

**PERSULPHATE OXIDATION OF PALM OIL  
MILL EFFLUENT (POME): POST TREATMENT  
PROCESS**

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**PERSULPHATE OXIDATION OF PALM OIL MILL EFFLUENT (POME):  
POST TREATMENT PROCESS**

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**A project report submitted in partial fulfilment of the requirements for the  
award of Bachelor of Engineering (Hons.) Environmental Engineering**

**Faculty of Engineering and Green Technology  
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## DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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### APPROVAL FOR SUBMISSION

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Specially dedicated to my beloved grandfather and parents.

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**PERSULPHATE OXIDATION OF PALM OIL MILL EFFLUENT (POME):  
POST TREATMENT PROCESS**

**ABSTRACT**

The effectiveness of  $S_2O_8^{2-}$  oxidation and  $S_2O_8^{2-}/H_2O_2$  oxidation as post treatment of POME were investigated. To the best of our knowledge, this is the first experimental study of  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidations as treatment of biologically treated POME (BIOTPOME). The removal efficiencies of chemical oxygen demand (COD), ammoniacal nitrogen ( $NH_3-N$ ), colour and suspended solids (SS) were 36.8 %, 47.6 %, 57.7 % and 90.6 %, respectively by using  $S_2O_8^{2-}$  oxidation under certain operation conditions ( $S_2O_8^{2-} : COD_i = 2.0 : 1.0$ , pH 11 and reaction time, 20 min). In  $S_2O_8^{2-}/H_2O_2$  oxidation, 35.8 % COD, 75.8 %  $NH_3-N$ , 87.8 % colour and 87.1 % SS were achieved in removal efficiencies under the operational conditions ( $S_2O_8^{2-} : COD_i = 2.0 : 1.0$ , dosage of  $H_2O_2 / S_2O_8^{2-} = 2.45 \text{ g}/1.63 \text{ g}$  at pH 11 in 20 min contact time). For COD, the maximum removal efficiency obtained was 56.9 % in  $S_2O_8^{2-}/H_2O_2$  oxidation ( $S_2O_8^{2-} : COD_i = 2.0 : 1.0$  and dosage of  $H_2O_2 / S_2O_8^{2-} = 2.45 \text{ g}/1.63 \text{ g}$  at pH 8.4 in 20 min reaction time). The study has proved that  $S_2O_8^{2-}/H_2O_2$  oxidation have potentials in removing  $NH_3-N$  of BIOTPOME under pH 11. However, the best COD removal was obtained at pH = 8.4.



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## LIST OF SYMBOLS / ABBREVIATIONS

AOPs	Advanced Oxidation Processes
BIOTPOME	Biologically Treated Palm Oil Mill Effluent
BOD	Biochemical Oxygen Demand
CKPO	Crude Palm Kernel Oil
COD	Chemical Oxygen Demand
COD <sub>i</sub>	Chemical Oxygen Demand (Initial)
CPO	Crude Palm Oil
CT	Contact Time
EFB	Empty Fruit Brunches
EQA	Environmental Quality Act
EGSB	Expanded Granular Sludge Bed
FFB	Fresh Fruit Brunches
HUASB	Hybrid Up-flow Anaerobic Sludge Blanket
HRT	Hydraulic Residence Time
ISCO	In Situ Chemical Oxidation
OG	Oil and Grease
PKS	Palm Kernel Shells
POME	Palm Oil Mill Effluent
PPF	Palm Press Fibres
ROS	Reactive Oxygen Species
RSM	Response Surface Methodology
SS	Suspended Solids
TDS	Total Dissolved Solids
TN	Total Nitrogen
TS	Total Solids
UV	Ultraviolet
VS	Volatile Solids
NH <sub>3</sub>	Ammonia
NH <sub>3</sub> -N	Ammoniacal nitrogen
NH <sub>4</sub> <sup>+</sup>	Ammonium
S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> /H <sub>2</sub> O <sub>2</sub>	Combined Hydrogen Peroxide and Persulphate
HCl	Hydrochloric acid
H <sup>+</sup>	Hydrogen ion
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HSO <sub>4</sub> <sup>-</sup>	Hydrogen sulphate ions
HO <sub>2</sub> <sup>-</sup>	Hydroperoxide anion
HO <sub>2</sub> <sup>•</sup>	Hydroperoxyl
OH <sup>•</sup>	Hydroxyl radical

