

**Kinetic Models on Fenton Oxidation of Refractory Organic Pollutants
in Aqueous Medium**

by

Amir Aiman bin Dzul kifli

13652

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical)

MAY 2014

Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL)

Approved by,

(Assoc. Prof. Dr Sekhar Bhattacharjee)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH PERAK
MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AMIR AIMAN BIN DZULKIFFLI

ABSTRACT

Advanced Oxidation Process (AOP) has been developed for the wastewater treatment through generation of highly reactive hydroxyl radical which offers a complete removal of organics owing to its greater efficiency in mineralization. Fenton's oxidation, being one of the AOPs, has been widely used to degrade pollutants due to the nature of its simple reaction. Organic contaminants are oxidized into carbon dioxide and water by the powerful hydroxyl radical oxidant during the Fenton's process. Irradiation of UV light to Fenton's oxidation of the amine wastes will strongly accelerate the rate of degradation of pollutants. The major aim for the author to perform this study is to simulate and develop a unified kinetic models on Fenton oxidation of refractory organic compound with respect to different operating parameters with the aid of engineering simulation software. The models can be used to predict the steady-state performance for Fenton degradation of organic compound in wastewater. Among the operating parameters being tested include the initial pH effect, the initial concentration of hydrogen peroxide and the effect of ferrous iron concentration. A kinetic study has been conducted on the chosen organic compound based on the availability of data from existing literature. The kinetic model developed was tested against several systems of different organic compounds, including phenol, guaiacol and monoethanolamine, to determine the feasibility of the model to predict the degradation of organic compounds in Fenton's reaction. The development of the model can be further improved in the future with the availability of data obtained from experimental procedure.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background of Study

The project is related to the degradation of refractory organic compound in wastewater treatment. This project will focus on the development of kinetic models on Fenton oxidation of organic pollutants in aqueous medium. Fenton oxidation is a type of advanced oxidation process (AOP) which involves chemical oxidizing agents in the presence of an appropriate catalyst and/or ultraviolet light (Legrini et al., 1993). As for Fenton reaction, the oxidant used is hydrogen peroxide (H_2O_2) (Dao and De Laat, 2011) and for Photo-Fenton reaction the oxidant is H_2O_2 with ferrous or ferric iron as the catalyst and in the presence of ultraviolet light. The effect of varying operating parameters in the effectiveness of refractory organic compound removal in waste water using Fenton's oxidation process will be studied by developing kinetic model for each organic compound and with the aid of simulation from engineering software such as MATLAB and POLYMATH. The three parameters of interest include; the effect of variation in pH, the effect of initial concentration of H_2O_2 , and the initial concentration of ferrous iron. The performance of degradation with respect to the parameters mentioned will be simulated with the aid of engineering software by measuring the efficiency of organic compound removal, total organic compound (TOC) removal or the level of chemical oxygen demand (COD) by comparing the results from models developed with the experimental results.

Fenton process has been widely used and adopted in the wastewater treatment for various types of industries due to the reduced use of oxidizing agents, such as hydrogen peroxide (Pontes et al., 2010). Ferrous iron and hydrogen peroxide are the key components for Fenton oxidation due to the ferrous iron properties which lack of toxicity and its easy removal from water. Hydrogen peroxide is environmentally benign due to its

slow decomposition into water and oxygen (Wang et al., 2011). Besides its application in the municipal and industrial water and wastewater treatment, Fenton oxidation is also applied in soil and groundwater treatment. The application of Fenton process in industries involved several stages including pH adjustment, oxidation and reduction reactions, neutralization and coagulation, and precipitation where the main operation parameters include H_2O_2 and Fe^{2+} doses, organic content and pH (Bensalah et al., 2011).

1.2 Problem Statement

Liquid effluents generated from the operation of a variety of chemistry-related industrial process contain toxic substances which are harmful not only to the environment but to human being as well. These liquid effluents are also released through a number of common household or agricultural applications. Improper management of these residues can cause contamination of the soil and of subterranean and surface water sources. Thus, in order to predict the performance of Fenton reaction in the degradation of organic compound, mathematical models are developed by fitting the model to the experimental data of the degradation of these organic compounds.

1.3 Objective and Scope of Study

1.3.1 Objectives

The aim of this project is to develop a unified mathematical model for the Fenton reaction to predict the performance of Fenton reaction in the degradation of refractory organic compound with respect to different operating parameters. The effectiveness is measured by the trend developed with the aid of engineering software for the simulation of the treatment of respective organic compound. The parameters used in this work include initial pH effect, initial concentration of H_2O_2 and initial concentration of Fe^{2+} for the selected organic compounds which are phenol, guaiacol and monoethanolamine respectively.

1.3.2 Scope of Study

This project involves the development of kinetic models of refractory organic compound degradation by Fenton oxidation. The mathematical models developed will be used to predict the degradation of respective organic compound. The degradation of organic compound varying in parameters ranging from pH, initial concentration of H₂O₂ and ferrous iron concentration are simulated with the proposed model and compared with the experimental results. Experimental results are obtained from experiments done by previous researchers for phenol, guaiacol and monoethanolamine.

1.4 Relevancy of the Project

- *Chemical Engineering* – Development of mathematical model for the prediction of Fenton's oxidation for organic compounds requires the knowledge on the principles of Fenton's process as well as organic chemistry.
- *Wide application of wastewater treatment* – The growing need in wastewater treatment is one of the driving forces for this project in which the development of mathematical model is important for the prediction of Fenton's degradation of organic compounds. Hence, with the development of unified model, the performance of organic compounds can be predicted.

1.5 Feasibility of the Project within the Scope and Time Frame

- *Scope of study* – This project was carried out within the scope of chemical engineering course as it encompasses various aspects of this field of study.
- *Time allocation (2 semesters)* – There are two parts in this project where the first part involves the pseudo steady state modelling of organic compounds based on the existing model. In the second part of this project, mechanistic model for a selected organic compound has been developed and the simulated results are compared with the existing experimental results.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW AND THEORY

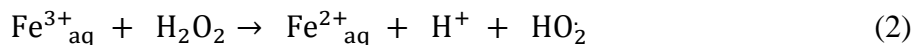
2.1 Overview of the Fenton's Oxidation

2.1.1 The Fenton's Reaction

The Fenton reaction is originated from the reaction of ferrous iron (II) with hydrogen peroxide (H_2O_2). This reaction was developed in the 1890s by Henry John Hortsman Fenton who first observed the oxidation of tartaric acid by a mixture of iron sulphate (FeSO_4) and H_2O_2 (Mwebi, 2005). The classical mechanism of Fenton reaction is a simple redox reaction in which ferrous iron (II) is oxidized to ferric iron (III) and H_2O_2 is reduced to hydroxide ion (OH^-) and the hydroxyl radical (OH^\bullet) by the following reaction (Machulek Jr et al., 2012).



The ferric iron produced in reaction (1) can be reduced back to ferrous iron by a second molecule of H_2O_2 by the following reaction:

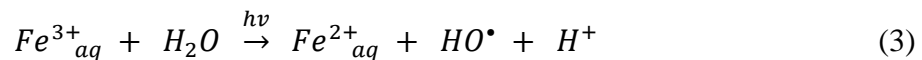


According to Machulek et al. (2012), the thermal reduction of ferric iron to ferrous iron in reaction (2) is much slower as compared to the initial reaction (1) thus requiring the addition of relatively large amount of ferrous iron to support the reduction process of ferric iron in reaction (2) in order to degrade the pollutant of interest. Fenton's reagent has been found effective in treating various industrial wastewater components such as

aromatic amines and wide variety of dyes, pesticides and surfactants as well as many other substances (Barbusiński, 2005).

2.1.2 The Photo-Fenton's Reaction

The Photo-Fenton reaction mainly consists of two reactions, the Fenton reaction (1) and the Photo-Reduction (reaction 3) (Tokumura et al., 2013). The rate of pollutants degradation by Fenton reaction is accelerated with the irradiation of UV or visible light due to the photochemical reduction of ferric iron (III) back to ferrous iron (II). The net reaction can be written as:



Ferrous iron (II) and hydroxyl radical are produced during the photoreaction of $Fe(OH)^{2+}$ (Pozdnyakov et al., 2000). Thus, Photo-Fenton reaction generates an additional hydroxyl radical which is responsible for the degradation of organic material alongside the regeneration of ferrous iron (II), the catalyst for reaction (1).

2.2 The Principles of Fenton's Process

2.2.1 General Pathway of Fenton's Process

The Fenton's degradation of organic compounds can be classified into four major stages which involves the formation of hydroxyl radical ($OH\cdot$) which is responsible in the degradation of organic compounds to form carbon dioxide and water. The first step is to determine the stoichiometric model for the degradation of the contaminants present in the effluent which will describe the chemical reactions that the contaminants undergo in the treatment. The general stoichiometric model for the degradation process through Fenton's oxidation is depicted in the figure below (Pontes et al., 2010).

