

CERTIFICATION OF APPROVAL

Sludge Disintegration using Fenton Treatment

by

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14248

A project dissertation submitted to be
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL)

Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 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.

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ABSTRACT

Activated sludge treatment has been widely applied to treat wastewater due to its advantages, including low running cost and high degradation efficiency. However, the cost of waste activated sludge treatment is notably high, representing more than half of the total operating costs of the wastewater treatment plant facilities. Thus, the study is conducted to investigate the optimum operating conditions on amount of $\text{H}_2\text{O}_2/\text{kg TS}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and reaction time for Fenton treatment of settled activated sludge. The experiments were conducted by varying the amount of Fenton's reagent, fixed at pH 3, allowing for selected reaction time following the Central Composite Design combinations by Design Expert software. For performance evaluation, mixed liquor volatile soluble solids (MLVSS), soluble chemical oxygen demand (sCOD), capillary suction time (CST) and extracellular polymeric substances (EPS) were measured. The optimum conditions were found to be 25 g $\text{H}_2\text{O}_2/\text{kg TS}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 14 and reaction time 1.5 h with MLVSS removal 23% to 28%, sCOD 5000 mg/L to 6200 mg/L, CST 129 s to 170 s and EPS 80 mg/L to 115 mg/L. In sum, within the study range of chemical dosages in this research, the mechanism of sludge disintegration in Fenton treatment reduced the sludge quantities, however, impaired its dewaterability.

ACKNOWLEDGEMENTS

First of all, I wish to extend my sincere appreciation to my supervisor, Dr. Mohamed Hasnain Isa for his help and supervision in conducting this study. His professional advice, guidance and motivation throughout the course tremendously helped me to a better understanding of environmental engineering. I would also like to extend my utmost appreciation to Mr. Gan Chin Heng for his precious and helpful comments and suggestions in my study.

I wish to express my heartfelt thanks to all the technicians of the Civil Engineering Environmental laboratory, especially Mr. Mohd. Khairul Anuar Jamaluddin for his technical assistance. My sincere appreciation also extends to all my colleagues who have provided assistance and views.

Last but not least, special thanks go to my family members for their patience, support and understanding over the entire period of my studies.

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CHAPTER ONE

INTRODUCTION

1.1 Background of Study

As a fundamental of biological wastewater treatment technology, the removal of dissolved and particulate biodegradable constituents and stabilization of organic matter found in the wastewater is accomplished using a variety of microorganisms. Activated sludge system has been widely used since it offers major advantages over alternative treatment strategies such as lower operating costs, highly efficient degradation and removal of organic and inorganic compounds (Tokumura et al., 2007). However, an inevitable drawback of the system is the excess biomass produced during the treatment process. Often, the sludge management is one of the most critical and expensive problems for a treatment plant operation. Therefore, effective treatment of excess sludge is very important. Over the past 30 years, a wide

variety of treatment technologies have been studied, developed, and applied for the minimization of sludge production.

In general, advanced oxidation processes (AOPs) are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products. AOPs typically involve the generation and use of hydroxyl free radical (HO^\bullet) as a strong oxidant to destroy organic compounds that cannot be oxidized by conventional oxidants. Second to fluorine, the hydroxyl radical is the strongest oxidant known (Metcalf & Eddy, 2003). It reacts unselectively once being formed and the dissolved constituents will be quickly and completely fragmented and converted into small inorganic molecules, by a series of oxidation reactions. These hydroxyl radicals can be produced with the help of other oxidizing agents (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). A variety of technologies have been developed since the late 19th century in order to yield a maximum production of hydroxyl free radical through pre-programmed dosages, sequences and combinations of these reagents. The various technologies are summarized in Table 1.1 (Metcalf & Eddy, 2003), according to whether ozone is used in the reaction.

This study focuses on one particular advanced oxidation process, the Fenton process. It is composed of four successive stages, which are pH adjustment at low acidic values, oxidation, neutralization and coagulation (Sahinkaya, 2014). Its oxidation mechanism depends on the production of the reactive hydroxyl (HO^\bullet) radical in the acidic condition by catalytic decomposition (in the presence of Fe^{2+}) of hydrogen peroxide (H_2O_2). It is an attractive oxidation system because iron is an abundant, non-toxic element and H_2O_2 is environmentally safe.

Table 1.1 Advanced oxidation processes used in sludge treatment
(Metcalf & Eddy, 2003)

Ozone-based processes	Non-ozone-based processes
Ozone at elevated pH (8 to >10)	$\text{H}_2\text{O}_2 + \text{UV}$
Ozone + UV_{254} (also applicable in the gas phase)	$\text{H}_2\text{O}_2 + \text{ferrous salt}$ (Fenton process)
Ozone + H_2O_2	$\text{H}_2\text{O}_2 + \text{UV} + \text{ferrous salt}$ (photo-Fenton process)

Ozone + UV ₂₅₄ + H ₂ O ₂	Electron-beam indication
Ozone + TiO ₂	Electrohydraulic cavitation
Ozone + TiO ₂ + H ₂ O ₂	Ultrasonics
Ozone + electron-beam indication	Nonthermal plasmas
Ozone + ultrasonics	Pulsed corona discharges
	Photocatalysis (UV + TiO ₂)
	Gamma radiolysis
	Catalytic oxidation
	Supercritical water oxidation

1.2 Problem Statement

Activated sludge process has been widely applied to treat wastewater due to its advantages including low running cost and high degradation efficiency: their effluents can meet stringent discharge standards thus ensuring a minimum residual impact on the aquatic environment (Dewil et al., 2004). Through their microbial activity (i.e. oxidation, conversion of organic matter and synthesis of new cells), these biological processes produce huge amounts of waste activated sludge (WAS), called biosolids or biomass. The higher collection rates and disposal of the WAS is a significant drawback inherent to most biological processes. Dewil et al. (2004) pointed out that this individual process mainly contributes to its total operation costs, reaching as high as 35-50%. He and Wei (2010) estimated that the operating cost has increased over the years, reaching 50-60% in total in their study. There is now increasing concern about the operating cost. Much attention has been focused on the advanced sludge treatment processes in order to reduce the amount of sludge production and to improve the dewaterability of the sludge as well as its biodegradability. Advanced oxidation processes (AOPs) are emerging alternative technologies for efficient removal of organic wastewater pollutants with high chemical stability and/or low biodegradability. These AOPs operate near-ambient temperature and pressure and generate strongly oxidizing radical species (primarily HO[•]) for complete decomposition of organic pollutants into non-toxic products like CO₂, H₂O and inorganic salts.

1.3 Objective

The main objective of this study is to investigate the effect of operating parameters (amount of H_2O_2 required, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and reaction time) on sludge disintegration and dewaterability by Fenton treatment.

1.4 Scope of Study

This study focuses on the Fenton process and determines the effects of main operational parameters (i.e. ferrous ion and hydrogen peroxide dosages per sludge concentration) on degradability and dewaterability of the sludge. Optimum operating conditions for sludge degradation are also determined.

1.5 Thesis Organization

This thesis has been organized into the following five chapters:

Chapter 1 introduces the waste activated sludge and its disposal, problem statement, objectives and scope of the study.

Chapter 2 presents a brief review of the advantages of Fenton-based advanced oxidation process. Principles of Fenton chemistry and application of the reaction in previous studies are also discussed.

Chapter 3 presents the methodology of the study – sludge sampling, experimental procedures for Fenton, response surface methodology and analytical methods for the selected responses.

Chapter 4 presents the characteristics of raw waste activated sludge, the results of Fenton treatment, followed by discussion.

Chapter 5 recaps the scope of the study and research method, concluding the results and findings of the study along with suggestions for future work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

Excess sludge produced by biological wastewater treatments such as activated sludge system has recently become a big issue. The disposal of excess sludge may account up to 50% of the total operating cost of a treatment plant. Therefore, the growing quantities of sludge generated require advanced treatment processes that are capable of achieving significant cuts in mass and volume. Technologies that combine efficient sludge mass and volume reductions with compliance to the legal restrictions and the production of reusable sludge products at relatively low costs represent the most desirable solutions.

2.2 Advantages of Fenton-based Advanced Oxidation Process (AOP)

Among all AOPs, oxidation systems based on the Fenton reagent (hydrogen peroxide and iron catalyst) have been widely implemented to remove recalcitrant organic compounds during wastewater remediation (Bokare et al, 2014). The reasons for the widespread applicability of Fenton oxidation processes include the following: (1) oxidizing radicals are generated at ambient pressure and temperature, which saves the cost of having complicated reactor facilities, (2) the simple and flexible nature enables easy implementation, (3) the generation of HO[•] is completed within the shortest reaction time among all other AOPs, (4) the use of cheap, moderately reactive and easy-to-handle reagents (ferrous salts and H₂O₂), and (5) the low commercial cost with ample supply of iron catalysts (Bokare et al., 2014). These are consistent with the suggestion from Sahinkaya et al. (2014), stating that the low initial capital cost and simple and cheap operation are the most important advantages of the Fenton process.