$O_3$	Ozonation
$SO_5^{2-}$	Peroxomonosulphate
$S_2O_8^{2-}$	Peroxydisulphate / Persulphate
NaOH	Sodium hydroxide
$Na_2S_2O_8$	Sodium persulphate
$SO_4^{2-}$	Sulphate ion
$SO_4^{\cdot-}$	Sulphate radical
$O_2^{\cdot-}$	Superoxide
$^{\circ}C$	Degree Celcius
g	Gram
hr	Hour (s)
L	Litre
mg/L	Miligram per Litre
mL	Mililitre
mS/cm	Mili-Siemens per Centimeter
min	Minute(s)
M	Molarity
NTU	Nephelometric Turbidity Units
PtCo	Platinum Cobalt
rpm	Revolutions per Minute
tons/hr	Tonnes per hour



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

The development of oil palm plantation has rapid growth in Asian countries especially Malaysia and Indonesia (Varkkey, 2012). Oil palm is one of versatile oil crops exploited in agriculture field of Malaysia. It has been reported that oil palm has become the most important subsector in agriculture production in year 2013 which contributed 36.7 % of added value of agriculture sector compared to rubber, forestry and logging, livestock, fisheries, aquaculture as well as other agriculture according to Department of Statistics, Malaysia (MPC, 2014). Large demand of products of oil palm by China, European Union, United State of America and Vietnam such oversea countries has led to economics boost of Malaysia (MPOB, 2014).

The solid waste and wastewater generated from oil palm industry have also increased due to the large demand on production of palm oil. The residues of oil palm tree such as trunks, fronds, empty fruit brunches, fibres and kernel shell are the wastes produced in solid form from those industries while the wastewater is known as palm oil mill effluent (POME). Overall wastes are called lignocellulosic biomass (Abdullah and Sulaiman, 2013). The wastes can cause environment destruction and induce pollution issue if directly discharge to the environment. Awareness among public and government on environment pollution issue therefore have raised. Many environmental regulations and initiatives are implemented for wastes reduction or zero waste discharge nowadays. The reuse of wastes and energy harness from wastes were also investigated to turn the wastes into value-added product. Thus, the

downstream system in palm oil industries has been greatly developed such as waste incineration, production of biogas and biofuel.

The downstream system for treating POME must be done accordingly before discharge it into water stream. POME primarily treated in biological treatment like open ponds system after waste oil recovery process (Loh et al., 2013). In Malaysia, the conventional oxidation ponds (anaerobic and aerobic) are the most common method to treat POME while for other processes like digestion tanks (anaerobic and aerobic), membrane filtration and physicochemical treatment are contributed in further degradation of contaminant in biologically treated POME (BIOTPOME) (Singh et al., 2010). For conventional anaerobic digestion treatment, it requires large land area and long hydraulic retention time although operation cost is low (Saeed et al., 2014).

Advanced oxidation processes (AOPs) are the technologies which effectively used to treat the organic contents from groundwater, municipal, industrial wastewater and sludge degradation since 1970s earlier (Ray et al., 2006). AOPs should be collaborated with biological treatment and act as post treatment in order to enhance the quality of BIOTPOME due to environment protection and human health. Landi and Naddeo (2011) mentioned that AOPs are encouraged to be utilized if the wastewater components are low biodegradability. The common mechanism of AOPs is the release of hydroxyl radical ( $\text{OH}^{\bullet}$ ) from strong oxidant in the water by photochemical process (e.g., ultraviolet radiation (UV) with ozonation ( $\text{O}_3$ ), hydrogen peroxide) and non-photochemical process (e.g., electron beam irradiation) (Bekbolet, 2011).

