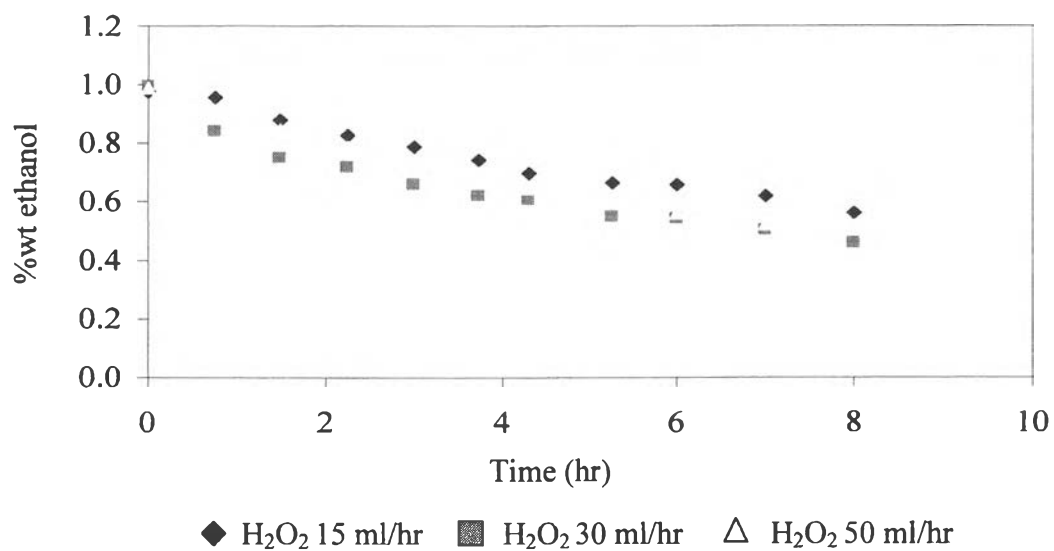


Figure 4.12 The concentration of ethanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different hydrogen peroxide flow rates.

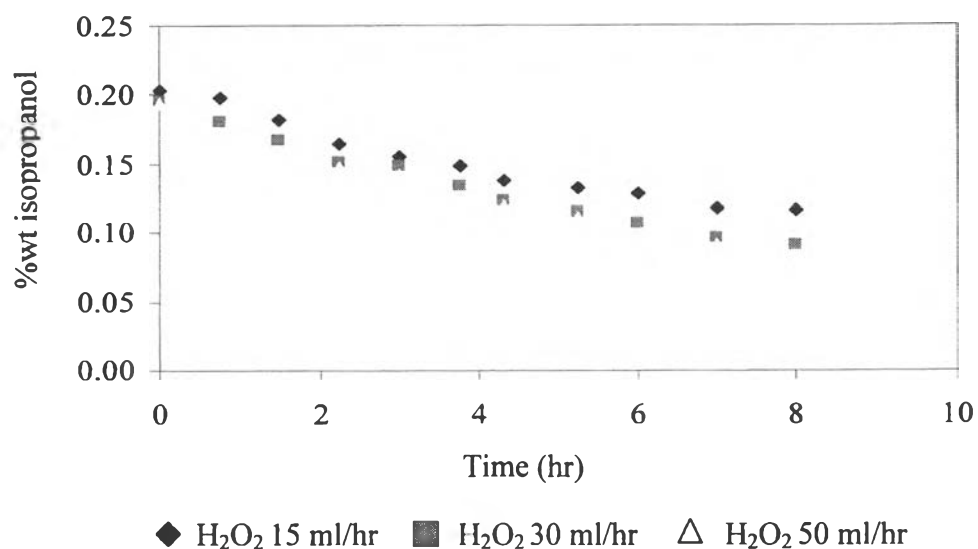


Figure 4.13 The concentration of isopropanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different hydrogen peroxide flow rates.

Table 4.2 COD of simulated wastewater treated using Fenton/Air (semi-batch) with different hydrogen peroxide flow rates

Time(hr)	COD(g/l)		
	H ₂ O ₂ 15 ml/hr	H ₂ O ₂ 30 ml/hr	H ₂ O ₂ 50 ml/hr
0	27.84	27.3	24.63
4	36.51	45.48	54.36
8	54.92	63.66	83.13

With varied air flow rate, when 30% v/v hydrogen peroxide with the flow rate of 30 ml/hr was fed in the Fenton system, containing 0.003 g ferrous sulfate at the ambient temperature, %TOC remaining reduced as shown in Figure 4.14. After six hours, %TOC remaining became constant. At high air flow rates, %TOC remaining was lower. Figures 4.15 and 4.16 represent % ethanol and isopropanol remaining reducing versus time, respectively. When air flow rate increased from 2 to 3 l/min, % ethanol and isopropanol remaining did not reduce much. COD as shown in Table 4.3 still increased. COD at any air flow rate were very similar.

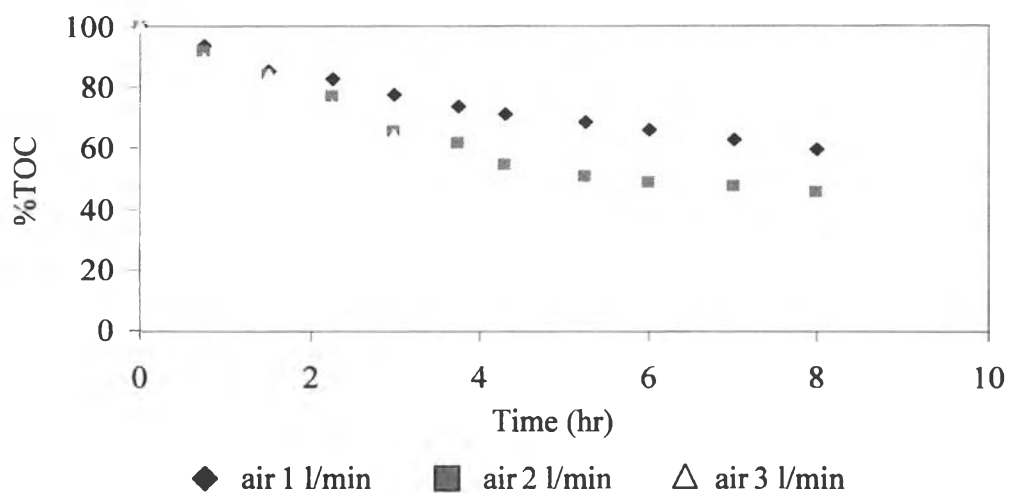


Figure 4.14 % TOC remaining along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different air flow rates.