2.3 Fenton Chemistry Principles

Numerous applications of hydrogen peroxide (H_2O_2) in the removal of pollutants from wastewater, such as sulphites, hydrochlorites, nitrites, cyanides and chlorine, are known (Venkatadri and Peeters, 1993). Other related uses include the bleaching of pulp and paper and organic synthesis. However, oxidation by H_2O_2 alone is not desirable for treating high concentrations of certain refractory contaminants due to low rates of reactions at reasonable H_2O_2 concentrations (Neyens et al., 2002).

In 1894, Henry John Horstman Fenton first discovered the activation of H_2O_2 by ferrous ions (Fe^{2+}) to oxidize tartaric acid (Barbusi ski, 2009). This oxidation process is also alternatively known as “Fenton reaction”. The mixture of hydrogen peroxide and ferrous ion was later named after the scientist, as the “Fenton reagent”. The hydroxyl radicals (HO^\bullet) are generated via a complex reaction sequence, initiated by ferrous ions and propagated by ferric ions (Fe^{3+}).



In this process, hydrogen peroxide (H_2O_2) acts as oxidizing agent. According to Dewil et al. (2004), hydrogen peroxide is a strong oxidant (standard potential 1.80 and 0.87V at pH 0 and 14, respectively). Transition metal salts (in this case, iron salts) can activate H_2O_2 to form the hydroxyl radicals which are stronger oxidants than H_2O_2 itself (oxidation potential 2.8V). This favors the rate of reactions at reasonable H_2O_2 concentration. The relative oxidizing power of the hydroxyl radical, along with other common oxidants, is summarized in Table 2.1.

Table 2.1 Comparison of oxidizing potential of various oxidizing agents
(Metcalf & Eddy, 2003)

Oxidizing agent	Electrochemical oxidation potential (EOP), V
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

Furthermore, the newly formed ferric ions (Fe^{3+}) may catalyze H_2O_2 , causing it to be decomposed into water and oxygen, forming ferrous ions and radicals at the same time (Neyens et al., 2002).



The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction (Walling and Goosen, 1973; De Laat and Gallard, 1999).



Eq. 2.8 implies that H_2O_2 can act as an OH^\bullet scavenger as well as an oxidizing agent as shown in Eq. (2.2). Considering the process of H_2O_2 decomposition into water,

Walling (1975) expressed concern on the pH conditioning of the Fenton reagent and summed up the overall Fenton chemistry as



Eq. 2.8 highlights the presence of H^+ in the decomposition of H_2O_2 . This suggests and an acidic environment is favorable for producing larger amount of hydroxyl radicals. This concept is supported by several experimental studies, which consistently agreed on pH 3 is the most optimum for Fenton oxidation (Sahinkaya et al., 2014; Neyens et al., 2002; Erden and Filibeli, 2011; Hickey et al., 1995).

2.4 Sludge Disintegration Mechanism

The free radicals generated by the Fenton process then engage in secondary reactions and attack organic molecules by radical addition, hydrogen abstraction, electron transfer and radical combination. Metcalf & Eddy (2003) simplified these reactions as follows:

- a. Radical addition. Hydroxyl radical reacts with unsaturated or aliphatic organic compound and produces organic radical which can further be oxidized by oxygen or ferrous iron until a stable oxidized end product is formed.



- b. Hydrogen abstraction. Generated hydroxyl radical can be used to remove hydrogen from an organic compound forming an organic radical. This initiates a chain reaction with oxygen, producing a peroxy radical, which can react with another organic compound, and so on.



- c. Electron transfer. Electron transfer results in the formation of ions with a higher valence. Oxidation of a monoatomic negative ion will result in the formation of an atom or a free radical.



- d. Radical combination. Two radicals form a stable product.



Oxidation of the refractory organic compounds by Fenton's reagent is rapid and exothermic and, in principle, should result in the oxidation (or conversion) of contaminants to primarily carbon dioxide and water (Bokare et al., 2014).

The inclusion of HO[•] disintegration technology into the sludge treatment process has been studied by a number of researchers in the past. At the microscopic level, these hydroxyl radicals react with the sludge flocs and microbial cells, and extract the intracellular materials into the liquid phase of biological sludge (Sahinkaya et al., 2014). Erden and Filibeli (2009) described the sludge disintegration mechanism as disruption of the microbial cells in the sludge, thereby destroying the cell walls and releasing the cell content so that these substances contained in the cell are solubilized. Tokumura et al. (2007) characterized it as a decomposition method of the cell wall of a microbe. The rupture of cell wall renders the microbe unable to maintain its form and becomes protein, which is easy for the subsequent decomposition. Therefore, the effect of cell rupture by disintegration can be estimated by soluble protein concentration because the cytoplasm of microorganisms is mainly composed of protein (Sahinkaya et al., 2014).

2.5 Applications of Fenton Process in Previous Studies

There are several studies on sludge disintegration via Fenton oxidation process using Fe²⁺. The main concerns of these studies are similar, that is to tackle the problem of excess biomass for activated sludge system.

Comparisons with previous studies were made and their findings were compatible to one another. Sahinkaya et al. (2014) dedicated their study to determine the optimum operating conditions for Fenton process, including pH, catalyst iron dosage, hydrogen peroxide dosage in affecting the performance of classical Fenton process (CTP) and “Fenton-type processes” (FTP). Sahinkaya et al. (2014) concluded the optimum conditions as catalyst Fe²⁺ dosage = 4 g/kg TS, H₂O₂ dosage = 40 g/kg TS and pH = 3. In a study carried out by Neyens et al. (2002), the optimum conditions were found to be catalyst Fe²⁺ dosage = 1.67 g/kg TS, H₂O₂ dosage = 25 g/kg TS and

pH = 3. In a similar study, Erden and Filibeli (2011) obtained the optimum conditions with 0.067 g Fe²⁺/g H₂O₂, and 60 g H₂O₂/kg dried solids (DS). All of these experiments were conducted for 1 hour at ambient temperature and pressure. Optimum conditions achieved by the previous researchers are summarized in Table 2.2.

Table 2.2 Optimum conditions of previous studies

Researchers	H ₂ O ₂ dosage	H ₂ O ₂ /Fe ²⁺ molar ratio
Sahinkaya et al. (2014)	40 g/kg TS	10
Neyens et al. (2003)	25 g/kg TS	15
Erden and Filibeli (2011)	60 g/kg TS	15

Similar studies were also done by He and Wei (2009) and Dewil et al. (2004) for the purposes of minimizing sludge production and drying performance, respectively. Their findings showed that Fenton oxidation process can effectively be used in WAS treatment. Not only was the dewaterability of sludge enhanced, but the solid content was also reduced. The effects of temperature, hydrogen peroxide concentration, pH and reaction time on the dewaterability of the sludge were tested. The process yielded a considerable reduction of dry solid contents (DS) and organic dry solid contents (ODS) and an improved dewaterability with a 30% reduction of the sludge volume when compared to the untreated sludge sample (Dewil et al., 2004).

Neyens et al. (2002) stated that the difficulty in activated sludge dewatering is mainly attributed to the presence of extracellular polymer (ECP). ECP is present in varying quantities of sewage sludge, occurring as either a highly hydrated capsule surrounding the bacterial cell wall or loose in solution as slime polymers. It is thought to aid the survival of the bacterial cell by preventing desiccation and acting as ion-exchange resin, controlling the ionic movement from solution into the cell.

Erden and Filibeli (2009) conducted their experiments in two stages and deduced that cell lysis transforming cell content into the medium is the first, and breakdown of extracellular polymeric substances (EPS) fraction in the sludge is the second stage of floc disintegration. Besides, the second stage of digestion enhanced the degradation of protein contents of sludge. Neyens et al. (2004) also concluded that oxidation

degrades EPS proteins and polysaccharides, reducing the EPS water retention properties and promotes flocculation which reduces the amount of fine flocs.

In examining the sludge disintegration, He and Wei (2009) observed that the treatment resulted in colour change from dark brown (activated sludge slurry before disintegration) to pale gray (degraded sample). Similar to the conclusion by Neyens et al. (2004), the microscopic observation indicated that the number and size of activated sludge flocs were decreased by the Fenton oxidation process.

In accordance with these reports, a series of experiments was planned and carried out to understand performances of the Fenton oxidation process.

CHAPTER THREE

METHODOLOGY

3.1 Sludge Sampling

In this study, waste activated sludge (WAS) was obtained from the return pipe from secondary clarifier sludge hopper of the sewage wastewater treatment plant in Universiti Teknologi PETRONAS. The sludge sample was allowed and stored in the cold room at 4 °C prior to use.

3.2 Experimental Procedures

The Fenton treatment was performed in a beaker, containing 500 mL of sludge at ambient temperature and pressure. The pH of the sludge was adjusted to the 3 using 95~98% H₂SO₄. Ferrous sulfate (FeSO₄•7H₂O) and hydrogen peroxide (H₂O₂) was added according to the selected H₂O₂/TS and H₂O₂/Fe²⁺ molar ratio simultaneously. The mixture was stirred gently during reaction. After the reaction, the sludge mixture was taken at selected reaction time, adjusted to pH above 10 with 48~50% NaOH to stop the Fenton reaction and mixed for 10 minutes for measurement of selected parameters.