## 1.2 Problem Statements

Chemical oxygen demand (COD) concentration and colour intensity were still high in effluent although POME has been treated in the conventional of biological treatments (Shahrifun et al., 2015; Chan et al., 2010; Vijayaraghanvan et al., 2007). COD concentration which exceeded 1000 mg/L may lead to eutrophication issue. High colour intensity will affect the photosynthesis process of aquatic plant due to sunlight blocking (Fadzil et al, 2013). Dark brown colour and high suspended solids of BIOTPOME may also not pleasant in terms of aesthetic after it is being discharged into the river which near residential area or tourism place. Ammoniacal-nitrogen compound is also another pollutant from palm oil mill effluent which may cause toxicity to aquatic life. Progressive acidosis is one of toxicity effect which cause low blood oxygen-carrying capacity in sensitive fish (Russo, 1985 cited in USEPA, 2013). Toxicity of ammonia ( $\text{NH}_3$ ) can inhibit nitrification process of nitrifying bacteria (Russo, 1985 cited in USEPA, 2013).

The final discharge of effluent from palm oil industries must follow the standard discharge limit under Environmental Quality Act 1974 which enforced by Department of Environment Malaysia. Biological treatment such as ponding system is well treating high strength organic wastewater like POME (Liew et al., 2015). However, for non-biodegradable organic content, it is hard to treat in biological treatment efficiently. Therefore, post treatment such as advanced oxidation process is imperative to further reduce the strength of POME and comply with the standard.

Up to date, there is no study reported on persulphate oxidation of POME. Persulphate oxidation is newer AOP alternative of in situ chemical oxidation (ISCO) technology for contaminated soil and groundwater remediation. Persulphate ( $\text{S}_2\text{O}_8^{2-}$ ) is one of strong oxidants which can produce high reactive radical, sulphate radical ( $\text{SO}_4^{\cdot-}$ ) to oxidize organic components in wastewater (Deng et al., 2014). Thus, it has great potential to treat wastewater such as BIOTPOME.

In this study, persulphate oxidation and combined hydrogen peroxide and persulphate ( $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$ ) oxidation were investigated as post treatment of POME to increase efficiencies of the removals of COD, ammoniacal nitrogen, colour and

suspended solids. pH, contact time as well as dosages of  $S_2O_8^{2-}$  and  $H_2O_2$  are the operational conditions used to achieve better removal efficiency of BIOTPOME.

### 1.3 Objectives

- i) To investigate the efficiency of persulphate ( $S_2O_8^{2-}$ ) oxidation in treating BIOTPOME.
- ii) To investigate the efficiency of combined hydrogen peroxide and persulphate ( $S_2O_8^{2-}/H_2O_2$ ) oxidation in treating BIOTPOME.

### 1.4 Outline of Report

Five chapters in total are included in this report. The first chapter describes the background of the study, problem statements and objectives accordingly. The second chapter includes a literature review part which implicates current significant researches on persulphate oxidation process. Third chapter is the methodology part which involves experimental procedures and analytical methods. The chapter four includes the studied results and discussion in this study. The last chapter consists of conclusion and recommendation.

## CHAPTER 2

### LITERATURE REVIEW

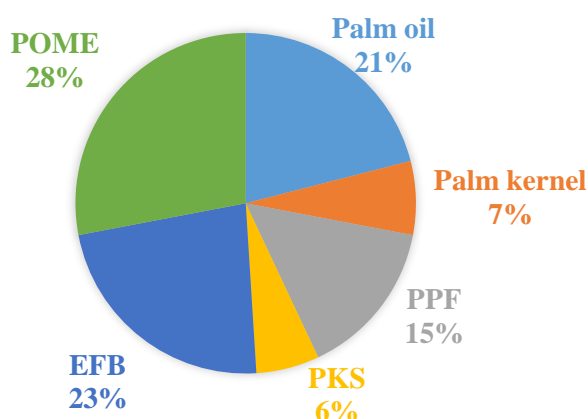
#### 2.1 Development and Production of Palm Oil in Malaysia

Oil palm plantation has been well developed in Malaysia since 1870s. Malaysia so far is the second largest palm oil production globally and around 19.2 million tonnes of palm oil was produced in year 2013 while Indonesia has produced the largest amount of palm oil around 28.4 million tonnes (Green Palm, 2015). According to Singh et al. (2010), the oil palm species planted in Malaysia is called *Elaeis guineensis* Jacq. or African oil palm, each hectare of oil palm results 10-35 tonnes of fresh fruit bunch in annual and economic life of oil palm tree can withstand for 20-25 years. Due to this agriculture product is demanded globally so the plantation area has increased in hectare year by year. Economics and Industry Development Division of Malaysia Palm Oil Board (2014b) has reported the plantation area of oil palm has expanded around 3.1 % from 5,229,739 ha (year 2013) to 5,392,235 ha (year 2014).