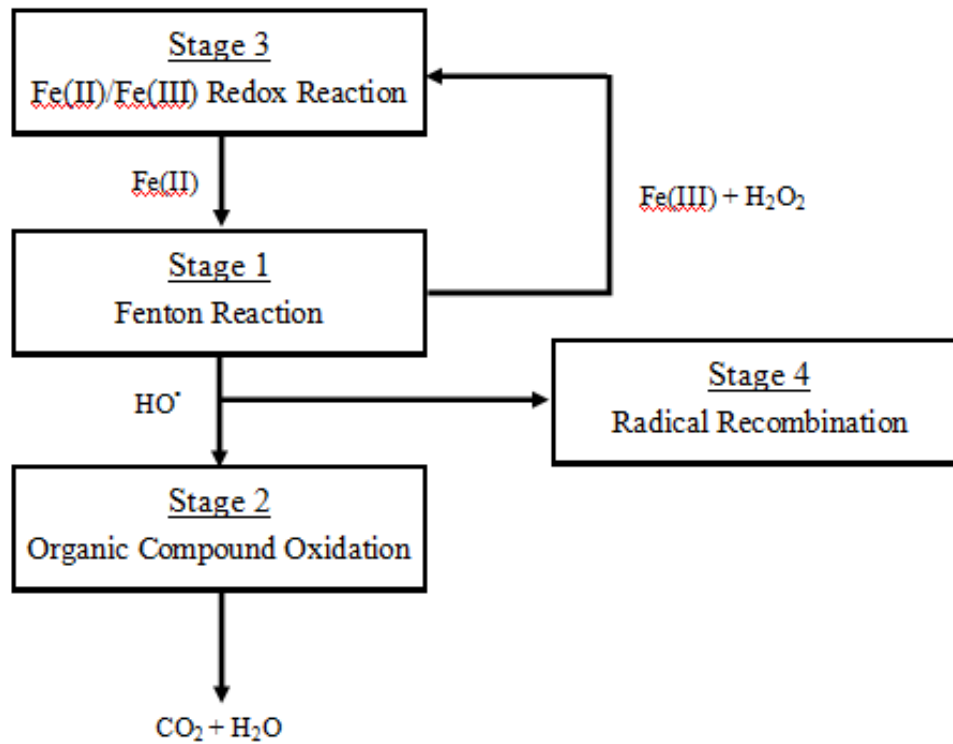
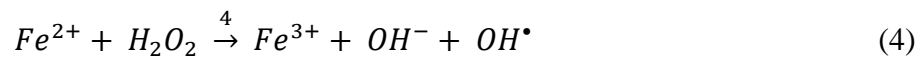


Figure 2.1: General structure of the Fenton's process pathway (Pontes et al., 2010)

Degradation of all organic compound will follow the same mechanism for Stage 1 and Stage 2, which are the Fenton reaction. The stoichiometric model for Stage 3 and Stage 4 will differ according to the organic compound of interest. The stoichiometric model for the organic compound degradation by the Fenton process is shown below for Stage 1 and Stage 2.

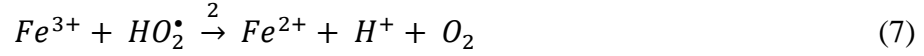
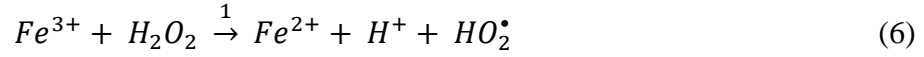
Stage 1 (Oxidation of Fe(II) to Fe(III)):



Stage 2 (Degradation of organic compound of interest, OC):



Stage 3 (Fe(II)/Fe(III) Redox Reaction):



From the stoichiometric model depicted for Stage 1, Stage 2 and Stage 3, the kinetic expression and mass balances for a batch operation mode of the relevant components in the model have been proposed as shown in the table below.

Kinetic expression	Mass balances on component model
$r_1 = k_1 \cdot [Fe^{3+}] \cdot [H_2O_2]$	$\frac{d[Fe^{3+}]}{dt} = r_4 - r_1 - r_2 - r_3$
$r_2 = k_2 \cdot [Fe^{3+}] \cdot [HO_2^\bullet]$	$\frac{d[Fe^{2+}]}{dt} = r_1 + r_2 + r_3 - r_4$
$r_3 = k_3 \cdot [Fe^{3+}] \cdot [O_2^{\bullet-}]$	$\frac{d[H_2O_2]}{dt} = -r_1 - r_4$
$r_4 = k_4 \cdot [Fe^{2+}] \cdot [H_2O_2]$	$\frac{d[HO_2^\bullet]}{dt} = r_1 - r_2$
$r_5 = k_5 \cdot [OC] \cdot [HO^\bullet]$	$\frac{d[HO^\bullet]}{dt} = r_4$
	$\frac{d[OC]}{dt} = -r_5$

For the purpose of developing the kinetic model, the rate of degradation of organic compound is assumed to be the pseudo first-order kinetic with the hypothesis of pseudo steady-state concentration of hydroxyl radical (Khamaruddin et al., 2011) which is in agreement with the experimental result of organic compound degradation done by Bensalah et al. (2011) where the plots of the organic compound concentration vs. time indicate a pseudo first-order kinetics.

$$-\frac{d[OC]}{dt} = k_5 \cdot [OC] \cdot [HO^\bullet] = k_{app} \cdot [OC] \quad (9)$$

where k_{app} is the apparent organic compound degradation rate constant which can be determined by integrating and rearranging equation (9) to form a linear equation, in which k_{app} is the slope of the linearized plot. Equation (9) can be integrated by setting the boundary condition $[OC] = [OC]_0$ for $t = 0$ and $[OC] = [OC]_t$ for $t = t$ which leads to Equation (10):

$$\int_{[OC]_0}^{[OC]_t} \frac{d[OC]}{[OC]} = \int_0^t k_{app} dt \quad (10)$$

$$\ln\left(\frac{[OC]_{t=0}}{[OC]_{t=t}}\right) = k_{app} \cdot t \quad (11)$$

The value of k_{app} from the plot of $\ln([OC]_{t=0}/[OC]_{t=t})$ vs. time (t) will determine the highest pseudo first-order rate constant and R^2 is the correlation coefficients used to predict the reliability of the equation. Once the value of k_{app} for the Fenton process have been determined, the rate constant for the reaction of organic compound with HO^\bullet radicals, k_{OC-HO^\bullet} , can be evaluated, in which competition kinetic model is one of the method which has been previously used by several authors (Bensalah et al., 2011)

2.3 The Effect of Different Parameters on the Fenton's Reaction

2.3.1 The Effect of pH

Based on the experiments conducted by previous researchers on the effect of varying pH to the Fenton's degradation of organic compound, the optimum value for Fenton's reaction to take place is in the range of 2.5 – 3.5 (Ebrahiem et al., 2013; Khamaruddin et al., 2011; Oancea and Meltzer, 2013). The effect of pH on the reaction efficiency is shown below:

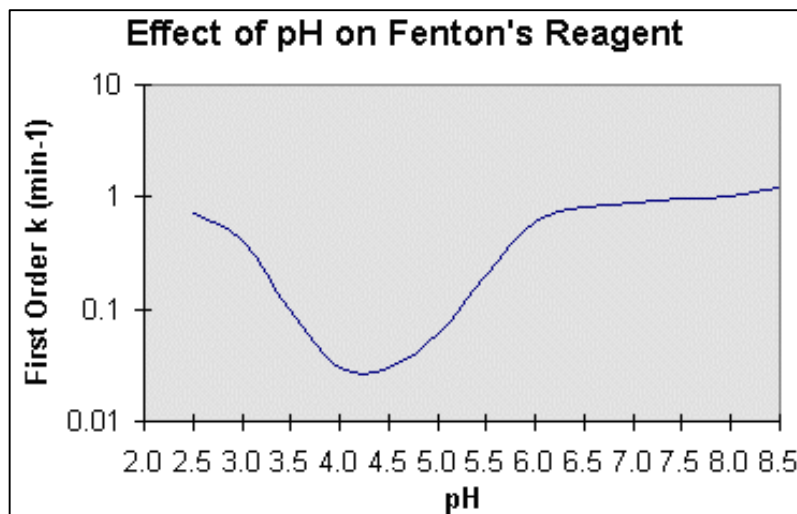


Figure 1.2: The effect of pH on the reaction efficiency (Bishop et al., 1968)

It can be observed that the optimum pH for the Fenton's reaction occurs between pH 3 and pH 6, in agreement with the previous experiment mentioned. The transition of iron from its hydrated ferrous iron form to a colloidal ferric species resulted in the drop of efficiency on the basic side where the ferric species catalytically decompose the hydrogen peroxide into oxygen and water, without the formation of hydroxyl radicals (Bishop et al., 1968).

2.3.2 The Effect of Ferrous Iron Concentration

In order to produce hydroxyl radical, hydrogen peroxide will need to react with iron to produce hydroxyl radical which is responsible in the degradation of organic compound. Increasing the iron concentration will increase the rate of removal of organic compound until a point is reached where further addition of iron becomes inefficient. Three factors typically influence the definition of iron concentration (Bishop et al., 1968):

- For ferrous iron concentration, there is an optimum amount of ferrous iron concentration for the degradation of organic compound where further increase in its concentration will result in decrease of organic compound degradation.

- The ratio of ferrous iron to substrate is also important in the degradation process where different composition will affect the reaction products distribution.

2.3.3 Effect of Temperature

The rate of reaction with Fenton's reagent increases with increasing temperature, where the effect can be clearly observed at temperatures less than 20 °C. The decomposition of hydrogen peroxide into oxygen and water will be accelerated when the temperature rises above 40-50 °C resulted in the decrease of the efficiency of hydrogen peroxide utilization (Bishop et al., 1968). As a practical matter, most commercial applications of Fenton's reagent occur temperatures between 20-40 °C.