3.3 Response Surface Methodology

Design Expert software was used to design the experiments for determining the optimum operating conditions and the statistical design was based on three operating parameters: g H₂O₂/kg TS, H₂O₂/Fe²⁺ molar ratio and reaction time. Their ranges were selected in accordance with previous studies (Table 2.2). Table 3.1 shows the coded levels and the factor values used in the experiments.

The experimental design consists of 20 runs of the Central Composite Design (for lower and upper levels of quantitative variables). Each numeric factor is varied over 5 levels: plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center-point. The correlations between the responses and the variables were obtained by a quadratic model. Myers and Montgomery (2002) pointed out that the model is adequate for predicting the responses in all experimental fields and developed the following equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j \quad (3.1)$$

where Y is the response, β_0 is the intercept constant, β_i , β_{ii} and β_{ij} are the coefficients for the first-order, the second order and the interaction effects, respectively. Besides, X is the coded value referring to the factor *i* (here between 1 to 3) and *k* is the number of variables.

Table 3.1 Central Composite Design of Response Surface Methodology

Independent Variable	Code	Coded Level				
		-1.68	-1	0	1	1.68
H ₂ O ₂ /kg TS (g)	A	9.77	20	35	50	60.23
H ₂ O ₂ /Fe ²⁺ molar ratio	B	3.27	6	10	14	16.73
Reaction time (h)	C	0.66	1	1.5	2	2.34

As shown in Table 3.2, all the tests are conducted following the design combinations by Design Expert software.

Table 3.2 List of experiment tabulated by Design Expert software

Run	g H ₂ O ₂ /kg TS	H ₂ O ₂ /Fe ²⁺ molar ratio	Reaction time (h)
1	35.0	10.0	0.66
2	50.0	6.0	1.00
3	50.0	14.0	1.00
4	20.0	14.0	1.00
5	20.0	6.0	1.00
6	35.0	16.7	1.50
7	9.8	10.0	1.50
8	35.0	10.0	1.50
9	35.0	10.0	1.50
10	35.0	10.0	1.50
11	60.2	10.0	1.50
12	35.0	10.0	1.50
13	35.0	3.3	1.50
14	35.0	10.0	1.50
15	35.0	10.0	1.50
16	20.0	6.0	2.00
17	20.0	14.0	2.00
18	50.0	6.0	2.00
19	50.0	14.0	2.00
20	35.0	10.0	2.34

3.4 Analytical Methods

A total of 8 responses were analyzed, consisting of total solids (TS), volatile solids (VS), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), soluble chemical oxygen demand (sCOD), capillary suction time (CST), EPS carbohydrates and proteins. pH measurement was performed using a pH meter (Hach sension 4) and a pH probe (Hach platinum series pH electrode model 51910, Hach Company). TS, VS, MLSS, MLVSS and CST were measured according to the Standard Methods (APHA et al, 2005), whereas sCOD was

measured by the Reactor Digestion Hach method No. 8000 (Hach, 2003) and the sample was filtered through 0.45 μ m membrane filter.

In terms of EPS, the measurement was divided into two categories, namely carbohydrates measurement and proteins measurement. For the carbohydrate characterization, sulfuric acid–UV method is proposed (Albalasmeh et al., 2013). A 1 mL aliquot of carbohydrate solution was rapidly mixed with 3 mL of concentrated sulfuric acid in a test tube and vortexed for 30 s. The temperature of the mixture rose rapidly within 10–15 s after addition of sulfuric acid. Then, the solution was cooled in ice for 2 min to bring it to room temperature. Finally, UV light absorption at 315 nm was read using UV spectrophotometer.

For the analysis of proteins, Bicinchoninic acid method (BCA) was employed (Zuriaga-Agustí et al., 2013). The BCA protein assay (Novagen) was based on a biuret reaction, which results in a protein assay with improved sensitivity and tolerance to interfering compounds compared to Lowry method. BSA (Sigma) was used as standard for doing the calibration curve to determine the protein concentration of each unknown sample. 50 μ L of standard or extracted sample was added to 1 mL of BCA working reagent. Then, the samples were incubated at 37 °C for 30 min. After cooling at room temperature, the samples were measured spectrophotometrically at 562 nm.

Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between process variables and the responses. The quality of the fit polynomial model was expressed by the coefficient of determination R^2 and Adj R^2 , and its statistical significance was checked by the F-test in Design Expert Software. Three-dimensional (3D) plots and their respective contour plots were obtained based on the effects of the two factors at three levels. Furthermore, the optimum region was identified based on the main parameters in the overlay plot. The adequacy of the regression equations was checked by comparing the experimental data with predicted values obtained from the equations. Detailed analysis on the model is presented in the following sections.

3.5 Gantt Chart

Main Tasks	First Semester / Week														Second Semester / Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of topic	█	█	█	█																								
Preliminary Literature Review				█	█	█	█																					
Extended Proposal																												
Continued Literature Review										█	█	█	█	█	█	█												
Proposal Defence																												
Interim Report																												
Experiments															█	█	█	█	█									
Data processing															█	█	█	█	█	█	█	█	█					
Progress Report																												
Pre-SEDEX																								█				
Submission of Draft Final Report																								█	█	█	█	
Submission of Technical Paper																												
Viva																												
Project Dissertation																												

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Sludge Characteristics

The waste activated sludge (WAS) samples were obtained from the Universiti Teknologi PETRONAS sewage treatment plant, which adopted extended aeration activated sludge system. The composition of influent wastewater is heavily attributed by various domestic activities in academic buildings, cafeteria and dormitories. The majority of its solids are from washwaters (sinks, baths, laundry, etc.) and human feces. The properties of WAS sludge were studied and tabulated in Table 4.1.

Table 4.1 Properties of waste activated sludge (WAS)

Parameters	Unit	Range	Mean
pH	-	6.34 – 7.40	6.87
Total solids (TS)	mg/L	31214 – 52560	41887
Volatile solids (VS)	mg/L	18640 – 32780	25710
Mixed liquor suspended solids (MLSS)	mg/L	12833 – 38571	25702
Mixed liquor volatile suspended solids (MLVSS)	mg/L	7000 – 26190	16595
Total chemical oxygen demand (TCOD)	mg/L	32172 – 51020	41596
Soluble chemical oxygen demand (sCOD)	mg/L	3029 – 4638	3834
Capillary suction time (CST)	s	136 – 144	140
EPS ^a carbohydrates	mg/L	20.62 – 22.34	21.5
EPS ^a proteins	mg/L	8.5 – 9.6	9.1

^a Extracellular polymeric substances

4.2 Statistical Analysis

The study ranges of the manipulating variables were chosen as amount of H₂O₂/kg TS from 9.77 g and 60.23 g, H₂O₂/Fe²⁺ molar ratio from 3.27 to 16.73 and reaction time from 0.66 h to 2.34 h. In accordance with previous literatures, the optimum reagent dosages for Fenton process range from 25 to 60 g H₂O₂/kg TS and 10 to 15 for H₂O₂/Fe²⁺ molar ratio. The effect of pH on Fenton treatment conditioning was excluded in this study because pH 3 has been proven experimentally as the optimum value (Sahinkaya et al., 2014; Neyens et al., 2002; Erden and Filibeli, 2011; Hickey et al., 1995).

The models for MLVSS removal, sCOD, CST and EPS (Y₁, Y₂, Y₃ and Y₄) were generated by Design Expert Software after the experimental data was keyed in. The following fitted regression models (equation in terms of coded values for the regressors) were obtained to quantitatively investigate the effects of H₂O₂/kg TS (A), H₂O₂/Fe²⁺ molar ratio (B) and reaction time (C) on the Fenton process performance.

MLVSS removal:

$$Y_1 = 21.29 + 1.39A + 2.67B + 0.67C - 0.017A^2 + 1.34B^2 + 1.34C^2 - 0.89AB + 1.25AC - 0.31BC \quad (4.1)$$

sCOD:

$$Y_2 = 5452.00 + 349.55A + 45.00B - 19.46C - 75.56A^2 - 119.76B^2 + 80.78C^2 + 78.54AB - 31.11AC - 287.91BC \quad (4.2)$$

CST:

$$Y_3 = 170.25 + 17.50A + 6.96B + 0.31C - 3.42A^2 - 0.24B^2 + 1.53C^2 + 7.25AB - 6.75AC - 7.00BC \quad (4.3)$$

EPS:

$$Y_4 = 59.24 - 4.79A + 0.21B - 13.29C + 4.85A^2 + 11.84B^2 + 2.14C^2 - 4.56AB + 16.14AC + 1.71BC \quad (4.4)$$

From Eqs. 4.1, 4.2, 4.3 and 4.4, it can be observed that the values of the sum of a constant (β_0), 21.29, 5452.00, 170.25 and 59.24, represent the predicted performance of MLVSS removal, sCOD, CST and EPS, respectively at coded level “0”. The positive sign in first order terms indicates that the manipulating variable is directly proportional to the respective output responses whereas the negative sign in first order terms indicates that the parameter inversely proportional to the responses. For example, MLVSS removal, sCOD, CST and EPS rise with increasing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (+2.67B, +45.00B, +6.96B and +0.21B). Relatively, lower values were found be associated with the reaction time (C), meaning that reaction time has less effect on the Fenton reaction compared to amount of $\text{H}_2\text{O}_2/\text{kg TS}$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio.