The main products of oil palm are crude palm oil (CPO) and crude palm kernel oil (CPKO). In 2011, totally 13.7 % CPO and CPKO production in Malaysia has resulted from global production of vegetable oils (MPOC, 2012). Palm oil is hugely demanded and imported by China, EU, USA, Pakistan, Vietnam and Japan etc. A total of 11.22 million tonnes of palm oil from Malaysia exports to overseas countries (MPOB, 2014b). Because of daily products manufactured are mainly derived from oil palm, this reflects high economic value on oil palm and significance of oils and fats production from oil palm in Malaysia.

### 2.1.1 Wastes Generation from Palm Oil Processing

During palm oil processing, biomass wastes such as palm press fibres (PPF), palm kernel shells (PKS), empty fruit bunches (EFB), and palm oil mill effluent (POME) are generated (Hassan et al., 2013). Figure 2.1 shows the waste and product generated per bunch of fresh fruit bunches (FFB) (Abdullah and Sulaiman, 2013). From Figure 2.1, the largest portion of waste generated from palm oil mills is POME which has 28 % by weight to FFB compared to EFB, PKS and PPF. Ahmad and other authors (2003) mentioned every tonne of CPO produced will utilize 5-7 tonnes of water and over 50 % of the water are eventually become POME. According to Malaysia Palm Oil Production Council, an average of about 53 million m<sup>3</sup> POME is generated annually based on 14.8 million tonnes of palm oil production in 2005 (Lorestani, 2006).



**Figure 2.1 Generation of Product and Waste for Each Bunch of FFB (Abdullah and Sulaiman, 2013).**

### 2.1.2 Alternatives for Wastes Reduction

In order to achieve waste reduction, clean development mechanism for biogas capturing (Chuen and Yusoff, 2012) and roundtable on sustainable palm oil for biofuel generated from biomass waste (Lee and Ofori-Baoteng, 2013) are two of projects implemented under cooperation of government with palm oil mills in

Malaysia. The waste products like fruit fibres and palm kernel shells are used as fuel and the steam energy harnessed will be utilised in palm oil mills (Abdullah and Sulaiman, 2013). Another researches mentioned EFB is potential renewable energy which has converted into biofuel using different technologies and served as an alternative source for fossil fuel to achieve zero carbon emission (Joseph, 2010; Olisa and Kotingo, 2014).

For POME, it has significant amount of nutrients and high contents of biodegradable organics that will cause negative impact on environment. It tends to present as a potential contaminant instead of a potential raw material (Madaki and Seng, 2013a). Thus, POME treatments are needed to minimize the effluent contained contaminant before discharge into any watercourse. POME treatment will be further discussed section by section.

## **2.2 Palm Oil Mill Effluent (POME) Generation and Characteristics**

As illustrated in Figure 2.1, around 28 % of waste generated from palm oil industry is palm oil mill effluent (POME). POME is an intractable wastewater which has thick brown in appearance and inducing unpleasant olfactory from palm oil extraction. POME discharged is normally as hot as 80-90 °C coupled with water, oil and fine suspended solids in composition (Liew et al., 2015). It is a form of colloidal suspension which mainly come from hydrocyclone wastewater (4 %), sterilizer wastewater (36 %) and clarification wastewater (60 %), accordingly (Liew et al., 2015; Wu et al., 2010; DOE, 1999).

POME is non-toxic wastewater since no addition of any chemicals in oil extraction process (Rupani et al., 2010). However, it comprises nutrients such as nitrogen and phosphorous as well as other insignificant mineral constituents (Mohammed et al., 2014). Table 2.1 shows typical characteristics of POME produced from palm oil mills (MPOB, 2014a). The composition of POME can be fluctuated by different crop season, quality of oil palm fruit bunches and particular process being carried out anytime (Madaki and Seng, 2013b).