2.3.4 The Effect of Reaction Time

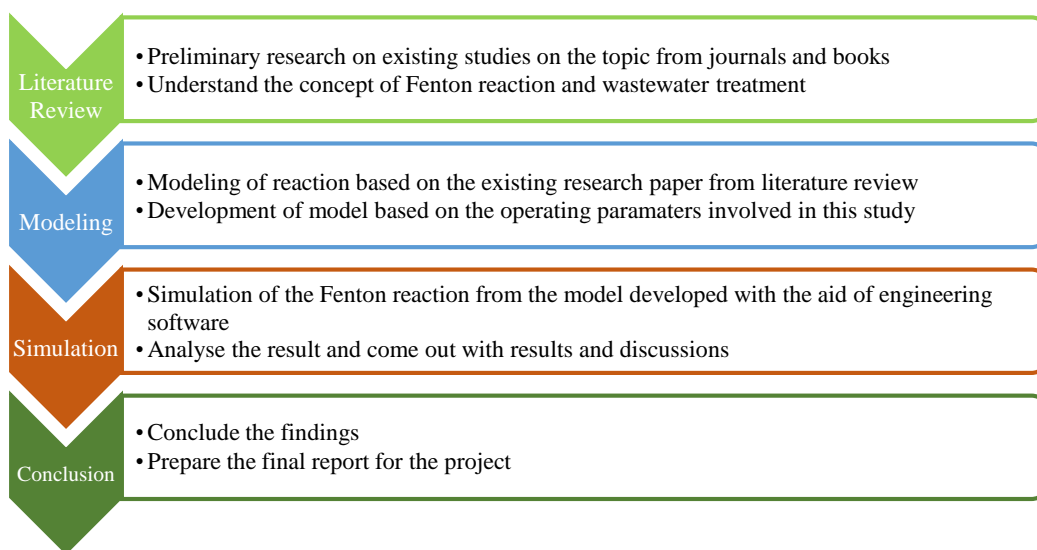
Among the variables that affect the total time needed for the completion of a Fenton's reaction will be the dose of catalyst and the wastewater strength itself. For simpler phenol oxidation, typical reaction times are 30 – 60 minutes (Feng and Le-Cheng, 2004; Pontes et al., 2010). The reaction will take longer time for more complex and concentrated wastes where for such cases, the reaction can be done in several steps by adding both ferrous iron and hydrogen peroxide which may be more effective and safer than increasing the initial charges (Bishop et al., 1968).

CHAPTER 3

METHODOLOGY

3. METHODOLOGY

3.1 Project Flow Chart



3.2 Project Work

The project is divided into two sections where the first section is the validation of the existing model from previous works. In this section, different organic compounds are used to predict the effectiveness of the model which employs two reaction pathways, radical reactions and complex reaction which was developed by Feng and Le-Cheng (2004) in their work for phenol degradation. Guaiacol and MEA are used as organic compounds of interest to validate this model. In the second section of this work, kinetic study of specific organic compound, which is phenol, has been developed based on the

principle reactions of Fenton process and the intermediates formed in between. The results from the model are then compared with the experimental results from existing literature.

3.2.1 Kinetic Study for the Validation of Unified Model

For the development of global kinetic model, the degradation of organic compound is assumed to follow two pathways, complex reaction and radical reaction. Feng and Le-Cheng (2004) have developed the kinetic model based on these two reactions and validated the model with the experimental data of phenol degradation in Fenton degradation. It is of the best interest in this work to validate this model to guaiacol and monoethanolamine.

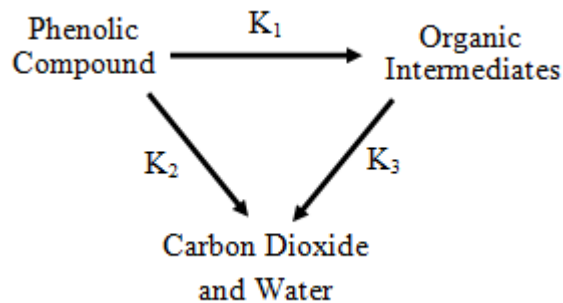


Figure 2.1: The principle pathways of organic compounds degradation (Feng and Le-Cheng, 2004)

Figure 3.1 represents the possible reaction pathways of organic compounds where organic compounds or phenolic compounds can proceed through complex reaction or radical reaction. In complex reaction, organic compounds undergo direct degradation to the final substrates, carbon dioxide and water. In radical reaction, the organic compound is first converted into organic intermediates such as acetic acid and maleic acid by hydroxyl radical before undergoing further degradation into water and carbon dioxide. All reactions in Figure 3.1 have been assumed to follow pseudo-first-order kinetics and can be represented as:

$$-\frac{d[PC]}{dt} = (K_1 + K_2)[PC] \quad (12)$$

$$-\frac{d[OI]}{dt} = K_3[OI] - K_2[PC] \quad (13)$$

Where PC and OI represent phenolic compound and organic intermediate respectively. K_i is related to the aforementioned parameters which are pH, H_2O_2 dosage and initial concentration of ferrous iron. Integrating both equations from the initial conditions at time, $t = 0$ and combining them, yields (Feng and Le-Cheng, 2004):

$$\frac{[PC + OI]}{[PC + OI]_0} = \frac{K_2}{K_1 + K_2 - K_3} e^{-K_3 t} + \frac{K_1 - K_3}{K_1 + K_2 - K_3} e^{-(K_1 + K_2)t} \quad (14)$$

Total concentration of organic substituents is presented by $[PC+OI]$ or total chemical oxygen demand (COD) where $[PC+OI]_0$ (COD_0) is the concentration at $t = 0$.

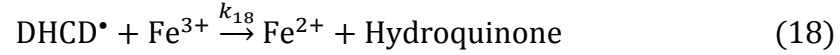
$$[PC + OI] = [COD]_0 \left[\frac{K_2}{K_1 + K_2 - K_3} e^{-K_3 t} + \frac{K_1 - K_3}{K_1 + K_2 - K_3} e^{-(K_1 + K_2)t} \right] \quad (15)$$

This model is then used to predict the degradation of guaiacol and MEA in this work by solving the nonlinear multiple regression of K_1 , K_2 and K_3 respectively by using MATLAB software.

3.2.2 Mechanistic Study of Phenol Degradation

Various products can be considered when studying phenol oxidation in Fenton's reaction. The concentration of phenol (C_6H_6O), catechol and hydroquinone were measured in course of reaction for three different experiments with different H_2O_2 concentrations conducted by Pontes et al. (2010). The initial concentrations of ferrous iron and phenol are kept constant at $1.0 \times 10^{-3} \text{ mol L}^{-1}$ and $12.1 \times 10^{-3} \text{ mol L}^{-1}$ respectively while the temperature is held constant at $30 \text{ }^\circ\text{C}$ and at $\text{pH} = 3.0$.

For the model development of phenol degradation in Fenton process, the principal reactions of Fenton process in Eq. 1 and Eq. 2 have been considered together with the following set of reactions for phenol degradation in Eqs. 16-20.



Where: $DHCD^\bullet$ = di-hydroxyl-cyclohexa-di-enyl radical

$THCD^\bullet$ = di-hydroxyl-cyclohexa-di-enyl radical

The rate of formation of perhydroxyl radical in Eq. 2 has been neglected because it is much slower than the rate of formation of hydroxyl radical itself (Gallard and De Laat, 2000). Eqs. 17 and 18 have also been neglected in the development of this model because of the fast reaction between ferric iron and the radicals. Considering that the degradation of phenol apparently follows pseudo first-order kinetics in the whole process, the reaction rate of phenol could be defined as Eq. 21.

$$r_{C_6H_6O} = -\frac{d[C_6H_6O]}{dt} = k_{16}[C_6H_6O][HO^\bullet] = k_{ap}[C_6H_6O] \quad (21)$$

where, $r_{C_6H_6O}$ denotes the rate of consumption of phenol, $[C_6H_6O]$ and $[HO^\bullet]$ are the concentrations of hydroxyl radical and phenol respectively and k_{ap} is the pseudo first-order rate constants and equals to $k_{16}[HO^\bullet]$. Performing the integration and applying initial conditions $[C_6H_6O] = [C_6H_6O]_0$ at $t = 0$ and $[C_6H_6O] = [C_6H_6O]$ at $t = t$ gives

$$\ln\left(\frac{[C_6H_6O]}{[C_6H_6O]_0}\right) = k_{ap}t \quad (22)$$

By plotting the values of $\ln([C_6H_6O]_0/[C_6H_6O])$ as a function of reaction time, first-order kinetics with respect to phenol could be obtained, as shown in the figure 3.2 together with the linear correlation coefficients (R^2) and k_{ap} or the slopes of the first-order kinetics which are shown in the table 3.1.

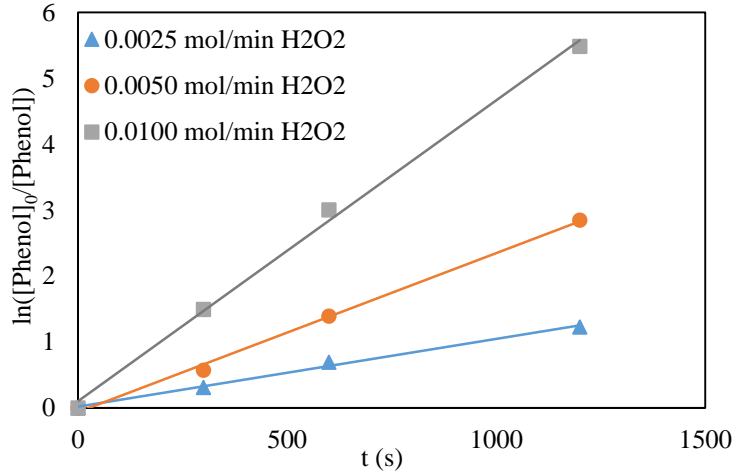


Figure 3.2: Fitting of the experimental data to first order reaction kinetics for different dosing rate of H₂O₂

Table 3.1: The first-order rate constant and linear correlation coefficients from Figure 3.2.