Table 4.2 shows the central composite design (CCD) in the form of a 2^3 full factorial design with 6 additional experimental trials (run number 8, 9, 10, 12, 14 and 15) as replicates of the central point and actual experimental results and predicted results from the model at each assay. These central points are replicated by Design Expert Software to get a good estimation of the experimental error, since they have the same values for all three manipulating variables (operating parameters). In addition, each manipulating variable is presented with their respective coded level in accordance with Table 3.1 Central Composite Design of Response Surface Methodology.

Table 4.2 Central Composite Design for the Study of Operating Conditions of Fenton Process

Run no.	Experimental Design			Performance							
	A: g H ₂ O ₂ /kg TS (Code)	B: H ₂ O ₂ /Fe ²⁺ molar ratio (Code)	C: Reaction time (Code)	Actual (Experimental data)				Predicted (by software)			
				MLVSS removal (%)	sCOD (mg/L)	CST (s)	EPS (mg/L)	MLVSS removal (%)	sCOD (mg/L)	CST (s)	EPS (mg/L)
1	35.0 (0)	10.0 (0)	0.66 (-1.68)	23.61	5554.9	173	95.50	23.95	5713.2	174	87.71
2	50.0 (1)	6.0 (-1)	1.00 (-1)	20.88	5277.1	179	70.72	20.27	5326.1	171	76.45
3	50.0 (1)	14.0 (1)	1.00 (-1)	23.84	6226.0	219	62.89	24.43	6149.0	213	64.33
4	20.0 (-1)	14.0 (1)	1.00 (-1)	26.66	5315.3	141	91.63	25.93	5230.6	150	115.32
5	20.0 (-1)	6.0 (-1)	1.00 (-1)	19.19	4981.7	129	117.32	18.19	4721.9	137	109.20
6	35.0 (0)	16.7 (1.68)	1.50 (0)	26.39	5125.6	188	117.92	26.53	5189.0	181	93.16
7	9.8 (-1.68)	10.0 (0)	1.50 (0)	16.87	4369.6	154	94.46	18.90	4650.4	131	81.08
8	35.0 (0)	10.0 (0)	1.50 (0)	22.01	5382.2	172	54.34	21.29	5452.0	170	60.91
9	35.0 (0)	10.0 (0)	1.50 (0)	21.55	5294.0	176	61.88	21.29	5452.0	170	60.91
10	35.0 (0)	10.0 (0)	1.50 (0)	21.21	5184.2	162	61.32	21.29	5452.0	170	60.91
11	60.2 (1.68)	10.0 (0)	1.50 (0)	23.58	5921.8	176	68.36	23.58	5826.2	190	64.95
12	35.0 (0)	10.0 (0)	1.50 (0)	21.48	5727.6	168	86.76	21.29	5452.0	170	60.91

Table 4.2 Central Composite Design for the Study of Operating Conditions of Fenton Process (continued)

Run no.	Experimental Design			Performance							
	A: g H ₂ O ₂ /kg TS (Code)	B: H ₂ O ₂ /Fe ²⁺ molar ratio (Code)	C: Reaction time (Code)	Actual (Experimental data)				Predicted (by software)			
				MLVSS removal (%)	sCOD (mg/L)	CST (s)	EPS (mg/L)	MLVSS removal (%)	sCOD (mg/L)	CST (s)	EPS (mg/L)
13	35.0 (0)	3.3 (-1.68)	1.50 (0)	15.65	4915.8	160	84.46	17.55	5037.6	158	92.43
14	35.0 (0)	10.0 (0)	1.50 (0)	20.77	5603.0	170	49.97	21.29	5452.0	170	60.91
15	35.0 (0)	10.0 (0)	1.50 (0)	21.05	5552.8	172	48.30	21.29	5452.0	170	60.91
16	20.0 (-1)	6.0 (-1)	2.00 (1)	19.69	5375.0	153	36.48	17.66	5321.0	165	46.91
17	20.0 (-1)	14.0 (1)	2.00 (1)	24.99	4858.1	136	53.74	24.17	4678.1	150	59.89
18	50.0 (1)	6.0 (-1)	2.00 (1)	25.43	5847.1	175	90.53	24.72	5800.8	172	78.72
19	50.0 (1)	14.0 (1)	2.00 (1)	28.10	5343.2	188	53.46	27.66	5472.1	186	73.46
20	35.0 (0)	10.0 (0)	2.34 (1.68)	24.53	5620.9	185	52.01	26.21	5647.8	175	43.01

The analysis of variance (ANOVA) for response surface quadratic model is shown in Table 4.3. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination and can be used to navigate the design space defined by the CCD. The AP values for all the responses are greater than 4 in the present study. The probability of lack of fit (PLOF) describes the variation of the data around the fitted model. If the PLOF is less than 0.05, the model is significant. The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% (Beg et al., 2003). In this case, all three responses fit the data well can are considered reproducible.

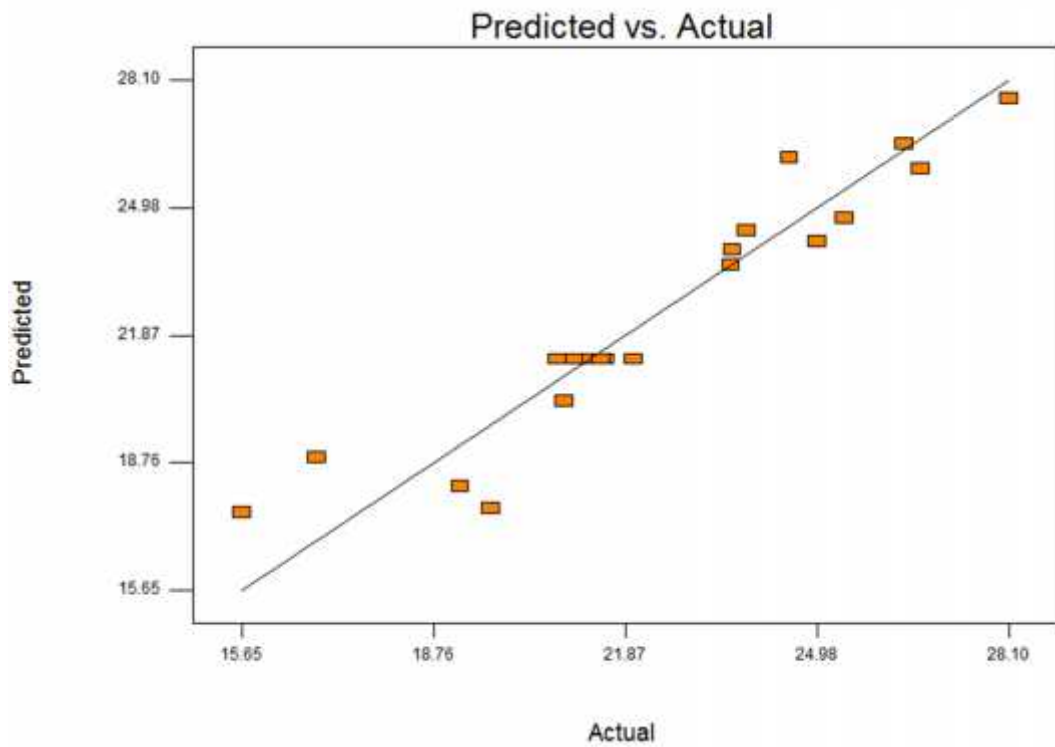
Table 4.3 ANOVA for Response Surface Quadratic Model

Response	AP	PLOF	CV	R ²
MLVSS Removal (%)	10.263	19.51	6.23	0.9007
sCOD (mg/L)	9.672	1.28	4.08	0.8549
CST (s)	9.215	13.19	7.47	0.7971
EPS (mg/L)	6.418	13.35	22.13	0.7394

AP: adequate precision; PLOF: probability of lack of fit; CV: coefficient of variance

Diagnostic plots of the predicted versus actual values can determine the model satisfactoriness by indicating an agreement between the actual data and the one obtained from the model. The R² coefficient gives the proportion of the total variation in the response predicted by the model and a value close to 1 is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. The R² coefficient should be at least 0.80 for a good fit of the model (Olmez, 2009). The R² coefficient is found to be close to 1 (0.9007 for MLVSS removal), indicating that the regression models explained the prediction well. The R² coefficient of sCOD and CST are considerably low (0.8549 and 0.7971, respectively) but the values are acceptable. The diagnostic plots of each response are shown in Figure 4.1.