**Table 2.1 Characteristics of POME (MPOB, 2014a).**

<b>Parameter</b>	<b>Range</b>
Biochemical oxygen demand	10,250 – 43,750
Chemical oxygen demand	15,000 – 100,000
Total solids	11,500 – 79,000
Suspended solids	5,000 – 54,000
Volatile solids	9,000 – 72,000
Ammoniacal nitrogen	4 – 80
Oil and grease	130 – 18,000
Total nitrogen	180 – 1,400
pH	3.4 – 5.2

\*All units in mg/L exclude pH

### **2.3 Regulatory Standards for Palm Oil Mill Effluent**

The regulation implemented for wastewater discharge from palm oil industry under Environmental Quality Act (EQA) 1974 [ACT 127] is called the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 (DOE,1999). Environmental quality regulations for oil palm industry are become stringent in Malaysia. Effluent standards and effluent charges under licensing system were operated under Malaysia government in the early 90's (Igwe and Onyegbado, 2007).

Typical parameter limits for wastewater of palm oil mill which stated in Second Schedule of Regulation 12(2) and (3) of Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 is shown as Table 2.2 (DOE, 1999). The parameters shown in Table 2.2 are the key point of decision on whether the wastewater is allowed to be discharged into watercourse. For the environmentally sensitive areas in Sabah and Sarawak, for example Kinabatangan River, DOE has stricter the effluents limit for BOD which cannot exceed 20 mg/L since 2006 (Madaki and Seng, 2013a). Effluent charges or penalty will be imposed on industry which has not fulfilled the wastewater discharge standards.

**Table 2.2 Effluent Discharge Standards for Wastewater from Palm Oil Mill (DOE, 1999)**

<b>Parameters</b>	<b>Allowable limits</b>
Biochemical oxygen demand (30 °C)	100
Chemical oxygen demand	1000*
Total solids	1500*
Suspended solids	400
Ammoniacal nitrogen	150
Oil and grease	50
Total nitrogen	200
pH	5.0 - 9.0
Temperature (°C)	45

\*No change in discharge standard after 1982 (Aris et al., 2008)

\*\*All units in mg/L exclude pH

## **2.4 POME Treatment**

There are many technologies introduced to treat POME. Conventional biological treatments are aerobic digestion, anaerobic digestion as well as combined aerobic-anaerobic digestion system. Bioreactor system has also been introduced in POME treatment with its advantages. For instance, pilot-scale study on bioreactor system, anaerobic expanded granular sludge bed (EGSB) reactors is investigated to achieve the better enhancement on COD removal of POME. Chemical treatments like coagulation-flocculation and membrane separation technologies are also the current treatment for POME.

### **2.4.1 Conventional POME Treatment**

Due to high removal efficiency in treatment, low construction and operation costs needed and ease of maintenance, ponding system is favourable in wastewater treatment (Wong, 1980). This system is widely used in POME treatment in Malaysia although large land area required for treatment ponds and long retention time of treatment (Abdurahman et al., 2013). There were around 85 % of effluent treatment in oil palm industry has installed the ponding system (Ahmad and Krimly, 2014). Series arrangement of anaerobic, facultative and aerobic open ponding is one of conventional biological treatment system for POME in Malaysia (Aris et al., 2008).

Before anaerobic treatment, facultative or aerobic ponding for 30 d - 45 d hydraulic residence time (HRT) should be conducted. POME first feeds to cooling pond for 1 d HRT and acidification pond for 2 d - 4 d HRT as pre-treatment (Tong and Jaafar, 2006). Anaerobic pond is important stage for POME in reduction of biodegradable organic loadings. With little input of external energy required and less production of biosolids as benefits of anaerobic digestion, most of organic content is disintegrate into methane gases, carbon dioxide and little hydrogen sulphide (Tong and Jaafar, 2006). Facultative or aerobic ponds are subsequently as additional processes for further degradation of BOD amount to ensure the effluent meet the discharge standards (Salihu and Alam, 2012).