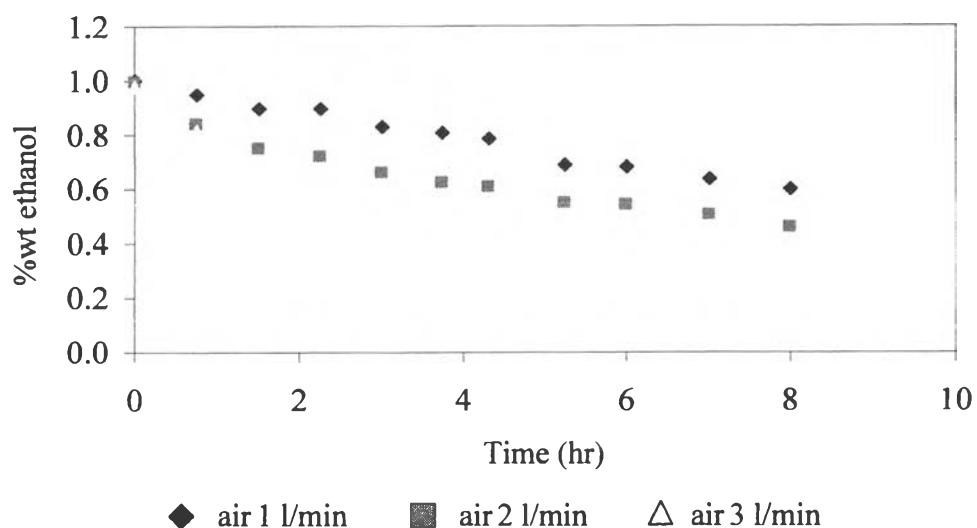


Figure 4.15 The concentration of ethanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different air flow rates.

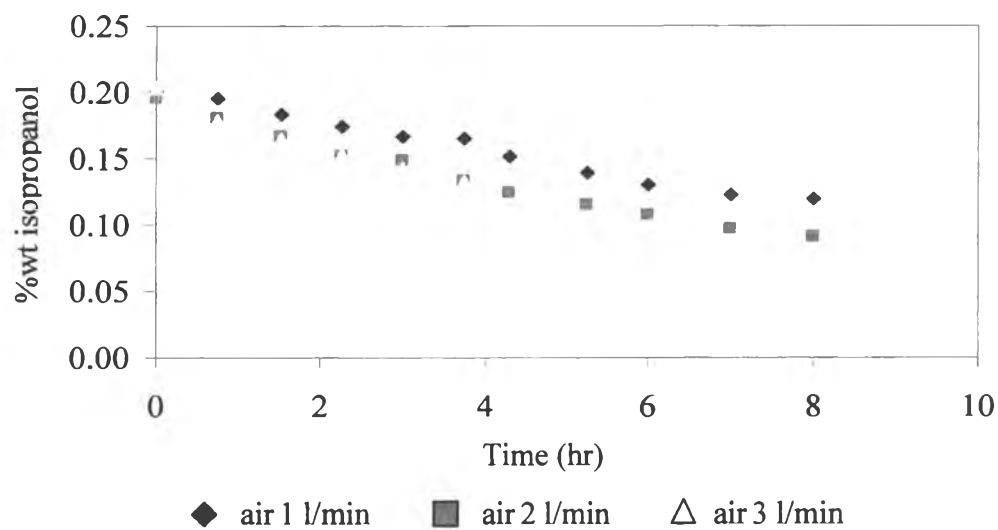


Figure 4.16 The concentration of isopropanol along time-on-stream when the simulated wastewater was treated using Fenton/Air (semi-batch) with different air flow rates.

Table 4.3 COD of the simulated wastewater treated using Fenton/Air (semi-batch) with different air flow rates

Time(hr)	COD(g/l)		
	H ₂ O ₂ 15 ml/hr	H ₂ O ₂ 30 ml/hr	H ₂ O ₂ 50 ml/hr
0	26.05	27.30	27.24
4	44.29	45.48	46.62
8	62.61	63.66	64.15

4.2 Modeling

4.2.1 Fenton Process

The method to determine K, α , and β values was Nonlinear Least-Square method, which used trial and error approach. The overall kinetic rate expression was used to evaluate the values of these constants by fitting the equations with the experimental data. FORTRAN program was written to solve the equations by Euler method. K, α , and β values at various ferrous sulfate amounts were shown in Table 4.4.

$$\frac{-d[CC_i]}{dt} = k[\text{ethanol}]^\alpha [\text{isopropanol}]^\beta [\text{OH}^\bullet]^r \quad (4.1)$$

Table 4.4 Summary of K, α , β , and γ values for Fenton (semi-batch) with different ferrous sulfate amounts

FeSO ₄ (g)	K (M ² s ⁻¹)	α	β	γ	% error
0.0030	1.6*10 ⁹	0.6	1.0	1.1	4.12
0.0075	1.8*10 ⁹	0.7	1.0	1.2	4.03
0.0113	1.7*10 ⁹	0.5	1.0	1.2	3.01
0.0150	1.6*10 ⁹	0.65	1.0	1.1	3.19
Total	1.68*10 ⁹	0.61	1.0	1.15	

Table 4.4 shows K, α , β , and γ values at various amount of ferrous sulfate (0.0030, 0.0075, 0.0113 and 0.0150 g). Average K value, α , β , and γ was 1.68*10⁹ M²s⁻¹, 0.61, 1.0, and 1.15, respectively.