(a)



(b)

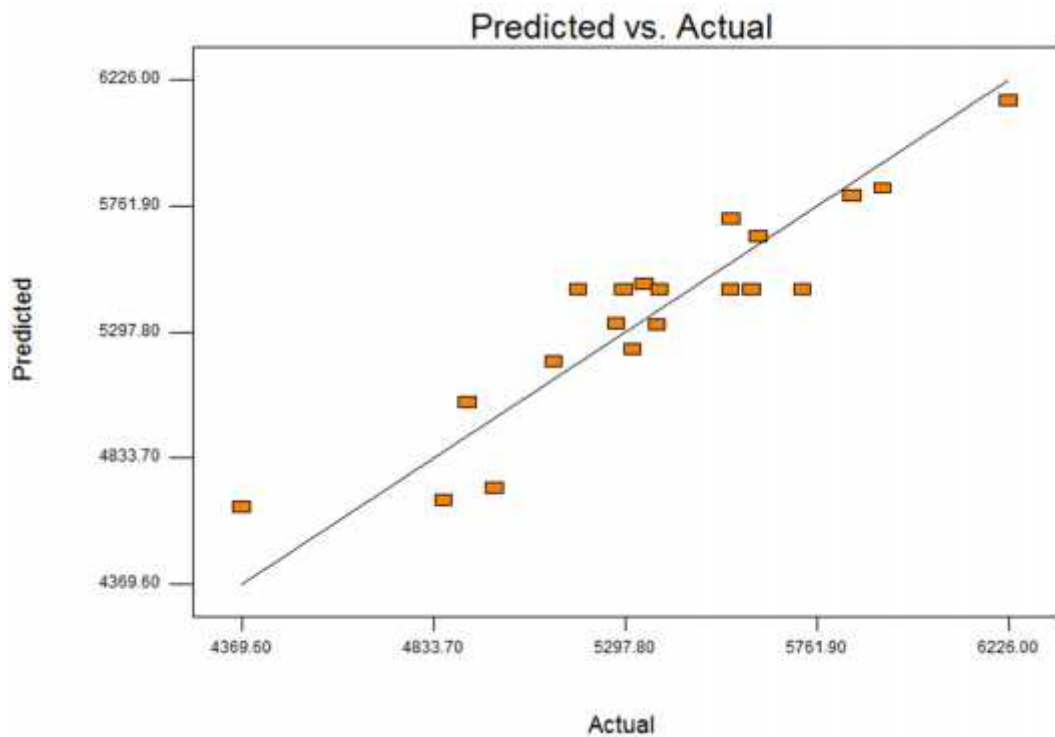
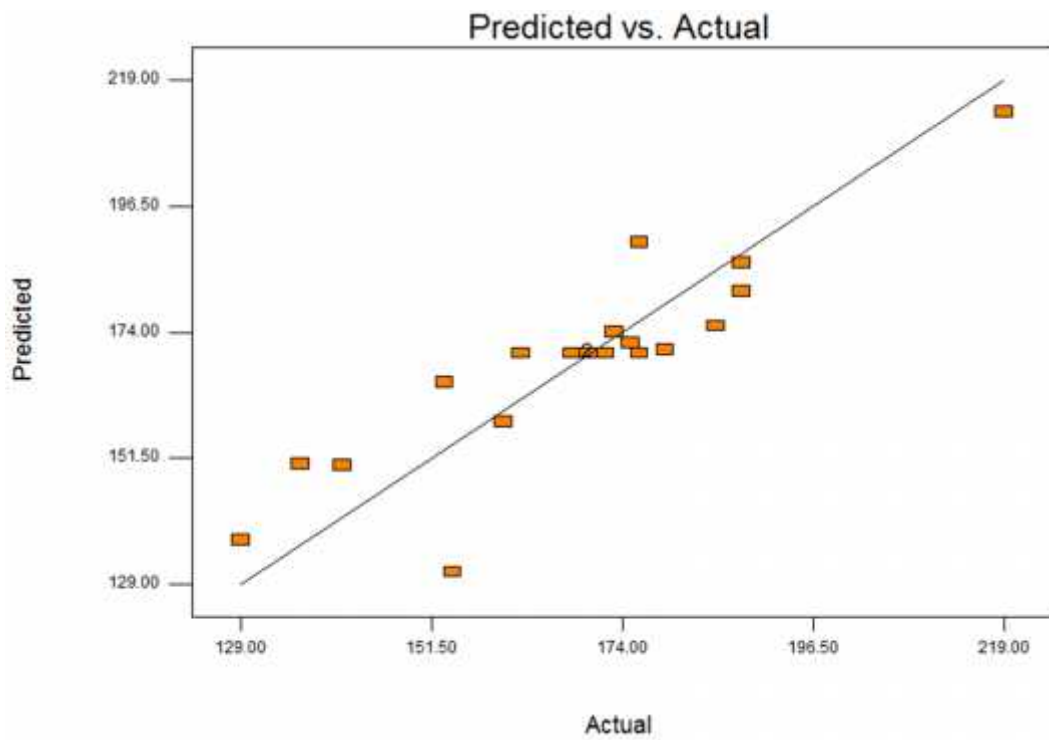


Fig. 4.1 Predicted versus Actual Plot for (a) MLVSS Removal ($R^2 = 0.9007$), (b) sCOD ($R^2 = 0.8549$), and (c) CST ($R^2 = 0.7971$) (d) EPS ($R^2 = 0.7394$)

(c)



(d)

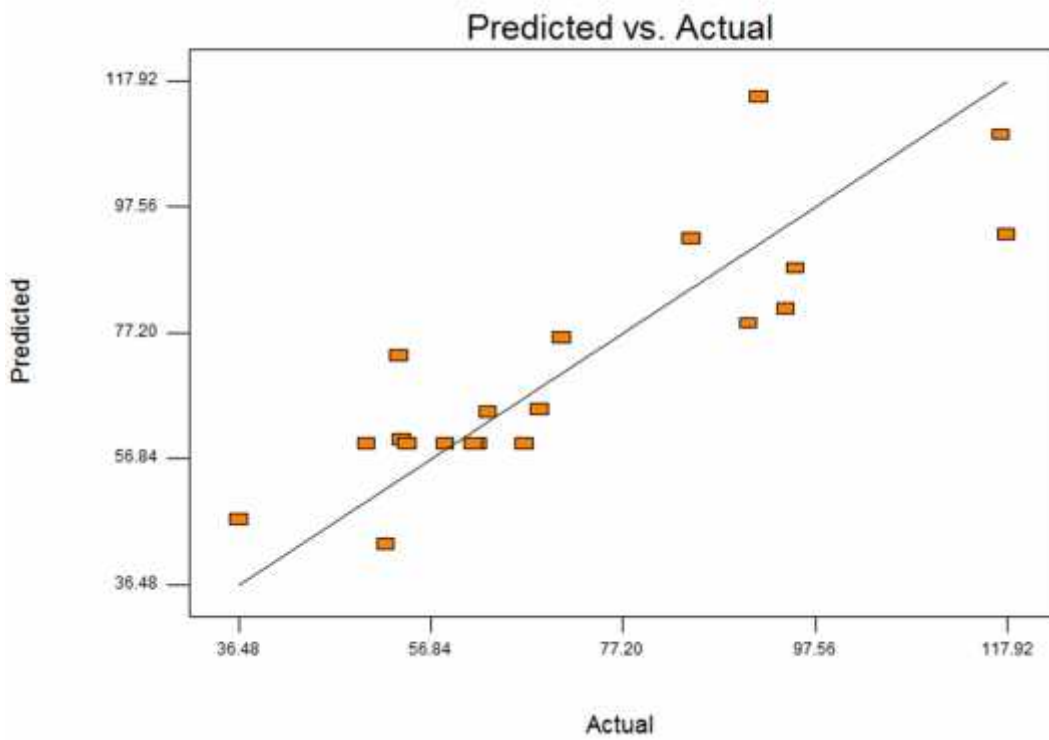
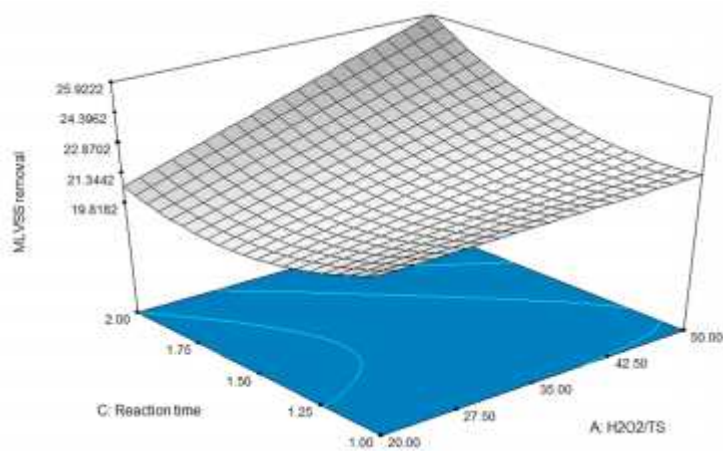


Fig. 4.1 Predicted versus Actual Plot for (a) MLVSS Removal ($R^2 = 0.9007$), (b) sCOD ($R^2 = 0.8549$), and (c) CST ($R^2 = 0.7971$) (d) EPS ($R^2 = 0.7394$) (continued)

4.3 Process Analysis

The response surface plots for MLVSS removal, sCOD and CST are shown in the form of three-dimensional contour plots (Figures 4.2, 4.3 and 4.4). The three-dimensional contour plots represent the responses (MLVSS removal, sCOD, CST and EPS) on the H_2O_2 dosage and reaction time (Figure 4.2), $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and reaction time (Fig. 4.3) and H_2O_2 dosage and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (Figure 4.4). The interactions of the manipulating variables are discussed in the later section.