### **2.4.2 Current POME Treatment Technologies**

Modification on conventional treatment is one of solution to improve the quality of POME wastewater discharge. Ismail et al. (2013) introduced the combined system which is conventional ponding system and adsorption as POME treatment in mill. Zeolite was the adsorbent used in adsorption process because it has potential to reduce heavy metal. A significant reduction in BOD concentration, heavy metals and turbidity in POME has been resulted under adsorption treatment.

Bioreactor or tank system is also applied in palm oil industry nowadays in order to capture the biogas for electric energy production. It has advantages such as less land is required, short HRT and more environmentally sound (Narasimhulu and Nanganuru, 2010). Wang et al. (2015) treated POME using anaerobic EGSB reactors and about 94.89 % COD removal was achieved with 3587 mg/L COD of effluent. Another research was hybrid up-flow anaerobic sludge blanket (HUASB) reactor equipped with anaerobic filter and removed up to 97 % COD of POME (Badroldin, 2010).

There have also other studies on current technologies in order to increase efficiency in treating POME. POME can also be treated using chemical precipitation such as coagulation and flocculation (Tan et al., 2006). Membrane separation technology like ultrafiltration is also studied with adsorption as pre-treatment and reduction of large amount of contaminants were achieved up to 90 % (Azmi and Yunus, 2014).

## **2.5 POME Post Treatment**

The POME treated by biological treatment is known as biologically treated POME (BIOTPOME). Fadzil et al. (2013) and Idris et al. (2010) reported that the POME needs secondary treatment due to insufficient removal in colour and COD prior to discharge into watercourse. Environmental issues will rise if it directly discharges into the watercourse. In Malaysia, POME is viewed as the main cause of aquatic pollution although it is chemical free and no toxicity (Embrandiri et al., 2013).

Presence of colour in treated POME has brought unpleasant view and caused low light penetration in the water lead to bad influence on aquatic systems (Bello et al., 2014). This condition affects the photosynthesis of aquatic plant and subsequent in low amount of oxygen produced which may bring effect on fishes and other lives after. Successive amount of organic and nutrient contents in term of COD will introduce eutrophication problem and further increases the amount of oxygen

depleted in water (Fadzil et al., 2013). Aquatic system will no longer sustain and a vicious cycle will be brought to human in the end.

Post treatment is necessary for treated POME to produce effluent which meet allowable discharge limits before released into watercourse. Especially in COD and colour removal using conventional biological system, the value of COD was still exceeded 1000 mg/L. The EGSB reactor system of Wang et al. (2015) has produced effluent which was exceed 3000 mg/L COD value. The colouration of POME has not been reduced after anaerobic and aerobic biological system due to composition like lignin, phenolic compounds and repolymerization of colouring compounds (Mohammed and Chong, 2014). To date, the advanced oxidation technologies such H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, Fenton's Reagent, radiation, photolysis and electrochemical processes have a great potential in wastewater treatment.

### **2.5.1 Advanced Oxidation Processes**

Advanced oxidation processes (AOPs) are one of technologies which involves the mechanism of highly reactive radicals generated such as hydroxyl radical (Ameta et al., 2012) and degradation of contaminants by the oxidants. Table 2.3 shows common used oxidants in advanced oxidation processes with redox potentials (Ray et al., 2006; Huling and Pivetz, 2006). It has potential to treat the non-biodegradable compounds of the BIOTPOME compared to available physical and chemical treatments (Fadzil et al., 2013). AOPs have also been mentioned in targeting resistant biodegradable compounds reduction in wastewater as pre-treatment and the intermediate product formed under oxidation mechanism can be degraded by microorganisms in subsequent biological treatment system but this approach is costly (Lofrano et al., 2011).