H ₂ O ₂ Feed Flow Rate (mol/min)	k_{ap} (s ⁻¹)	R^2
0.0025	0.0010282	0.9943
0.0050	0.0024110	0.9974
0.0100	0.0045634	0.9972

The correlation coefficient, R^2 , varying from 0.9943 to 0.9974, indicates that the first-order kinetics provides a reasonable description of the Fenton oxidation. The reaction rate of hydroxyl radical, r_{HO^\bullet} , could be expressed as Eq. 23.

$$r_{HO^\bullet} = k_1[Fe^{2+}][H_2O_2] - k_{16}[C_6H_6O][HO^\bullet] - k_{19}[Catechol][HO^\bullet] - k_{20}[hydroquinone][HO^\bullet] \quad (23)$$

According to the steady-state assumption, the value of r_{HO^\bullet} is 0. Rearranging Eq. 23 into Eq. 24 results in.

$$\begin{aligned} k_1[Fe^{2+}][H_2O_2] &= k_{16}[C_6H_6O][HO^\bullet] + k_{19}[Catechol][HO^\bullet] \\ &+ k_{20}[Hydroquinone][HO^\bullet] \end{aligned} \quad (24)$$

Then, the concentration of OH^\bullet could be expressed as Eq. 25.

$$[HO^\bullet] = \frac{k_1[Fe^{2+}][H_2O_2]}{k_{16}[C_6H_6O] + k_{19}[Catechol] + k_{20}[Hydroquinone]} \quad (25)$$

Substituting Eq. 25 into Eq. 21, the following equation based on the first-order reactions can be written as Eq. 26.

$$r_{C_6H_6O} = \frac{k_{16}[C_6H_6O] \cdot k_1[Fe^{2+}][H_2O_2]}{k_{16}[C_6H_6O] + k_{19}[Catechol] + k_{20}[Hydroquinone]} \quad (26)$$

Multiplying Eq. 26 with $\frac{1/k_{16}[C_6H_6O]}{1/k_{16}[C_6H_6O]}$ yields Eq. 27

$$\begin{aligned} r_{C_6H_6O} &= \frac{k_1[Fe^{2+}][H_2O_2]}{1 + \frac{k_{19}[Catechol]}{k_{16}[C_6H_6O]} + \frac{k_{20}[Hydroquinone]}{k_{16}[C_6H_6O]}} \\ &= k_{ap}[C_6H_6O] \end{aligned} \quad (27)$$

Eq. 27 can be rearranged into Eq. 28.

$$\begin{aligned} \frac{[Fe^{2+}][H_2O_2]}{[C_6H_6O]} &= \frac{k_{ap}}{k_1} + \frac{k_{ap} k_{19}}{k_1 k_{16}} \frac{[Catechol]}{[C_6H_6O]} \\ &+ \frac{k_{ap} k_{20}}{k_1 k_{16}} \frac{[Hydroquinone]}{[C_6H_6O]} \end{aligned} \quad (28)$$

The parameters k_{ap}/k_1 , $(k_{ap}/k_1)(k_{19}/k_{16})$ and $(k_{ap}/k_1)(k_{20}/k_{16})$, could be directly determined using multiple linear regression as shown in Appendix II provided that the concentration of intermediates products are known and the values are 5.27056×10^{-5} , -2.55326×10^{-6} and -8.06292×10^{-7} respectively. Referring to $k_{ap} = 4.5634 \times 10^{-3}$, $k_{HO\cdot}$ could be calculated as:

$$\begin{aligned} k_{HO\cdot} &= k_1 = (4.5634 \times 10^{-3}) / (5.27056 \times 10^{-5}) \\ &= 86.07 \end{aligned} \quad (29)$$

The values of k_{19}/k_{16} and k_{20}/k_{16} could be calculated as follows

$$\begin{aligned} \frac{k_{19}}{k_{16}} &= \frac{-2.55326 \times 10^{-6}}{5.27056 \times 10^{-5}} = -0.04844 \\ \frac{k_{20}}{k_{16}} &= \frac{-8.06292 \times 10^{-7}}{5.27056 \times 10^{-5}} = -0.01530 \end{aligned}$$

Therefore, the oxidation rate of phenol in the Fenton process can be expressed as:

$$r_{C_6H_6O} = \frac{86.07[Fe^{2+}][H_2O_2]}{1 - 0.04844 \frac{[Catechol]}{[C_6H_6O]} - 0.01530 \frac{[Hydroquinone]}{[C_6H_6O]}} \quad (30)$$

The values obtained from this model are validated with the experimental value of the phenol degradation (Pontes et al., 2010).

3.2.3 Simulation of Proposed Kinetic Model

After developing kinetic models based on the principal pathways of each organic compound degradation, parameter estimation consists of fitting the model to experimental data by searching the values of the model parameters that best describe these data. The model fitting is defined by an error criterion to be minimized, which is generally the sum

of the squares of the differences between the model predictions and the experimental data. One of the methods to solve for the model parameters includes either linear and/or nonlinear regression where multiple parameters need to be solved. With the aid of mathematical software such as MATLAB and POLYMATH, the regression can be done to fit an arbitrary model equation to a set of data points. The MATLAB function that accomplishes this is nlinfit. POLYMATH can also be used to fit a general nonlinear function model to independent variables from the experimental data where the regression will adjust the values of the model parameters to minimize the sum of squares of the deviations between the model predictions and the experimental data as mentioned earlier.

3.3 GANTT CHART AND KEY MILESTONE

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■												
2	Preliminary Research Work		■	■	■	■	■	■							
3	Submission of Extended Proposal							●							
4	Proposal Defence								■	■	■				
5	Project Work Continues										■	■	■	■	
6	Submission of Interim Draft Report														●
7	Submission of Interim Report														●

No	Detail Work	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
8	Project Work Continues	■	■	■	■	■	■	■								
9	Submission of Progress Report								●							
10	Project Work Continues								■	■	■	■	■			
11	Pre-EDX											●				
12	Submission of Draft Report												●			
13	Submission of Dissertation (Soft Bound)													●		
14	Submission of Technical Paper													●		
15	Oral Presentation														●	
16	Submission of Project Dissertation (Hard Bound)															●

■ Process ● Suggested Milestone

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

For the first part of this work, the unified model is used to predict the degradation of guaiacol and MEA based on the available experimental data with variation in parameters which include pH, dosage of H_2O_2 and initial concentration of ferrous iron. The kinetic model developed in the second part of this work is based on the experimental results of phenol degradation (Pontes et al., 2010) with variation in H_2O_2 concentration.

4.1 Guaiacol Degradation Prediction with the Unified Model

In this part, the model represented by Eq. is used to predict the performance of guaiacol degradation. MATLAB software is used to perform nonlinear multiple regression to obtain the values of K_1 , K_2 and K_3 respectively. Experimental data of guaiacol are obtained from previous work by Samet, Y., et al. (Samet et al., 2011).

4.1.1 Effect of Initial pH on Guaiacol Degradation

Fig. 4.1 shows the plot of experimental data on guaiacol degradation at different pH concentration done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.1. MATLAB coding for the nonlinear multiple regression is shown in the appendix I.

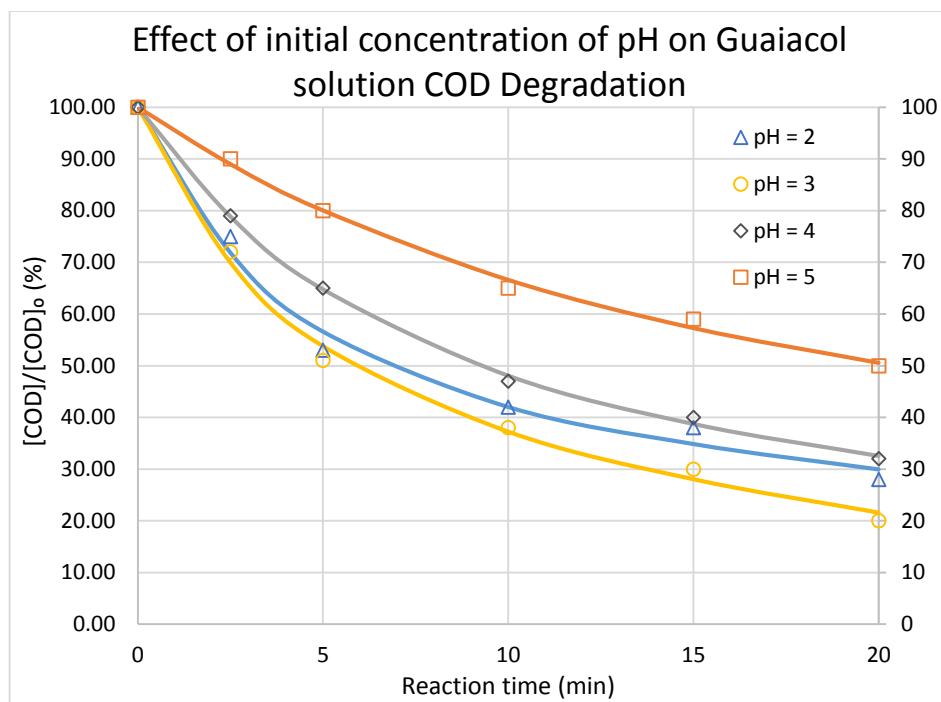


Figure 4.1: Effect of initial pH concentration on guaiacol solution COD degradation

Operational conditions: Dosing rate of H_2O_2 60 mg min^{-1} , $[\text{Fe}^{2+}]_0 = 8 \text{ mM}$ and temperature $40 \text{ }^\circ\text{C}$.

Table 4.1: Results of guaiacol degradation at different initial concentration of pH

	pH = 2	pH = 3	pH = 4	pH = 5
K_1	0.1525	0.1656	0.1037	0.0488
K_2	0.1341	0.1691	0.0940	0.0481
K_3	0.0276	0.0508	0.0279	0.0125
$K (K_1 + K_2)$	0.2866	0.3347	0.1977	0.0969
$\alpha (K_1/K_2)$	1.1372	0.9793	1.1032	1.0146

From the figure above, the initial pH value effective for the degradation of guaiacol through Fenton's process is at pH 3.0 where the production of hydroxyl radical is optimum in acidic conditions. Hydroxyl radical is produced through the decomposition of hydrogen peroxide in the presence of ferrous ions. The rate of degradation decreases when pH value deviates from 3.0.