(a)



(b)

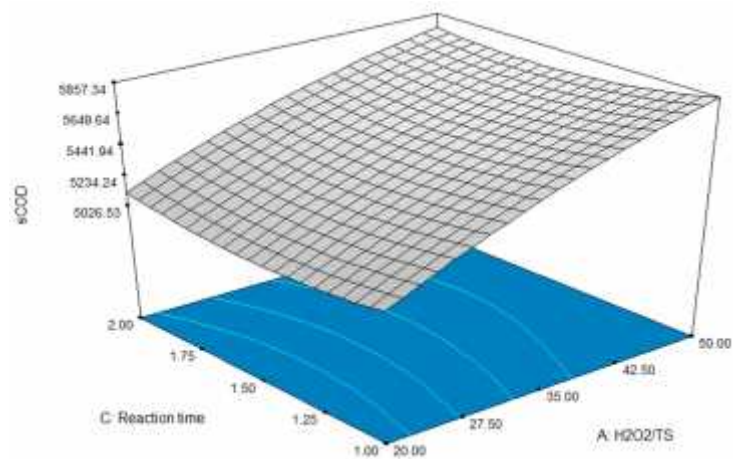
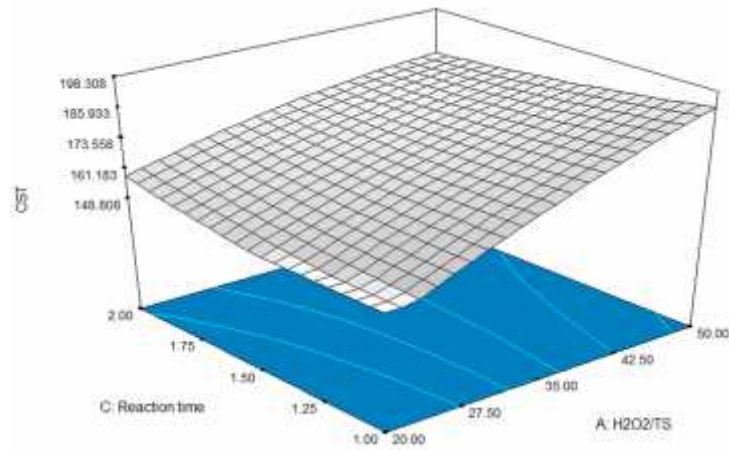


Fig. 4.2 Response Surface Plots of (a) MLVSS removal, (b) sCOD (c) CST and (d) EPS as a Function of H_2O_2 dosage (g/kg TS) and Reaction Time at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ Molar Ratio 10

(c)



(d)

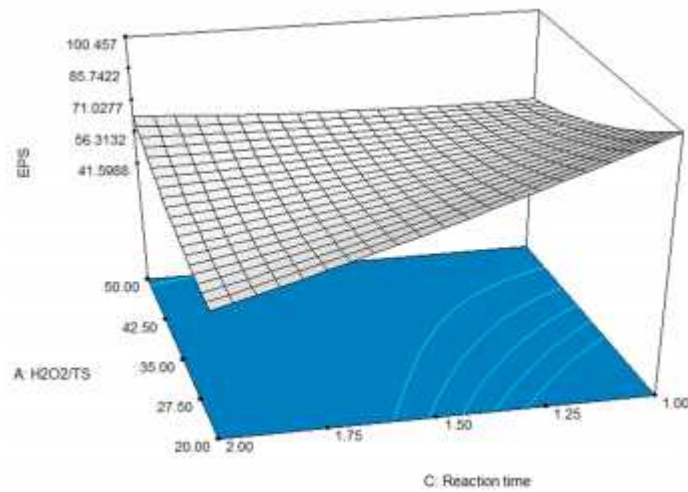
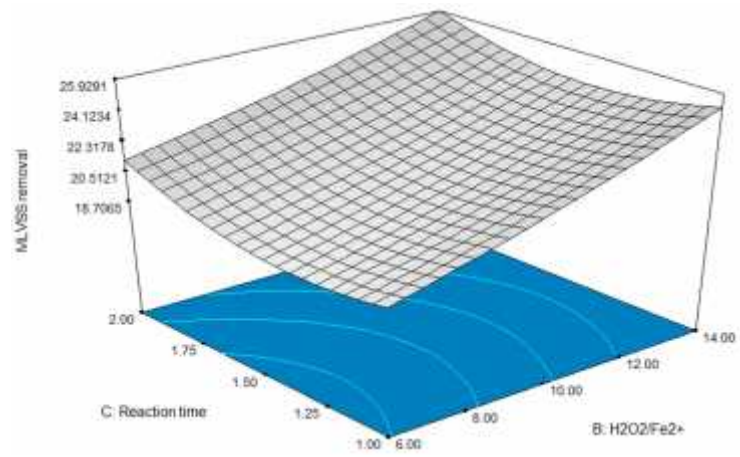
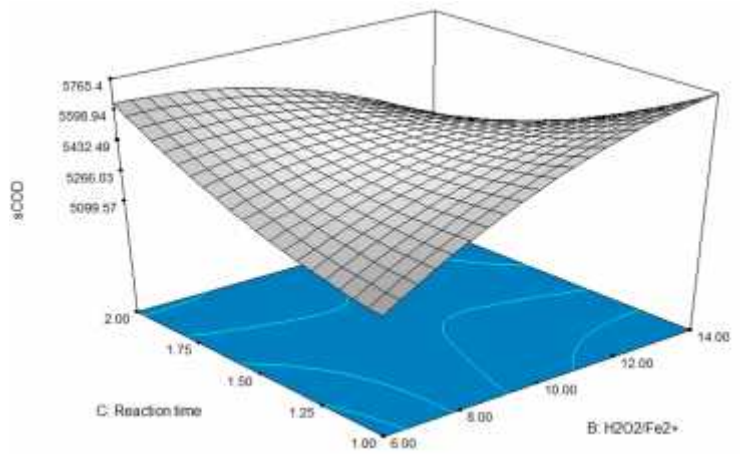


Fig. 4.2 Response Surface Plots of (a) MLVSS removal, (b) sCOD (c) CST and (d) EPS as a Function of H₂O₂ dosage (g/kg TS) and Reaction Time at H₂O₂/Fe²⁺ Molar Ratio 10 (continued)

(a)



(b)



(c)

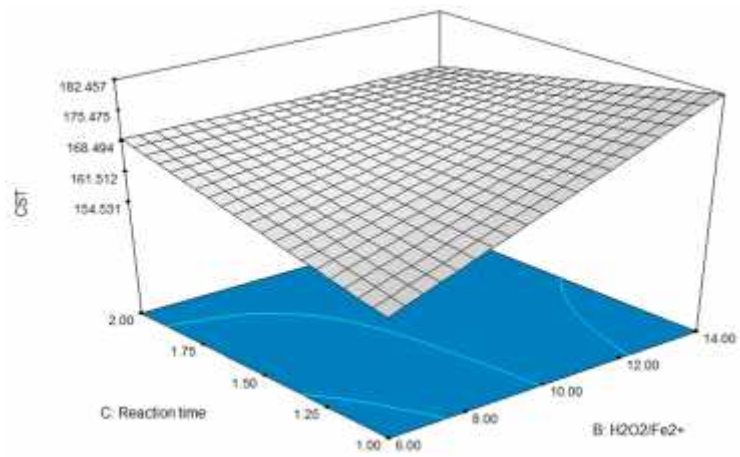


Fig. 4.3 Response Surface Plots of (a) MLVSS removal, (b) sCOD, (c) CST and (d) EPS as a Function of H₂O₂/Fe²⁺ Molar Ratio and Reaction Time at 35 g H₂O₂/kg TS

(d)

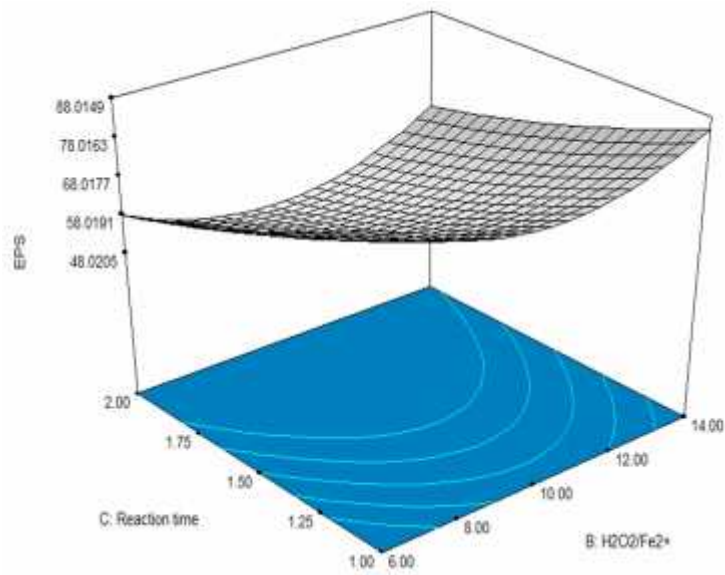


Fig. 4.3 Response Surface Plots of (a) MLVSS removal, (b) sCOD, (c) CST and (d) EPS as a Function of H₂O₂/Fe²⁺ Molar Ratio and Reaction Time at 35 g H₂O₂/kg TS (continued)