Figures 4.17 to 4.24 show the comparison of the experimental data and the predicted concentrations of ethanol and isopropanol at various ferrous sulfate amounts. 30 % v/v hydrogen peroxide flow rate was 30 ml/hr. Air flow rate was 2 ml/min. The concentration of ethanol and isopropanol from the model fit reasonably well with the experimental data.

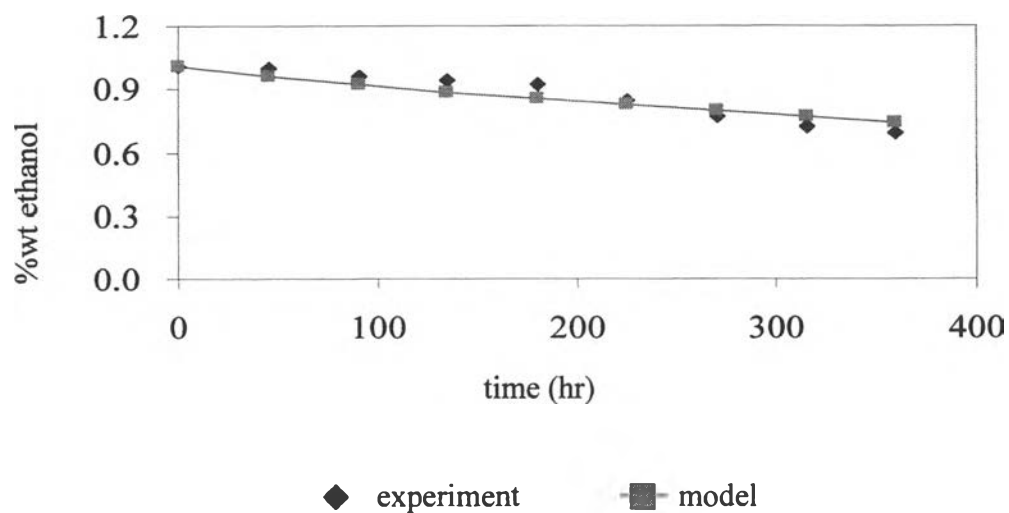


Figure 4.17 The comparison of the experiment and predicted concentrations of ethanol using Fenton process (0.003 g ferrous sulfate, 30 ml/hr H₂O₂ flow rate).

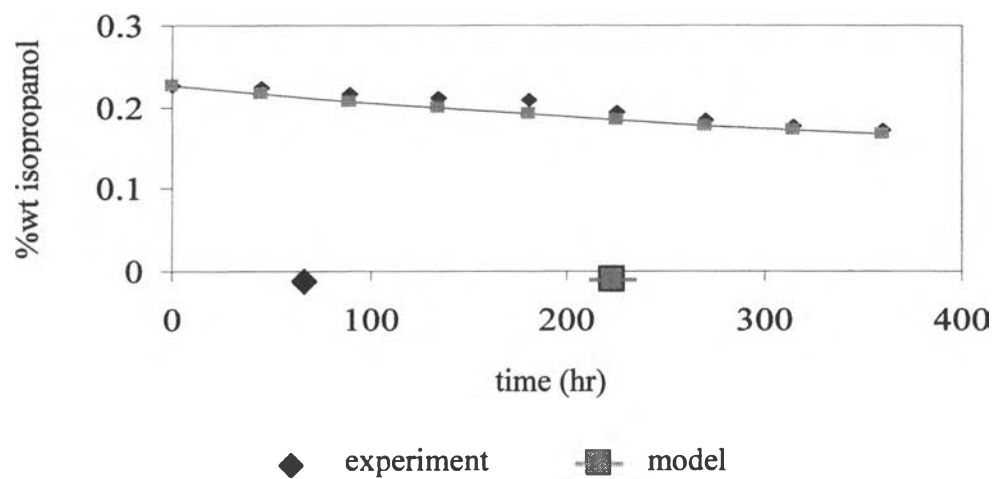


Figure 4.18 The comparison of the experiment and predicted concentrations of isopropanol using Fenton process (0.003 g ferrous sulfate, 30 ml/hr H₂O₂ flow rate).

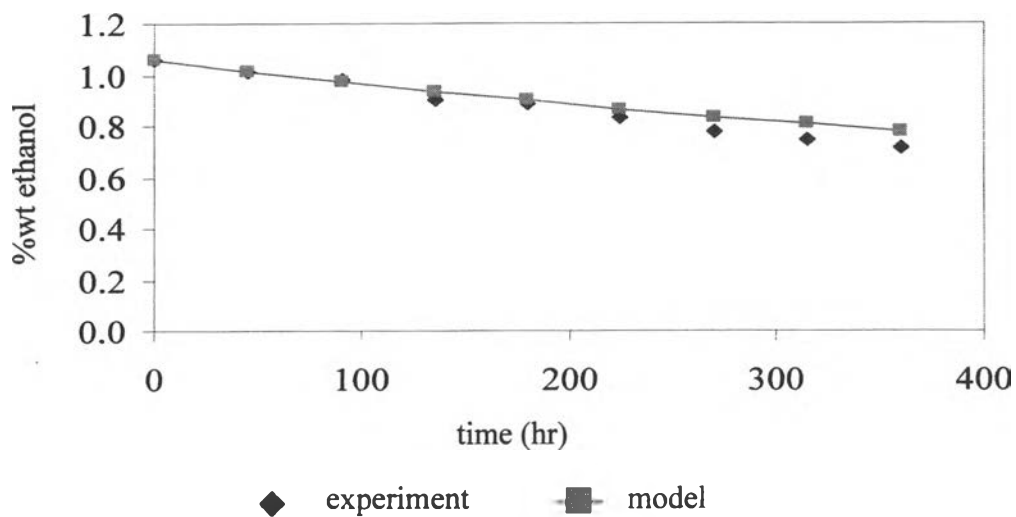


Figure 4.19 The comparison of the experiment and predicted concentrations of ethanol using Fenton process (0.0075 g ferrous sulfate, 30 ml/hr H_2O_2 flow rate).