The rate of guaiacol degradation is low at pH 2.0 due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ between ferric ions and hydrogen peroxide (Samet et al., 2011). High concentration of hydrogen ions resulted in the protonation of peroxide to form the stable oxonium ion H_3O_2^+ which subsequently increases the electrophilicity and stability of H_2O_2 and causes the decrease of H_2O_2 reactivity with Fe^{2+} . The high concentration of hydrogen ions also resulted in higher scavenging effect of hydroxyl radical by hydrogen ions (Feng and Le-Cheng, 2004). The rate of degradation is also slow for pH higher than 3.0 due to the formation of ferrous and ferric hydroxide complexes having lower catalytic capability than ferrous ions and as well as decomposition of hydrogen peroxide into oxygen and water, losing its oxidation ability (Gulkaya et al., 2006).

From the plot of experimental versus modelled data, the values of K_1 and K_2 for guaiacol degradation are the highest for pH 3.0, in agreement from previous investigations of different organic compounds degradation (Ahmadimoghaddam et al., 2010; Wang et al., 2011). This observation indicates that both complex oxidation of guaiacol and further oxidation of organic acid are promoted at pH 3.0. Decreasing the pH value from 3.0 to 2.0 shows a change in guaiacol degradation where the rate is also decreased. The values of K_1 , K_2 and K_3 increase as the pH is increased from 2.0 to 3.0 and then decrease as the pH is further increased to 4 and 5. The highest value for K_1 and K_2 appears at pH 3.0, indicating that guaiacol degradation favors radical reaction over complex reaction. The model can be used to well predict the degradation of guaiacol in Fenton's process.

4.1.2 Effect of the Dosing Rate of H₂O₂ on Guaiacol Degradation

Fig. 4.2 shows the plot of experimental data on guaiacol degradation at different dosing rate of hydrogen peroxide done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.2.

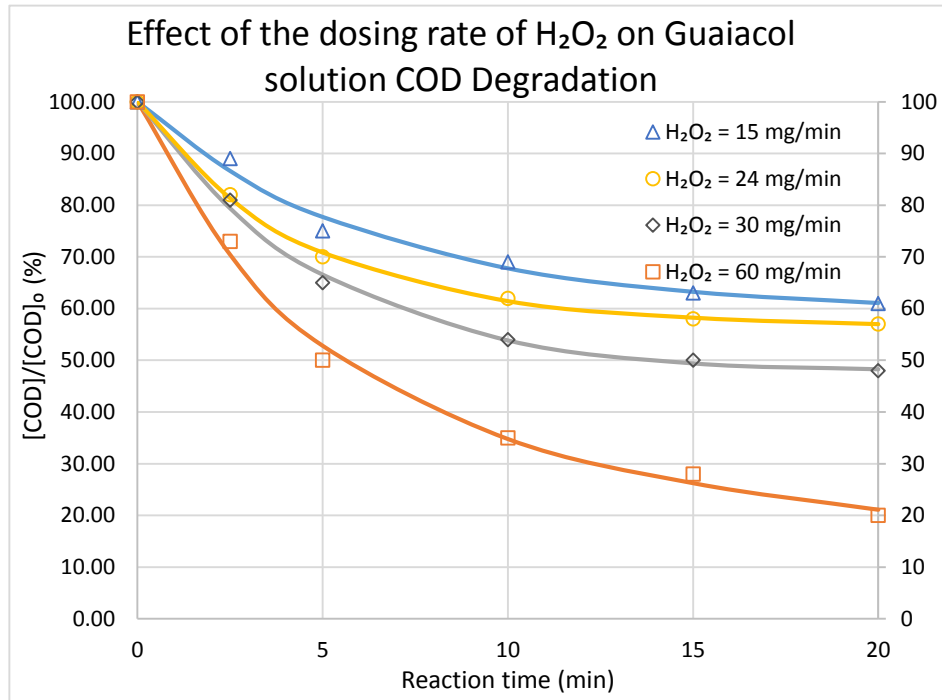


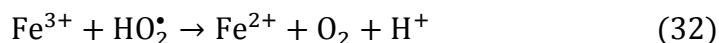
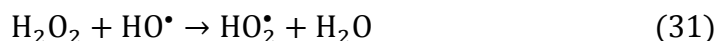
Figure 4.2: Effect of dosing rate of H₂O₂ on guaiacol solution COD degradation

Operational conditions: $[\text{Fe}^{2+}]_0 = 8 \text{ mM}$, temperature $40 \text{ }^\circ\text{C}$ and pH 3.0.

Table 4.2: Results of guaiacol degradation at different dosing rate of H₂O₂

	H ₂ O ₂ = 15 mg/min	H ₂ O ₂ = 24 mg/min	H ₂ O ₂ = 30 mg/min	H ₂ O ₂ = 60 mg/min
K_1	0.0652	0.0980	0.1033	0.1528
K_2	0.1001	0.1341	0.0807	0.0844
K_3	0.0011	0.0013	0.0045	0.0354
$K (K_1 + K_2)$	0.1653	0.2321	0.1840	0.2372
$\alpha (K_1/K_2)$	0.6513	0.7308	1.2800	1.8104

It can be observed from Fig. 4.2 that the rate of degradation of guaiacol increases with increasing dosing rate of H₂O₂. The higher the dosing rate of H₂O₂, the higher the rate of formation of hydroxyl radical which is responsible in the degradation of guaiacol. However, the concentration of H₂O₂ must not exceed the stoichiometric quantity where higher concentration of H₂O₂ will act as the hydroxyl radical scavenger (Harimurti et al., 2010). Simultaneous production of oxygen from the reaction between ferric ions and hydroperoxyl radical as shown in the equations below.



Eq. 31 has a bigger impact on the degradation of organic compound as compared to Eq. 32 because ferric ions are not present from the beginning. Thus, a very high concentration of hydrogen peroxide hinders efficient utilization of the hydroxyl radicals. The degradation of guaiacol through Fenton's process with varying dosing rate of H₂O₂ can be well predicted with the unified model based on the plotted experimental and calculated results.

It can be observed that from the calculated results that the radical reaction is not the preferred way for guaiacol degradation in Fenton's process. Degradation of guaiacol prefers the complex pathways due to its highest value of K₂. Nevertheless, this model can still be used to safely predict the guaiacol degradation at varying dosing rate of hydrogen peroxide. The low value of K₃ can be related to the inefficient removal of organic intermediates such as acetic acid and maleic acid or simply the residual COD.

4.1.3 Effect of Initial Concentration of Fe²⁺ Ion on Guaiacol Degradation

Fig. 4.3 shows the plot of experimental data on guaiacol degradation at different initial concentration of ferrous ion done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.3.

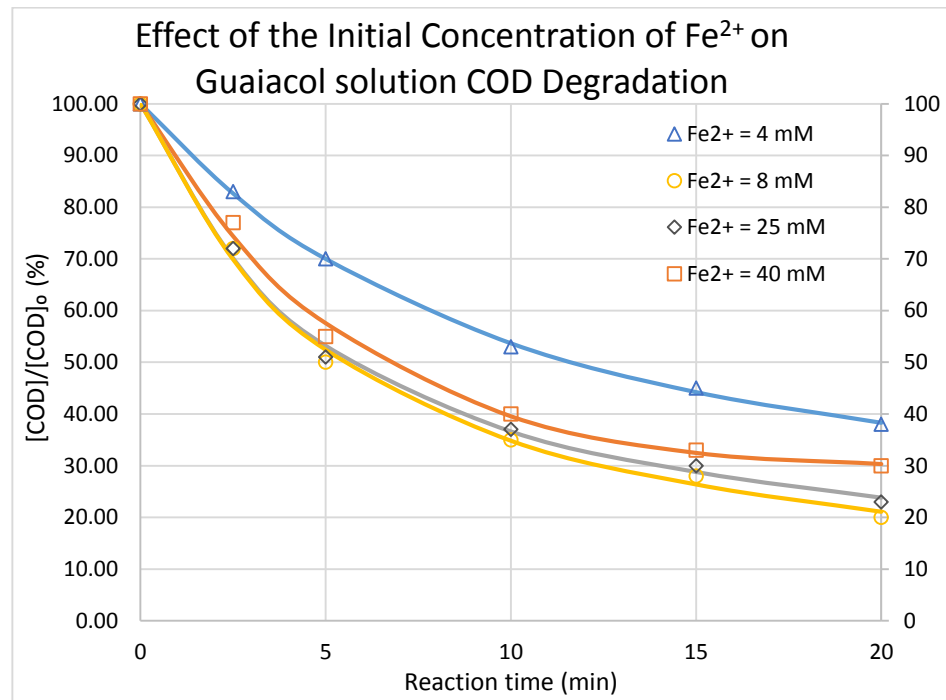


Figure 4.3: Effect of initial concentration of Fe²⁺ ion on guaiacol solution COD degradation

Operational conditions: Dosing rate of H₂O₂ 60 mg min⁻¹, pH 3.0 and temperature 40 °C

Table 1.3: Results of guaiacol degradation at different initial concentration of Fe²⁺

	Fe ²⁺ = 4 mM	Fe ²⁺ = 8 mM	Fe ²⁺ = 25 mM	Fe ²⁺ = 40 mM
K_1	0.0811	0.1579	0.1584	0.1252
K_2	0.0589	0.0972	0.1043	0.0368
K_3	0.0146	0.0386	0.0328	0.0129
$K (K_1 + K_2)$	0.1400	0.2551	0.2627	0.1620
$\alpha (K_1/K_2)$	1.3769	1.6245	1.5187	3.4022

From Fig. 4.3 it can be observed that the rate of degradation of guaiacol increases with increasing initial concentration of ferrous ion from 4 mM to 8 mM. However, the degradation decreases as the initial concentration of ferrous ion is increased to 40 mM. The increase in degradation of guaiacol from 4 mM to 8 mM can be explained by the fact that ferrous ion is the catalyst to produce very reactive hydroxyl radical from decomposition of hydrogen peroxide as shown in Eq. 1. Therefore, better degradation of guaiacol can be achieved with higher concentration of ferrous ion due to the increase in hydroxyl radical. However, when the ferrous ion concentration is increased from 8 mM to 25 mM and 40 mM, the rate of degradation decreases due to the competitive consumption of hydroxyl and perhydroxyl radicals (Samet et al., 2011). Another side effect of using higher concentration of ferrous ion will produce a higher amount of ferric ion sludge which is expensive to be treated and requires large quantity of chemicals as well as manpower (Ramirez et al., 2007).