(a)

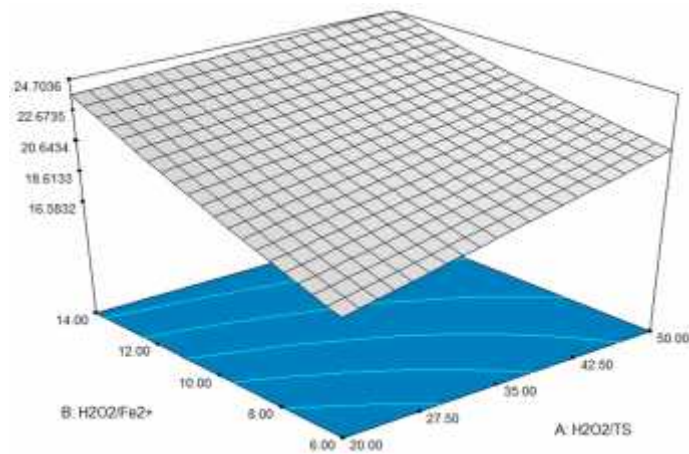
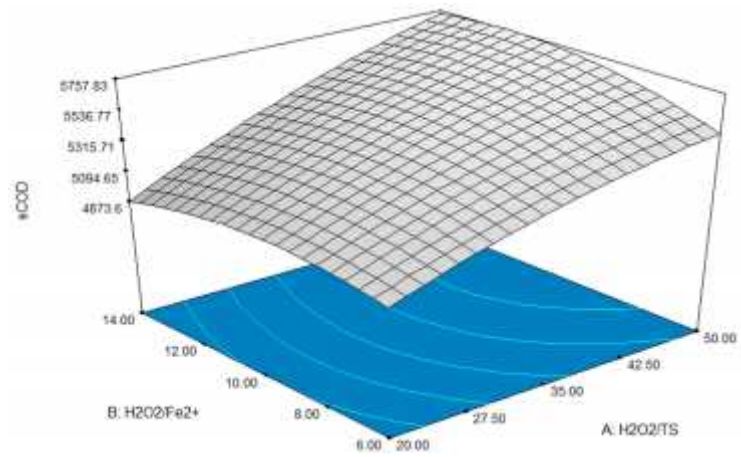
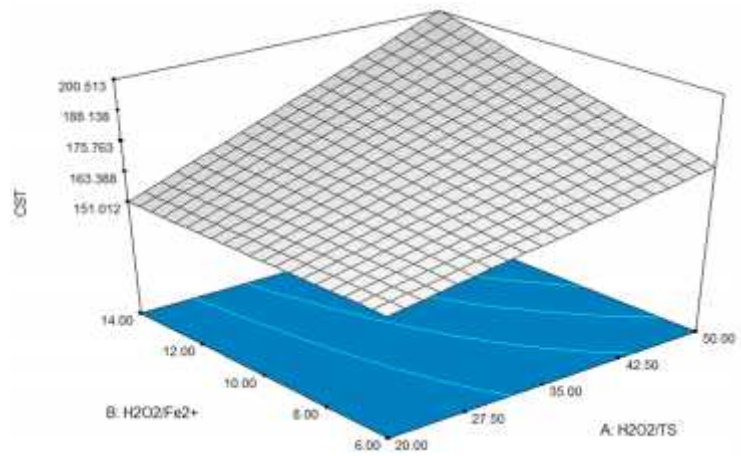


Fig. 4.4 Response Surface Plots of (a) MLVSS removal, (b) sCOD and (c) CST as a Function of H₂O₂ dosage (g/kg TS) and H₂O₂/Fe²⁺ Molar Ratio at Reaction Time of 1.5 h

(b)



(c)



(d)

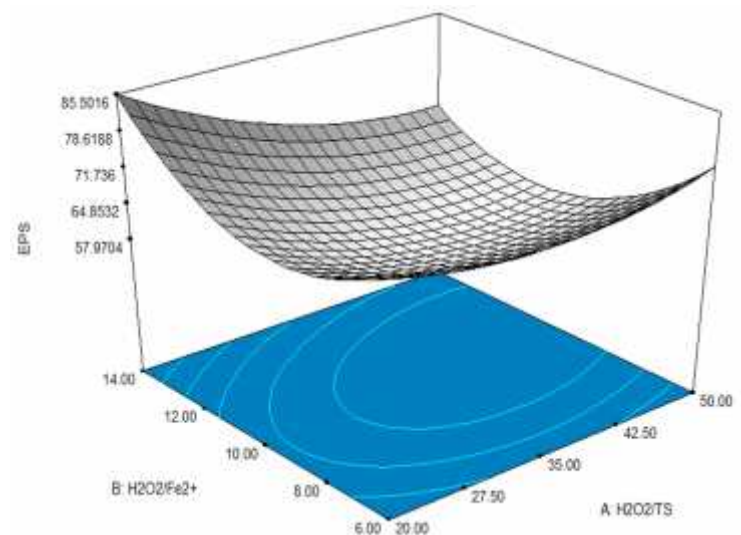


Fig. 4.4 Response Surface Plots of (a) MLVSS removal, (b) sCOD, (c) CST and (d) EPS as a Function of H₂O₂ dosage (g/kg TS) and H₂O₂/Fe²⁺ Molar Ratio at Reaction Time of 1.5 h (continued)

4.3.1 Effect of H₂O₂ dosage (g/kg TS)

Hydrogen peroxide is an oxidizing agent with oxidation potential of 2.8V (Metcalf & Eddy, 2003). Kim et al. (2008) supported that oxidation by hydrogen peroxide alone can reduce the sludge volume up to 33% removal of TS, even without the use of transition metal catalyst.

As illustrated in Figure 4.2, since increase in H₂O₂ dosage from 10 to 40 g/kg TS led to more production of HO[•] per unit volume in the solution, the collisions frequency between the reactants increases. The increase of HO[•] can rupture the cell wall and release its extracellular polymeric substances (Erden and Filibeli, 2009; Tokumura et al., 2007; Sahinkaya et al., 2014). Thus, the main contribution of excess sludge reduction can be derived from the MLVSS removal (He and Wei, 2009). As a result, the solids destruction efficiencies improved gradually from 16.87 % to 21 % for MLVSS removal. As an indication of sludge disintegration, the breakdown of the cellular structure led to release of its contents into soluble state, resulting in an increase in sCOD, from 3800 mg/L to nearly 6000 mg/L. A small drop in sCOD was observed when the reaction prolonged to 2 hours, implying continual oxidation process by other secondary reactions. This trend was parallel with the observation in EPS, where the highest values were obtained at shorter reaction time and the lowest values being found at longer reaction time.

Increasing dosages of H₂O₂ in Fenton reaction effectively improved the oxidation of organic matter. Nevertheless, the overdose of H₂O₂ in the reaction mixture can lead to decrease in the oxidation efficiency. This can be deduced by the observation that MLVSS removal only improved negligibly, with increasing H₂O₂ dosages, upon reaching 40 g/kg TS. This indicates that the sludge was solubilized at higher H₂O₂ dosages, leading to the release of carbohydrate and protein, followed by the release of lipid (Kim et al., 2008). Kim et al. (2008) reported that the intermediates such as short-chain carboxylic acid produced from ramified aliphatic chain by hydrogen peroxide are easily degraded by microorganisms. Sahinkaya et al. (2014) supported that during the breakdown of cell wall, the released organic substances are oxidized by HO[•] unselectively, due to its highly reactive behaviour.

Similar phenomena were also observed by other literatures, which agreed on H₂O₂ can act as radical scavenger at high concentration (Moradi and Ghanbari, 2014;

Sahinkaya et al., 2014; Neyens et al., 2002). This reaction leads to the production of hydroperoxyl radical, a species with much weaker oxidizing power compared to hydroxyl radical (Ting et al., 2008).



Therefore, the concentration of OH^\bullet decreases, in turn, decreases the solids degradation efficiencies.

The dewatering capacity of treated samples was determined by the measurement of capillary suction time (CST). The lower CST values indicate better dewatering capacity of sludge. Dewil et al. (2004) reported that the extracellular polymeric substances in the untreated sludge form a three-dimensional network, protecting the sludge cell from oxidation. A lot of water is contained within the voids of these flocs. Kim et al. (2008) also pointed out that the untreated sludge particles are bigger in size; coupled with relatively higher viscosity. These characteristics cause difficulty in the dewatering capacity of untreated sludge, giving it very high CST values.