**Table 2.3 Oxidant Types and Redox Potentials (Ray et al., 2006; Huling and Pivetz, 2006.).**

<b>Oxidants</b>	<b>Redox Potential, V</b>
Fluorine (F <sub>2</sub> )	3.0
Hydroxyl radical (OH <sup>•</sup> )	2.8
Sulphate radical (SO <sub>4</sub> <sup>•-</sup> )	2.6
Ozone (O <sub>3</sub> )	2.1
Persulphate (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	2.1
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1.8
Chlorine (Cl <sub>2</sub> )	1.4

Muruganandham et al. (2014) summarized that many oxidation processes are very efficient in treating wastewater such as O<sub>3</sub>, O<sub>3</sub> combined with catalysts, O<sub>3</sub> combined with UV, Fenton combined with hydrogen peroxide and photo-Fenton. Table 2.4 shows the different types of AOPs used for treating biologically treated POME. Aris et al. (2008) were investigated the ambient-Fenton and solar-Fenton oxidation process on biologically treated POME. The removal percentages of COD and colour were 75.2 % and 92.4 % in ambient-Fenton while for solar-Fenton process, resulted in 82.4 % and 95.1 % of COD with colour removal accordingly (Aris et al., 2008). By optimizing the Fenton oxidation on treated POME using response surface methodology (RSM) and at pH 3.5, 91.11 % and 97.36 % removal in COD and colour within 30 min reaction time (Saeed et al., 2014).

**Table 2.4 Advanced Oxidation Process Used to Treat BIOTPOME.**

<b>Treatments</b>	<b>Efficiencies of treatment</b>	<b>References</b>
Ambient-Fenton Process (initial COD: 1500 mg/L; initial colour: 1800 ADMI)	75.2 % COD removal 92.4 % colour removal	Aris et al., 2008
Solar-Fenton Process (initial COD: 1500 mg/L; initial colour: 1800 ADMI)	82.4 % COD removal 95.1 % colour removal	Aris et al., 2008
UV/Ferrioxalate/TiO <sub>2</sub> /O <sub>3</sub> (contact time: 4 hr)	100 % COD removal	Fadzil et al., 2013
Electrocoagulation (initial COD: 2030 mg/L)	75.4 % COD removal	Bashir et al., 2016

## 2.6 Persulphate Oxidation

Other than Fenton oxidation, persulphate oxidation process is another current technology that has received great attention in wastewater treatment. Persulphate oxidation is an advanced chemical oxidation which using persulphate anions as oxidant. Table 2.5 shows various wastewaters treated using persulphate oxidation in current years. Persulphate oxidation alone and hydrogen peroxide activated persulphate oxidation were the targeted treatments used for treating BIOTPOME wastewater. The details of persulphate oxidation include persulphate used, direct oxidation, radical oxidation, hydrogen peroxide as activator and operational conditions during experiment are further discussed.

**Table 2.5 Various Wastewater Using Persulphate Oxidation.**

<b>Wastewater types</b>	<b>Oxidation used</b>	<b>References</b>
Semi-aerobic stabilized landfill leachate	$O_3/S_2O_8^{2-}$ oxidation	Abu Amr et al., 2013
Anaerobic stabilized landfill leachate	$S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidations	Hilles et al., 2015
Azo dye - C. I. Direct Red 23	$S_2O_8^{2-}/Fe^0$ oxidation	Weng and Tsai, 2016
Dinitrotoluenes (DNTs) from industrial wastewater	Electro-activated persulphate oxidation	Chen et al., 2014

### 2.6.1 Persulphate

Persulphate or peroxydisulphate is general term which refers to anions such as peroxomonosulphate,  $SO_5^{2-}$  or peroxydisulphate,  $S_2O_8^{2-}$ . These anions can be found in persulphate salts such as potassium persulphate, sodium persulphate and ammonium persulphate. Sodium persulphate ( $Na_2S_2O_8$ ) is widely applied as source of oxidant for groundwater (Liang et al., 2007; Deng et al., 2014), contaminated soil (Zhao et al., 2013; Ko et al., 2012) and wastewater treatment (Epold and Dulova, 2015; Deng and Ezyske, 2011).  $Na_2S_2O_8$  is white crystallized powders with 238.1

g/mol in molecular weight. It is an inorganic oxidizing agent which has melting point at 180 °C (CDC, 2014).