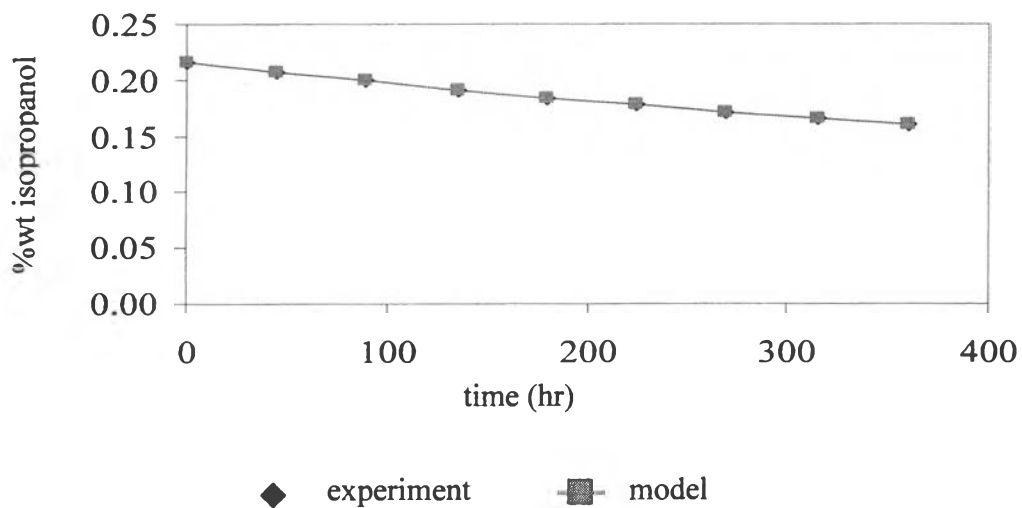


Figure 4.20 The comparison of the experiment and predicted concentrations of isopropanol using Fenton process (0.0075 g ferrous sulfate, 30 ml/hr H_2O_2 flow rate).

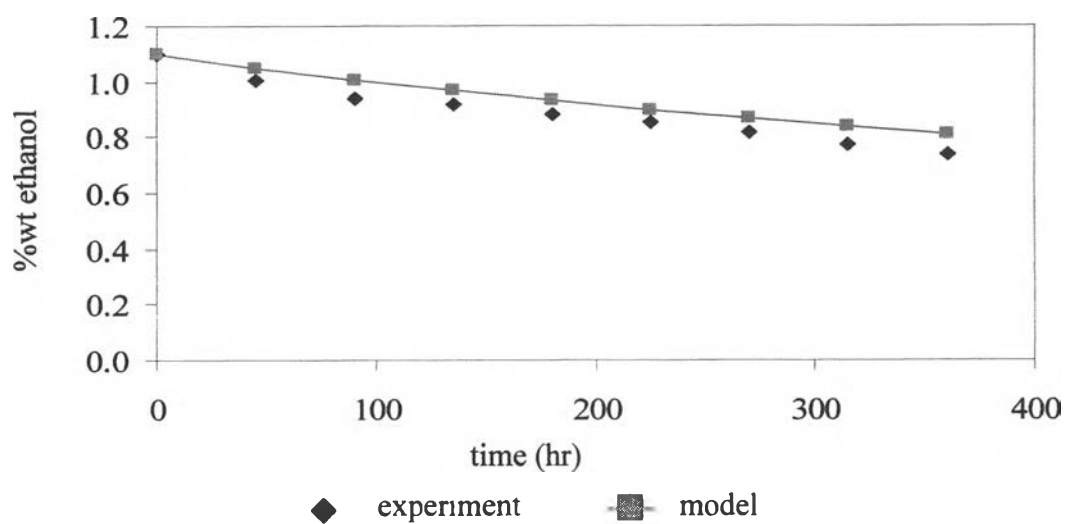


Figure 4.21 The comparison of the experiment and predicted concentrations of ethanol using Fenton process (0.0113 g ferrous sulfate, 30 ml/hr H_2O_2 flow rate).

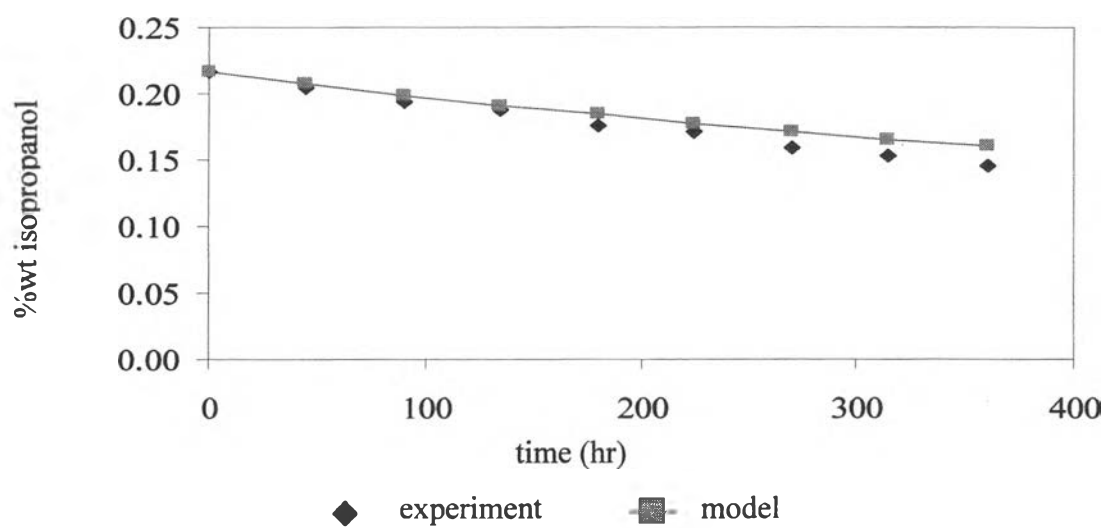


Figure 4.22 The comparison of the experiment and predicted concentrations of isopropanol using Fenton process (0.0113 g ferrous sulfate, 30 ml/hr H_2O_2 flow rate).