According to the results obtained from the simulation of guaiacol degradation for varying ferrous ion concentration, the values of K_1 is high enough to support the evidence that guaiacol follows the radical reaction for its degradation in Fenton's process. The value of K_3 however is still the highest as compared to the other three values. From the simulation of these parameters, guaiacol degradation can be sufficiently predicted by using this model.

4.2 Monoethanolamine Degradation Prediction with the Unified Model

The same unified model as shown in Eq. 15 is used to simulate the degradation of MEA in Fenton's process. The calculated results are then validated with the experimental results done by Harimurti et al. (2010) on the degradation of MEA in aqueous solution by Fenton's reagent. The values of K_1 , K_2 and K_3 are determined through nonlinear multiple regression and the results are as shown below.

4.2.1 Effect of Initial pH on MEA Degradation

Fig. 4.4 shows the plot of experimental data on MEA degradation at different initial concentration of ferrous ion done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.4.

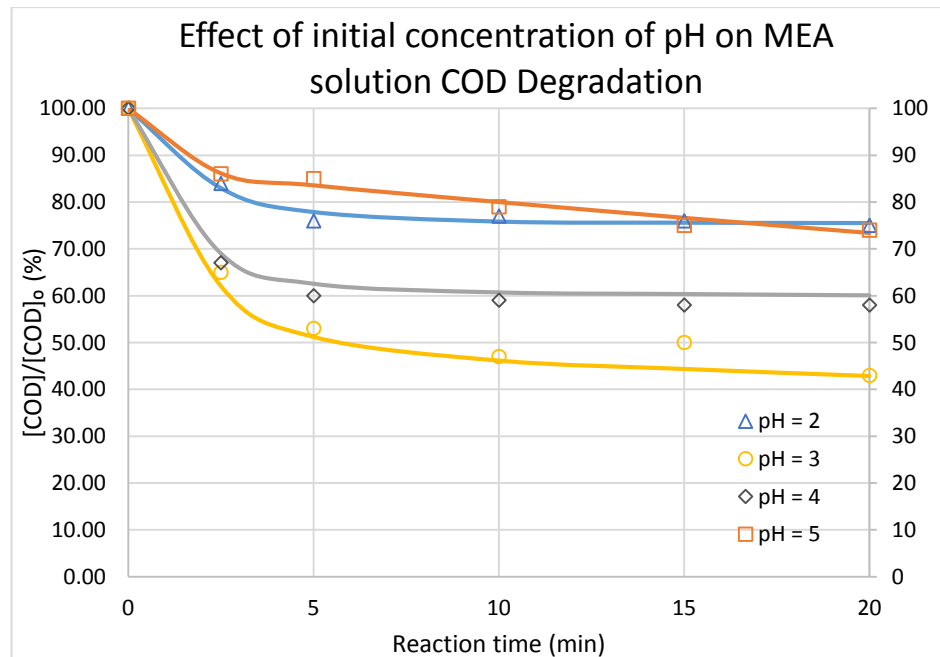


Figure 4.4: Effect of initial pH on monoethanolamine solution COD degradation

Table 4.4: Results of MEA degradation at different initial concentration of pH

	pH = 2	pH = 3	pH = 4	pH = 5
K_1	0.1169	0.2686	0.2459	0.1491
K_2	0.3649	0.2529	0.3861	0.9593
K_3	0.0002	0.0068	0.0009	0.0086
$K (K_1 + K_2)$	0.4818	0.5215	0.6320	1.1084
$\alpha (K_1/K_2)$	0.3204	1.0621	0.6369	0.1554

The degradation of MEA is effective at pH 3.0 in agreement with the degradation of guaiacol in the previous section where pH 3.0 is the optimum condition for the degradation to occur due to the acidic condition. Hydroxyl radicals are largely produced from the decomposition of H_2O_2 in this acidic range of pH. However, as stated before, the degradation performance decreases when pH value deviates is out of the 2.5-3.5 range (Khamaruddin et al., 2011; Oancea and Meltzer, 2013; Tokumura et al., 2013).

The reduce in the degradation of MEA in the lower pH range is due to several factors which include the formation of complex ion between ferric ion and hydrogen peroxide such as oxonium ion resulted from the solvating ability of hydrogen ion and the enhanced scavenging effect of hydroxyl radical by hydrogen ion. Protonation of hydrogen ion to form the stable oxonium ion is also another contributor to the decrease in MEA degradation in pH lower than 3.0. The degradation of MEA also decreases for pH more than 3.0 due to the decomposition of hydrogen peroxide to give water and carbon dioxide which resulted in losing of its oxidation ability (Gulkaya et al., 2006).

For the values of K_1 , K_2 and K_3 obtained from the nonlinear multiple regression of the unified model, it can be observed that the degradation of MEA can be predicted by this model. The degradation pathway of MEA can be assumed to follow radical reaction due to the highest value of K_1 and K_3 respectively.

4.2.2 Effect of Hydrogen Peroxide Concentration on MEA Degradation

Fig. 4.5 shows the plot of experimental data on MEA degradation at different hydrogen peroxide concentration done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.5.

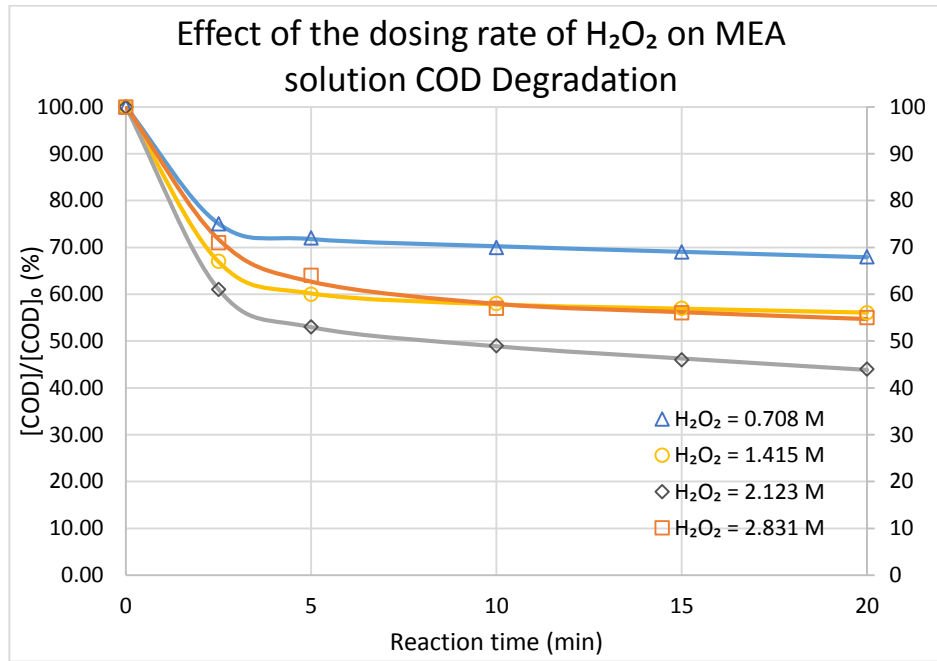


Figure 4.5: Effect of H_2O_2 concentration on MEA solution COD degradation

Table 4.5: Results of MEA degradation obtained for different H_2O_2 concentration

	$H_2O_2 = 0.708$ M	$H_2O_2 = 1.415$ M	$H_2O_2 = 2.123$ M	$H_2O_2 = 2.831$ M
K_1	0.2441	0.2677	0.3221	0.1924
K_2	0.6401	0.3899	0.3716	0.2888
K_3	0.0034	0.0030	0.0108	0.0052
$K (K_1 + K_2)$	0.8842	0.6576	0.6937	0.4812
$\alpha (K_1/K_2)$	0.3813	0.6866	0.8668	0.6662

The degradation of MEA is effective at the H_2O_2 of 2.123 M as shown in Fig. 4.5 above where any increase or decrease of H_2O_2 will result in the reduce of MEA degradation. Excess H_2O_2 concentration will result in the scavenging effect of hydroxyl radical. The same observation can be deduced from the discussion for the degradation of guaiacol where simultaneous generation of oxygen from the excess H_2O_2 concentration does not help in the degradation process (Harimurti et al., 2010). In the presence of higher concentration of H_2O_2 , organic compounds will have to compete with H_2O_2 to react with hydroxyl radical which will result in reduced treatment efficiency (Samet et al., 2011). The optimum concentration of H_2O_2 will depend on the type of organic compounds for the Fenton's oxidation.

From the calculated results presented in Table 4.5, it shows that the radical pathway is not the efficient way for MEA degradation (Feng and Le-Cheng, 2004). The value of K_1 and K_3 for H_2O_2 concentration of 2.831 M are not comparatively higher as compared to the values of K_1 and K_3 for other H_2O_2 concentration. The low value of K_3 indicates that the removal of organic intermediate such as acetic acid is not efficient resulted in the presence of trace amount of COD in the final substrate.