By the contribution of OH^\bullet , Fenton oxidation is capable of reducing the sludge particle sizes, decrease its viscosity, leading to a decrease in hydraulic shearing force on the particles. Results demonstrated that lower CST values were achieved at the range of 20 to 30 g H_2O_2 /kg TS. The CST values decreased with increasing dosages of H_2O_2 , upon reaching 20 g H_2O_2 /kg TS. The lowest CST values were found to be associated with 20 g H_2O_2 /kg TS.

Upon reaching the optimum amount of H_2O_2 , from 30 g/kg TS and above, the CST values increased with the dosages of H_2O_2 . The increase slowed down afterwards. It is thought that the oxidation process disintegrates the sludge EPS contents, gradually increasing the number of small particles (Dewil et al., 2004; Kim et al., 2008). The percentage of voids reduce, less air is trapped, which causes a more dense (compact) sludge structure. This explains why the CST values bound back for increasing dosages of H_2O_2 .

4.3.2 Effect of H₂O₂/Fe²⁺ Molar Ratio

Primarily, Fe²⁺ ions act as the catalyst for activating H₂O₂ to produce the OH[•] radicals. This forms the basic reaction of Fenton chemistry. In the absence of any competitive scavenging of either HO[•] or R[•], the use of excess concentration of Fe²⁺ and H₂O₂ should, in principle, completely convert all organic compounds into CO₂ and water (Bokare et al, 2014). However, the non-specific and enhanced reactivity of HO[•] towards both organic and inorganic substrates results in various competitive processes that negatively affect the organic oxidation process (Neyens et al., 2002). The relevant reactions are shown as below:



In Figure 4.3, the minimum values of CST were found towards H₂O₂/Fe²⁺ molar ratio of 6 at 35 g H₂O₂/kg TS. A lower value of H₂O₂/Fe²⁺ molar ratio implies that higher concentration of Fe²⁺ are added to the mixture with a fixed amount of H₂O₂ dosage/kg TS. The sludge disintegration improved with an increasing Fe(II)SO₄ dosage by more production of HO[•] in the solution. However, further decrease in H₂O₂/Fe²⁺ molar ratio did not improve the process efficiency as such CST remained in the range between 120 s to 130 s. The slowdown of efficiency can be attributed direct reaction of OH[•] radical with metal ions at high concentration of Fe²⁺ in Eq. 2.3.

On the other hand, a peak was observed at H₂O₂/Fe²⁺ molar ratio which ranges from 8 to 12, based on the surface plots of EPS and sCOD, respectively, indicating the optimum dosage of Fe²⁺ concentration for Fenton reaction.

4.3.3 Effect of Reaction Time

Figures 4.2 and 4.3 show that better performance in sludge disintegration were achieved at about 1.5 – 2.0 h at 35 g H₂O₂/kg TS and H₂O₂/Fe²⁺ molar ratio 10. The gradients of these curves along the axis of reaction time were found to be gentle, indicating that the effect of reaction time was not dominant, compared to the other

manipulating variables. Further increase in reaction time above 1.5 h did not improve the process significantly. It can be deduced that organics were rapidly degraded by the Fenton reagent and most organics removal occurred in 1.5 h.

4.4 Process Optimization

With multiple responses, the optimum operating conditions where all parameters simultaneously meet the desirable removal criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response value in the factor space and the regions that do fit the optimization criteria would be shaded (Mason et al., 2003). In order to obtain a moderately precise optimum zone, response limits as the desirable ranges were chosen for each parameter close to their acquired disintegration efficiencies – MLVSS removal 23% to 28%, sCOD 5000 mg/L to 6200 mg/L, CST 129 s to 170 s and EPS 80 mg/L to 115 mg/L (Fig. 4.6). The shaded region shows the optimum parameters – 25 g H₂O₂/kg TS, H₂O₂/Fe²⁺ molar ratio 14 and reaction time 1.5 h, and constitute the optimum operating conditions. The results are consistent with optimum conditions reported in the literature (Neyens et al.). As shown in Table 2.2, different operating conditions were achieved by Erden and Filibeli (2011) and Sahinkaya et al. (2014). That might result from the differences in the chemical and physical properties of the biological sludge used in the studies.

Table 4.4 Lower and Upper Limits of Measured Responses

Responses	Unit	Lower limit	Upper limit
MLVSS removal	%	23	28
sCOD	mg/L	5000	6200
EPS	mg/L	70	115
CST	s	130	170

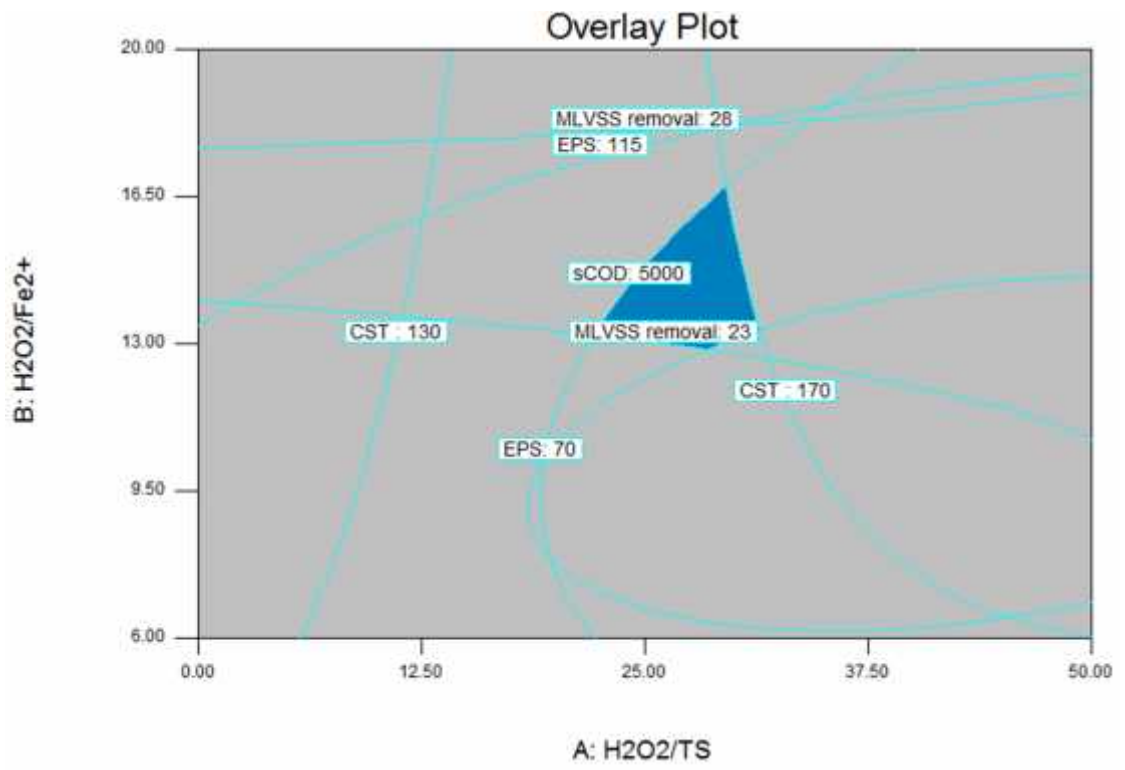


Fig. 4.5 Overlay Plot for Optimal Region at Reaction Time 1.5 h

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study focused on determining the optimum conditions of Fenton treatment for effective degradability and dewaterability of waste activated sludge (WAS). WAS samples were obtained from the return pipe from secondary clarifier sludge hopper of the sewage wastewater treatment plant in Universiti Teknologi PETRONAS. Optimum operating conditions of the Fenton treatment were determined using response surface methodology (RSM) by Design Expert Software. It was applied to optimize the three operating conditions of the treatment: $\text{H}_2\text{O}_2/\text{kg TS}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and reaction time. Removal of mixed liquor volatile suspended solids (MLVSS), soluble chemical oxygen demand (sCOD), capillary suction time (CST) and extracellular polymeric substances (EPS) were measured with a view to assess the treatment's efficiency.

Using RSM, the optimum operating conditions for Fenton treatment of the WAS were 25 g $\text{H}_2\text{O}_2/\text{kg TS}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 14 and reaction time 1.5 h with MLVSS removal 23% to 28%, sCOD 5000 mg/L to 6200 mg/L, CST 129 s to 170 s and EPS 80 mg/L to 115 mg/L. In term of biodegradability, MLVSS removal of the treatment was considered moderate, whereas the residual sCOD and EPS were considered high, due to the release of intracellular contents into soluble state. CST of the treated sludge increased, indicating reduced efficiency in dewatering properties. In conclusion, within the study range of chemical dosages in this research, the mechanism of sludge disintegration in Fenton treatment reduced the sludge quantities, however, impaired its dewaterability.

5.2 Recommendations for Future Work

Suggestions for future work for possible improvements and new directions:

1. To increase the range of parameters, which may help in increasing MLVSS removal as well as decreasing CST
2. To assess the potential of reusing the iron sludge formed during neutralization of the Fenton treatment
3. To assess the improvement in anaerobic digestion of the treated sludge

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