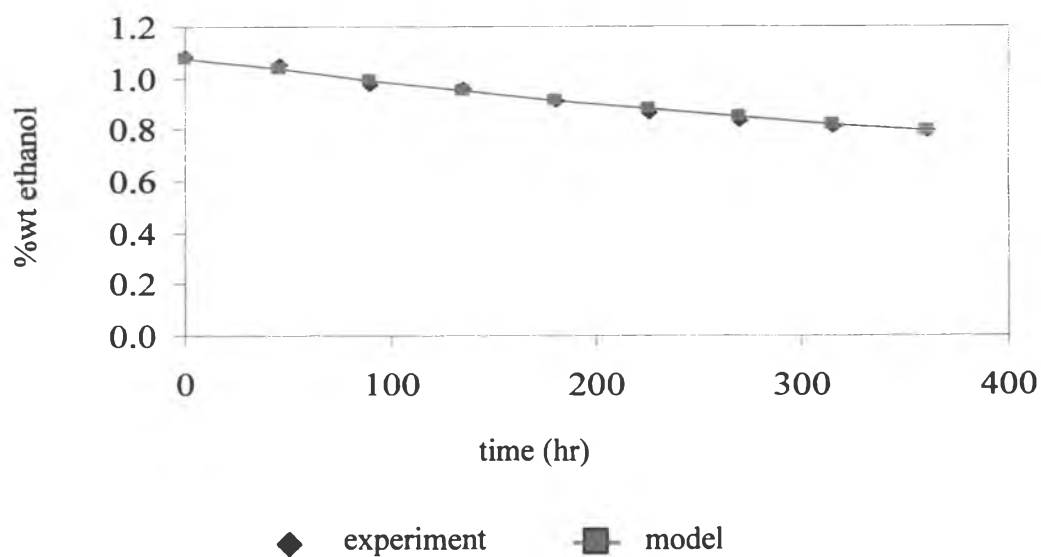


Figure 4.23 The comparison of the experiment and predicted concentrations of ethanol using Fenton process (0.015 g ferrous sulfate, 30 ml/hr H₂O₂ flow rate).

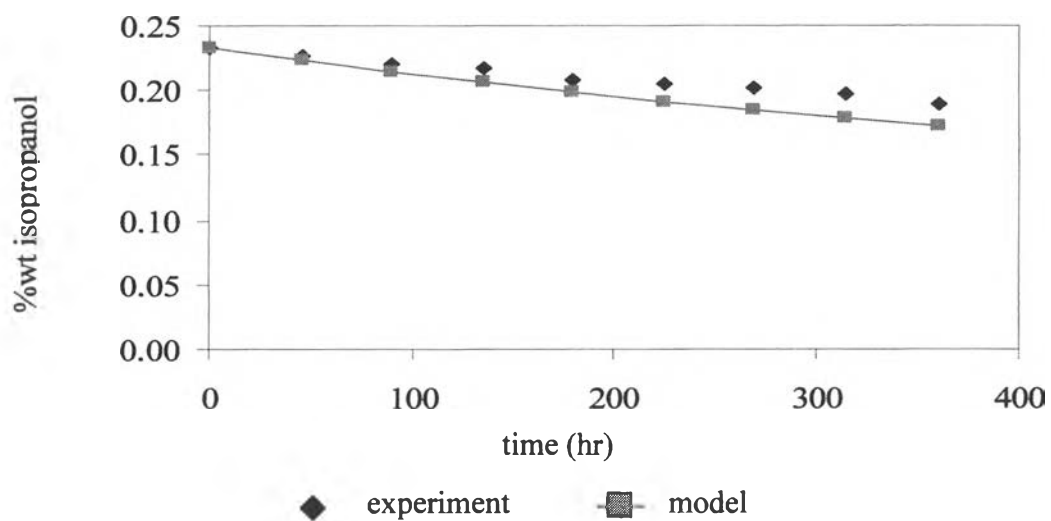


Figure 4.24 The comparison of the experiment and predicted concentrations of isopropanol using Fenton process (0.015 g ferrous sulfate, 30 ml/hr H₂O₂ flow rate).

4.2.2 Fenton/Air Process

The model for this process was composed of two parts: chemical oxidation and evaporation. The overall kinetic rate expression and evaporation equation (Equation 3.4 and 3.6) were used to describe the rate of change of concentration in organic contaminants. These equations were integrated with respect to time using Euler method. The values of constants were evaluated by fitting the overall kinetic rate expression and evaporation equation with the experimental data.

Figures 4.25 and 4.26 show comparison of the experimental data and the predicted concentrations of ethanol and isopropanol of Fenton/Air process with the H_2O_2 flow rate of 30 ml/hr, the air flow rate of 2 l/min, and 0.003 g ferrous sulfate. K-value was $1.68 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The concentration of ethanol and isopropanol from the model did not fit experimental data. The evaporation model was studied to check the enormous over-prediction of Fenton/Air process.