4.2.3 Effect of Ferrous Iron Dosing on MEA Degradation

Fig. 4.6 shows the plot of experimental data on MEA degradation at different ferrous iron dosing done by Samet et al. (2011) represented by the symbols and the modelled data from the unified model in Eq. 15 are represented by the lines. Parameter K_1 , K_2 and K_3 determined through nonlinear multiple regression by using MATLAB software are shown in Table 4.6.

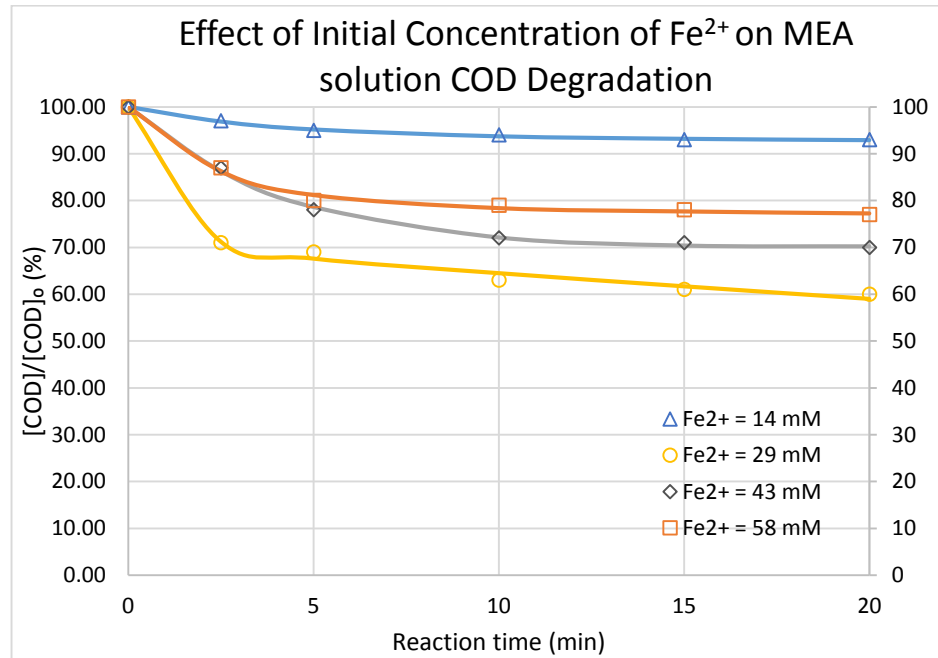


Figure 4.6: Effect of Fe²⁺ dosing on MEA solution COD degradation

Table 4.6: Results of MEA degradation for different Fe²⁺ dosing

	Fe ²⁺ = 14 mM	Fe ²⁺ = 29 mM	Fe ²⁺ = 43 mM	Fe ²⁺ = 58 mM
K_1	0.0168	0.3084	0.0721	0.0871
K_2	0.2413	0.7149	0.1543	0.3203
K_3	0.0004	0.0089	0.0016	0.0010
$K (K_1 + K_2)$	0.2581	1.0233	0.2264	0.4074
$\alpha (K_1/K_2)$	0.0696	0.4314	0.4673	0.2719

From Fig. 4.6, the rate of degradation of MEA is optimum at ferrous ion concentration of 29 mM. Increasing ferrous ion concentration resulted in the increasing of hydroxyl radical availability for the degradation of MEA according to the Eq. 1. Ferrous ion act as the catalyst for the formation of hydroxyl radical which will further degrade MEA into water and carbon dioxide. However, further increment of ferrous iron concentration from 29 mM to 43 mM and 58 mM resulted in the reduction of MEA degradation due to the competitive consumption of hydroxyl radical and perhydroxyl radical (Samet et al., 2011).

According to the calculated results in Table 4.6, the highest value of K_1 and K_3 are at ferrous ion with concentration of 29 mM which indicates that the degradation of MEA for different ferrous ion concentration favors the radical oxidation. It can be assumed that the degradation of MEA follows the unified model as shown in Eq. 15 based on the plot of calculated data and the experimental data.

4.3 Mechanistic Study of Phenol Degradation in Fenton's Process

From the model developed for the degradation of phenol in section 3.2.2, the model of phenol degradation in Fenton's process can be illustrated as below.

$$r_{C_6H_6O} = \frac{86.07[Fe^{2+}][H_2O_2]}{1 - 0.04844 \frac{[Catechol]}{[C_6H_6O]} - 0.01530 \frac{[Hydroquinone]}{[C_6H_6O]}}$$

In the development of the model, a set of reactions has been considered, Eqs. 16-20, where the intermediates formed are hydroquinone and catechol. The time evolution of phenol, hydroquinone, catechol and carbon dioxide can be obtained from the experimental results on the phenol degradation by the Fenton's process (Pontes et al., 2010).

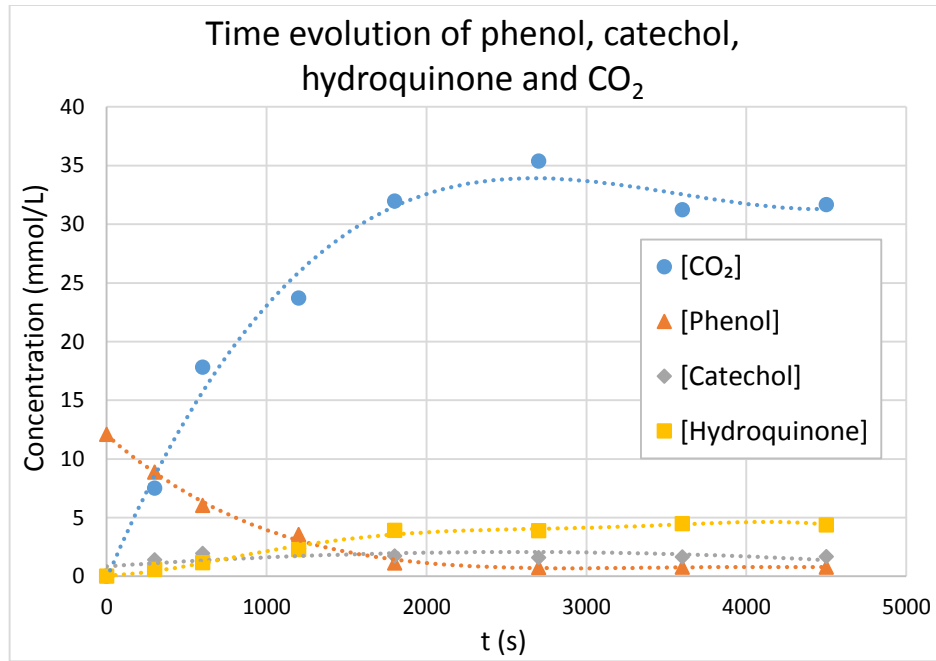


Figure 4.7: Experimental results for phenol degradation by the Fenton's process (Pontes et al., 2010)

By plotting the value of $\ln([\text{C}_6\text{H}_6\text{O}]_0/[\text{C}_6\text{H}_6\text{O}])$ as a function of reaction time from the derivation of Eq. 22, first-order kinetics with respect to phenol could be obtained as shown below with the linear correlation coefficients (R^2) and k_{ap} or the slopes of the first-order kinetics which are shown in the table 3.1. The values of k_{ap} are dependent on the hydrogen peroxide concentration and it is first order.

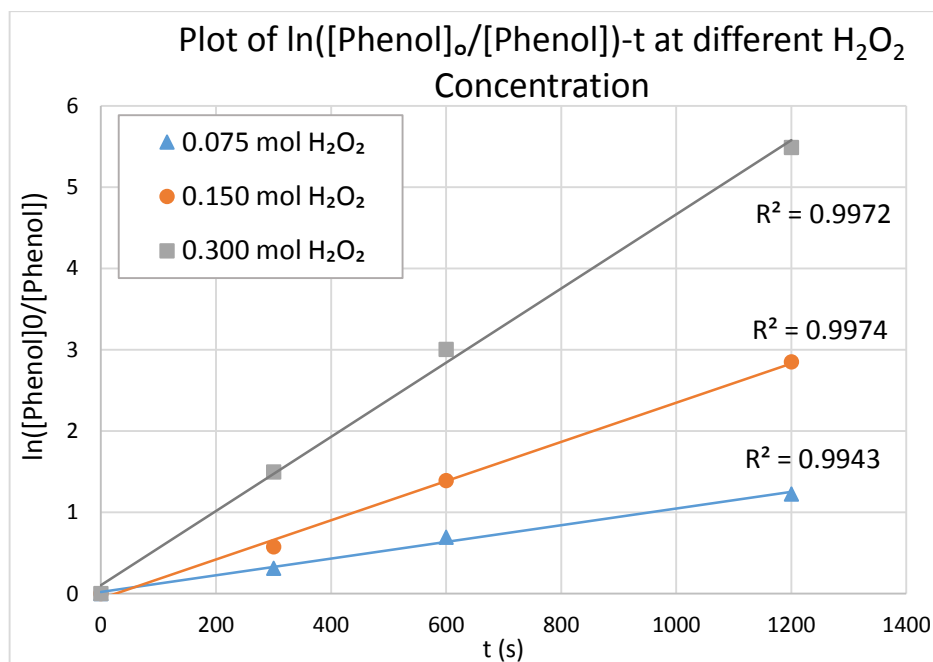


Figure 3: Fitting of the experimental data to first order reaction kinetics for different H₂O₂ dosing rate

The variation of the apparent rate constant (k_{ap}) values at different hydrogen peroxide concentration is plotted as below where it can be observed that the values of k_{ap} increases with increasing H₂O₂ concentration. The increase in H₂O₂ result in the increase of hydroxyl radical formation from Eq. 1 where ferrous iron acts as the catalyst for the decomposition of H₂O₂ into hydroxyl radical.