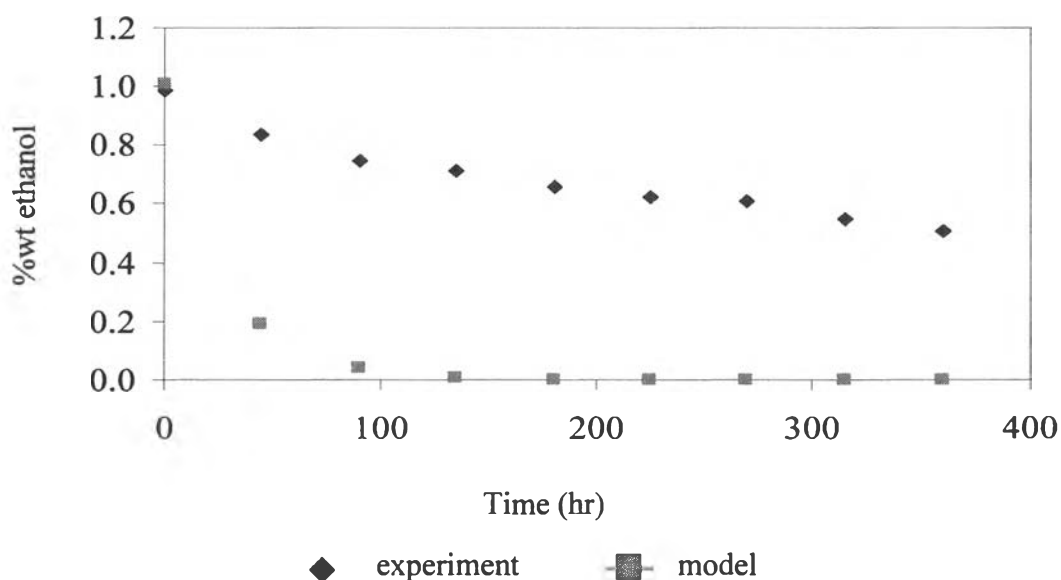


Figure 4.25 The comparison of the experiment and predicted concentrations of ethanol using Fenton/Air process (0.003 g ferrous sulfate, 30 ml/hr H_2O_2 flow rate, and 2 l/min air flow rate).

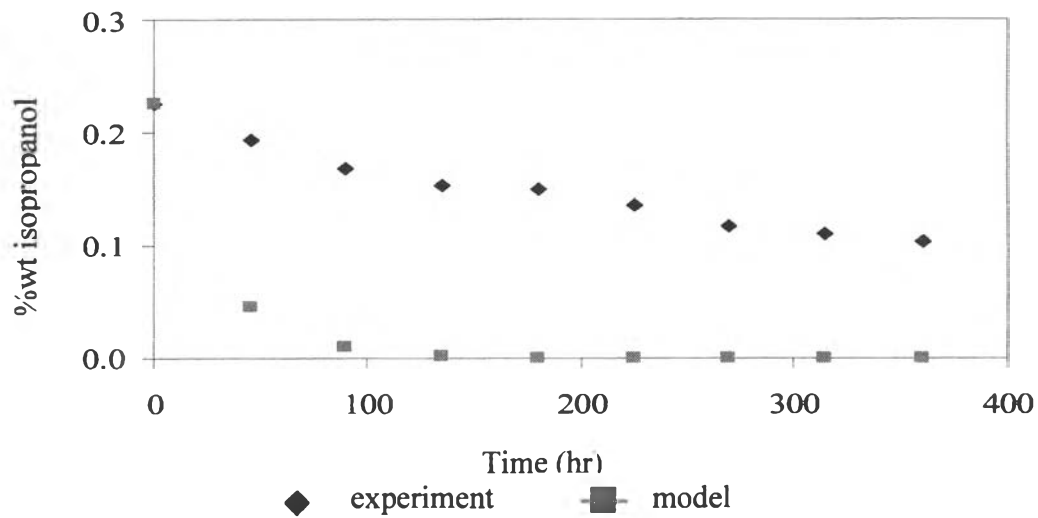


Figure 4.26 The comparison of the experiment and predicted concentrations of isopropanol using Fenton/Air process (0.003 g ferrous sulfate, 30 ml/hr H₂O₂ flow rate, and 2 l/min air flow rate).

Figures 4.27 to 4.32 represent the comparison of the experimental results and predicted concentrations of isopropanol with air at the flow rate of 1, 2, and 3 l/min, respectively. The air model did not fit with the experimental data. It can be concluded that the enormous over-prediction occurs from evaporation equation.

$$\frac{-d[CC_i]}{dt} = \left(\frac{Q}{22.4}\right)\left(\frac{M_i}{m_w}\right)(y_i) \quad (4.2)$$

The evaporation equation was derived from Equation 4.1. The model assumed equilibrium mole fraction of component *i* in the vapor phase (*y_i*) which was greater than *y_i* from experiments. This assumption can cause enormous error.

Model to describe evaporation based on Tock *et al.* (1993) which assumed equilibrium *y_i*. However, the system in this thesis is not equilibrium.

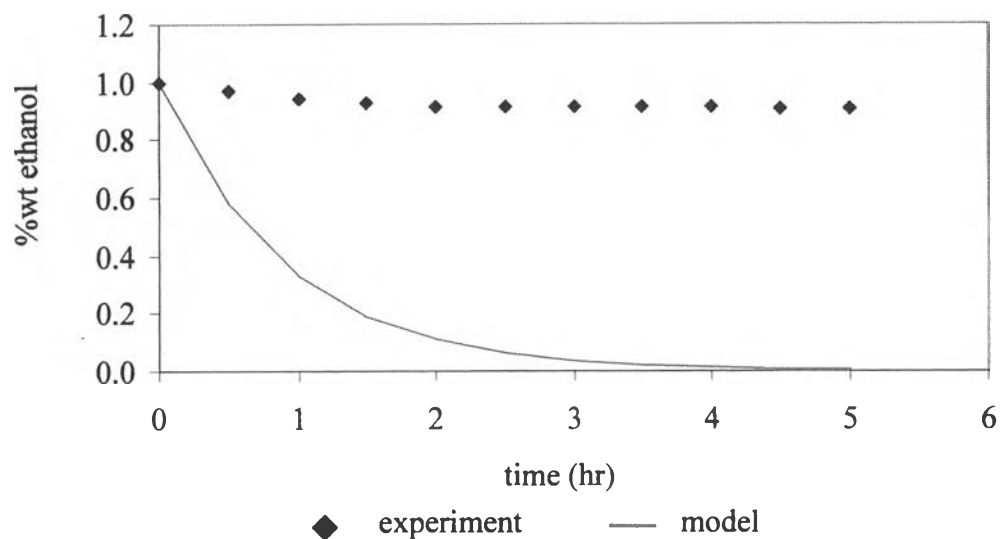


Figure 4.27 The comparison of the experiment and predicted concentrations of ethanol when only air with the flow rate of 1 l/min was fed into the system.

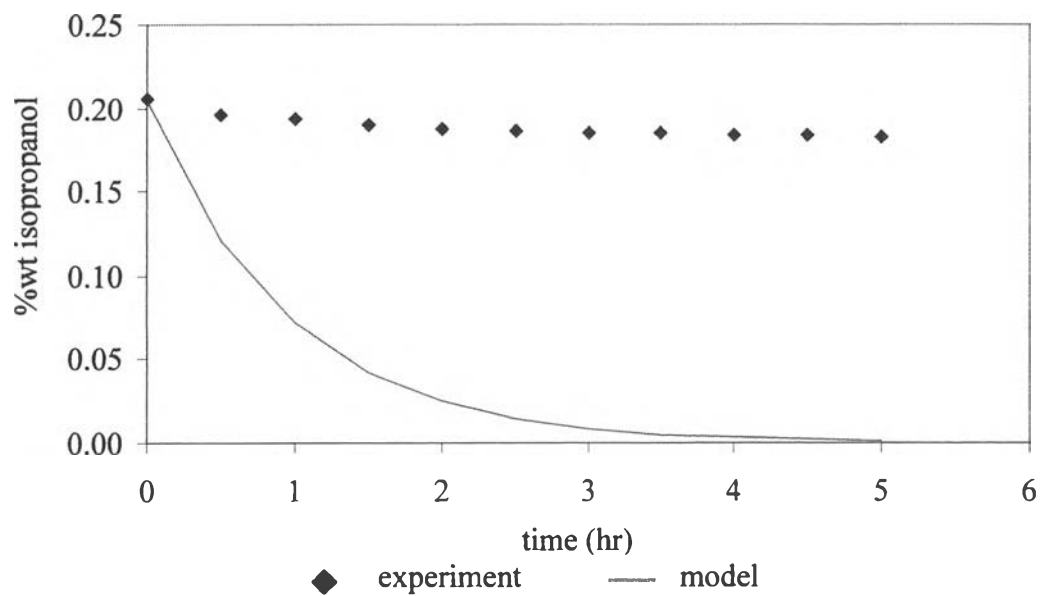


Figure 4.28 The comparison of the experiment and predicted concentrations of isopropanol when only air with the flow rate of 1 l/min was fed into the system).

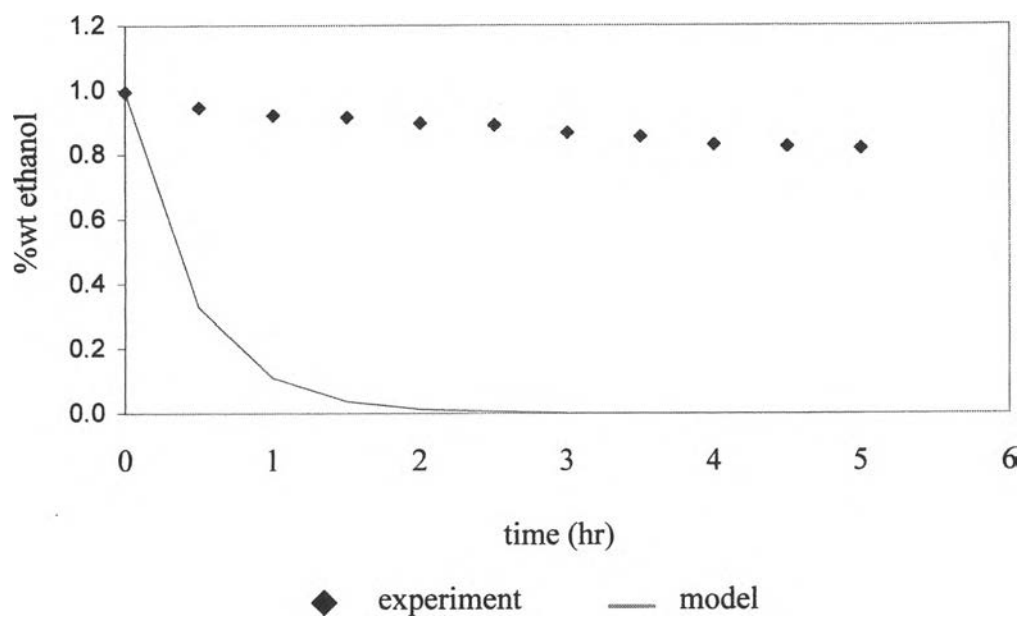


Figure 4.29 The comparison of the experiment and predicted concentrations of ethanol when only air with the flow rate of 2 l/min was fed into the system.