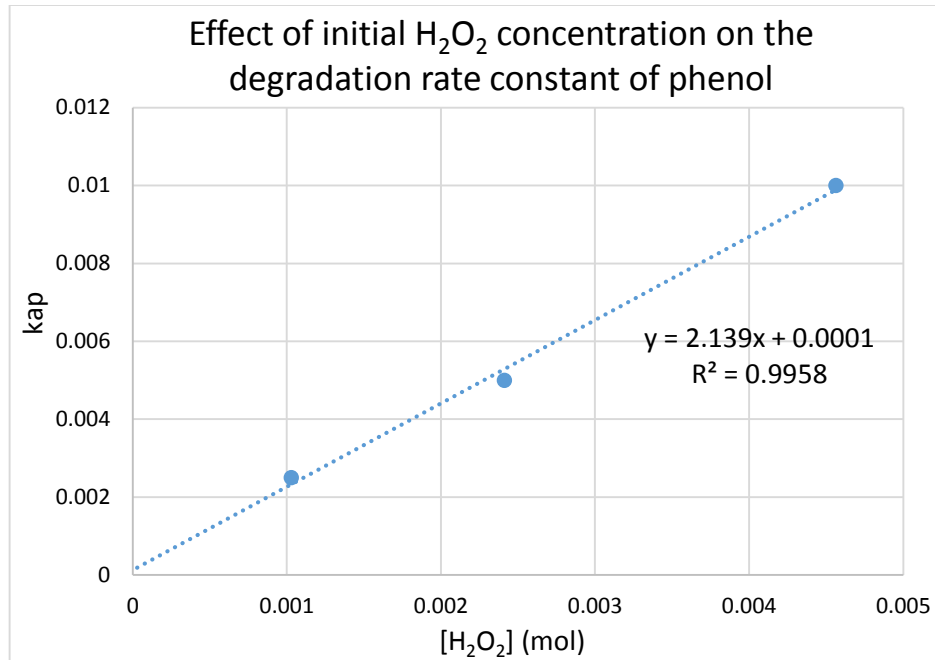


Figure 4.9: Evolution of k_{ap} at different H₂O₂ concentration for phenol degradation

The experimental values are then plotted against the calculated values from Eq. 30 by using multiple linear regression as shown in the appendix. The results are as shown below.

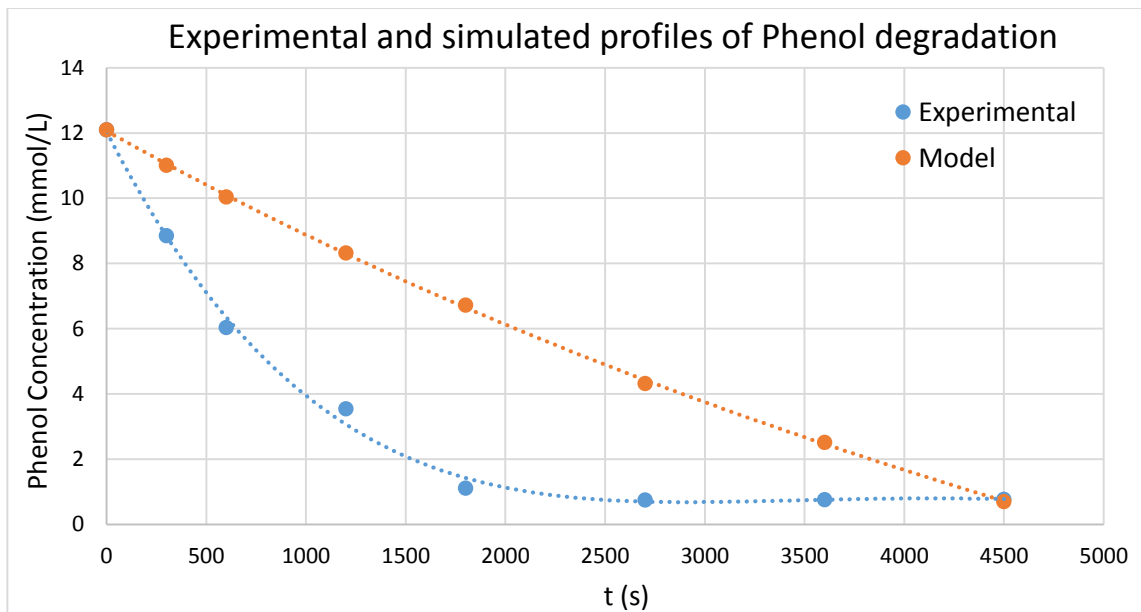


Figure 4.10: Calculated data from the mechanistic model and the experimental data (Pontes et al., 2010)

From Fig. 4.10, it can be observed that the degradation of phenol can be roughly predicted by using the model developed in section 3.2.2. The rate of degradation of phenol increases with the increase in H_2O_2 concentration to the increase in hydroxyl radical formed from Eq. 1.

For improvement of the model developed, it is suggested to establish a correction factor for the model in the future work. Consideration of higher order reaction can also be done for phenol degradation in order to better fit the experimental results.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The project addresses the mathematical modeling of the refractory organic compound degradation by the Fenton's oxidation. The kinetic model was developed by using the methods used by established research. In this project, the development of mathematical model was done based on these three operating parameters, namely pH variation, hydrogen peroxide concentration and ferrous iron concentration. The established model will be compared with the experimental results in order to develop a mathematical model which can be used to predict the performance of refractory organic compound degradation through the Fenton's oxidation. The project is within the capability of a final year student to be executed with the help and guidance from the supervisor and the coordinator. The feasibility of this project is well-suited with the time frame and can be completed within the allocated time. The student will also have the opportunity to explore in depth the use of engineering software such as MATLAB and POLYMATH in determining the model parameters. Thus, this project is a good platform for the student to experience working environment by solving real-life situations with the aid of engineering software. The model developed can be used to predict the performance of organic compounds degradation in Fenton's process for respective organic compounds. The unified model can be used to predict different organic compounds and preferred reaction pathways can also be predicted.

5.2 Recommendations

The suggested future work for this project will include the simulation of more organic compounds with the unified model to validate its effectiveness in predicting the organic compounds degradation. The simulated results can be validated with the established experimental data done by previous researchers on different parameters.

Besides that, the mechanistic model of phenol degradation developed in this project can be further improvised to obtain more complete simulation of experimental results for phenol degradation. The accuracy of the model can be improved by considering more sets of reactions and by introducing a correction factor for the developed model. Besides that, experimental work can also be conducted together with the development of the mechanistic model for the ease of experimental results analysis. Different parameters could be used in future work expansion where it will best represent the model developed. The improvisation of the model can be achieved by considering and comparing higher order reaction apart from the first-order reaction.

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APPENDICES

Appendix I

The values of K_1 , K_2 and K_3 are determined through non-linear regression method with the aid of MATLAB software as shown in the below.

```
clear
clc
clf
format compact
% the data
    x = [0, 2.5, 5, 10, 15, 20];
    y = [1, 0.62, 0.45, 0.36, 0.32, 0.30];
% the proposed model (fh is a handle to the function)
    fh = @(k,x) ((k(2)./(k(1)+k(2)-k(3)))*exp(-k(3)*x))+(((k(1)-
k(3))./(k(1)+k(2)-k(3)))*exp(-k(1)*x-k(2)*x));
% guess values for parameters
    k0 = [0.5000,0.5000,0.0500];
% plot the raw data
    plot (x,y,'s','markersize',5,'color',[0,0,0]);
    hold on
% determine the best fit values for coefficient (khat)
    khat = nlinfit(x,y,fh,k0);
% plot the fit
    xf = linspace (x(1), x(length(x)));
    plot(xf,fh(khat,xf),'linewidth',1,'color',[1,0,0]);
    legend('original data','fit data','location','Best')
% the result
    khat(1)
    khat(2)
    khat(3)
```

This model is then applied to other degradation of organic compounds where either the value of COD, TOC or BOD are available from the experimental data.

Appendix II

Multiple linear regression of developed model for phenol degradation.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.84649687
R Square	0.716556952
Adjusted R Square	0.635573224
Standard Error	3.23912E-06
Observations	10

<i>ANOVA</i>					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	2	1.85668E-10	9.28339E-11	8.848159609	0.012123565
Residual	7	7.34432E-11	1.04919E-11		
Total	9	2.59111E-10			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	5.27056E-05	2.4955E-06	21.12031333	1.34224E-07
X Variable 1	-2.55326E-06	8.82223E-06	-0.289412089	0.780650165
X Variable 2	-8.06292E-07	3.1358E-06	-0.257124759	0.80447666

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	5.2706E-05	2.496E-06	21.1203	1.34224E-07	4.681E-05	5.861E-05	4.680E-05	5.861E-05
X Variable 1	-2.553E-06	8.822E-06	-0.2894	0.780650165	-2.34E-05	1.831E-05	-2.34E-05	1.831E-05
X Variable 2	-8.063E-07	3.136E-06	-0.2571	0.80447666	-8.22E-06	6.609E-06	-8.22E-06	6.609E-06

RESIDUAL OUTPUT

<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>
1	5.27056E-05	3.16361E-07
2	5.22485E-05	-4.90886E-07
3	5.17349E-05	-1.17804E-07
4	5.05093E-05	-1.02148E-06
5	4.59397E-05	2.6455E-06
6	4.32169E-05	4.77514E-06
7	4.24901E-05	2.09225E-06
8	4.26339E-05	5.39893E-08
9	4.26909E-05	-2.74682E-06
10	4.27105E-05	-5.50625E-06