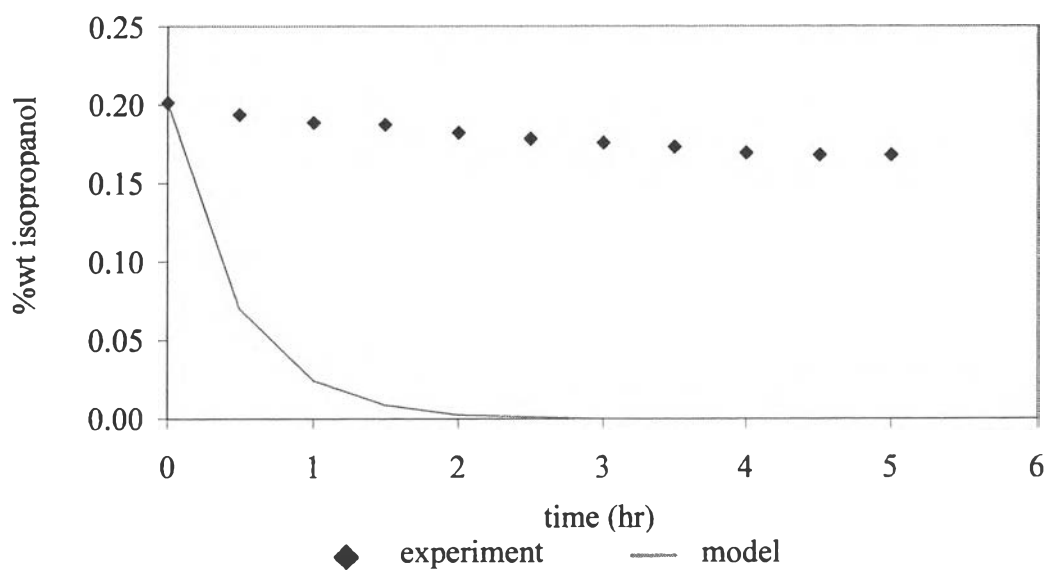


Figure 4.30 The comparison of the experiment and predicted concentrations of isopropanol when only air with the flow rate of 2 l/min was fed into the system.

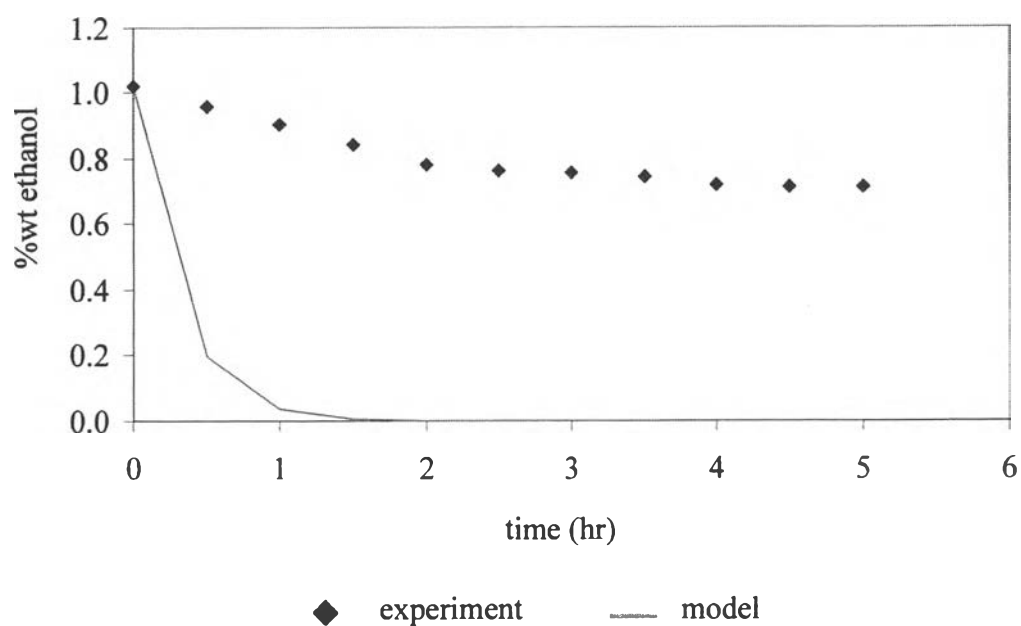


Figure 4.31 The comparison of the experiment and predicted concentrations of ethanol when only air with the flow rate of 3 l/min was fed into the system.

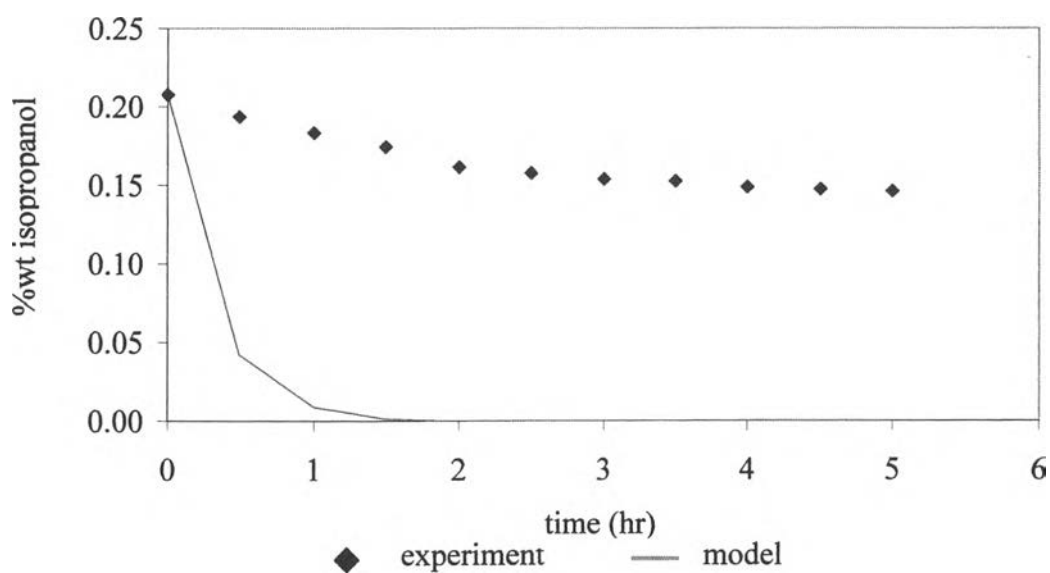


Figure 4.32 The comparison of the experiment and predicted concentrations of isopropanol when only air with the flow rate of 3 l/min was fed into the system.