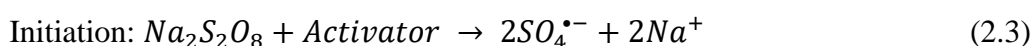
### 2.6.2 Direct Oxidation

Persulphate salt such as sodium persulphate will dissociate in water to form  $S_2O_8^{2-}$  with redox potential, 2.1 V. According to Kuşmlerek and other researchers (2015), some authors mentioned persulphate is non-selectively reactive compound, by comparing with hydrogen peroxide and ozone, it is comparatively stable at room temperature and longer lifetime when exposes in water. The potential oxidation-reduction for direct persulphate oxidation is shown as Equation (2.1) (Block et al., 2004). Hydrogen sulphate ions ( $HSO_4^-$ ) are produced and it may dissociate into sulphate ( $SO_4^{2-}$ ) ions and hydrogen ions ( $H^+$ ) in the end.

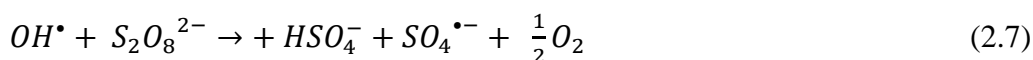
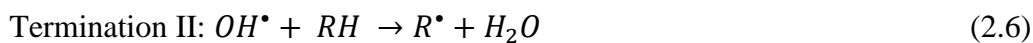


### 2.6.3 Radical Oxidation

The kinetics for degradation rate of organic compounds is slow (Bennedsen, 2014) so persulphate activation is crucial on generation of sulphate free radical ( $SO_4^{\bullet-}$ ) with redox potential (2.6 V). The persulphate can be activated using different methods, for instances, heat, low-valent metal, UV light, acidic or alkali pH and oxidants.  $OH^{\bullet}$  is also released and consumed through the initiation, propagation and termination reactions as shown in Eq. (2.3) - (2.6) when activator is employed (Cronk, 2008). As radicals from Eqs. (2.3), (2.4) and (2.7) has no reaction with reducing ions, it will result in production of sulphate salt as Eq. (2.8) (Ali, 2005).





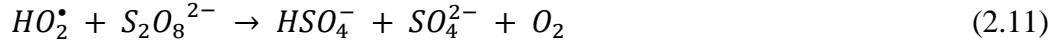
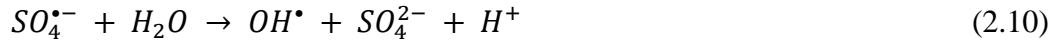
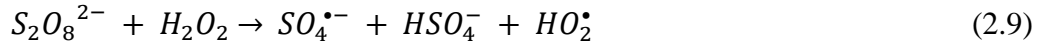


where RH and R<sup>•</sup> represent an organic matter and oxidized organic matter.

SO<sub>4</sub><sup>•-</sup> prefers in gaining electron from reduced substances and organic radical cation subsequently is produced through the reaction (Elloy, 2014). It is short-lived oxidant and potentially degrades organic substances through oxidation process which similar to OH<sup>•</sup> with a slight difference of mechanism. It can rapidly attack wide range of organic contaminants. SO<sub>4</sub><sup>•-</sup> has high electron affinity and able to oxidize aromatic with electron donating groups such as hydroxyl and amino group (Gau et al., 2010).

### 2.6.3.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) as Activator

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) has been proposed as activator in persulphate activation in recent years. It has potential functions as activator in the formation of SO<sub>4</sub><sup>•-</sup>, this system is known as dual oxidant system (Block et al., 2004). In this system, the reactivity of peroxide in reduction of targeted organic substances collaborates with improved stability of persulphate. Researchers proposed the peroxide activation mechanisms after chain initiation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as in Equation (2.3) and further reactions are shown in Equation (2.9) - (2.12) (Tsao and Wilmarth, 1960 cited in Epold and Dulova, 2015). Besides, termination steps of the oxidation are assumed to be happened as in Equation (2.13) - (2.16).



Another suggestion is the exothermic reactions of  $H_2O_2$  causing sulphate free radicals generation due to the heat generated (Robinson et al., 2004 cited in Bennedson, 2014). However, the function of  $H_2O_2$  in binary mixture of  $H_2O_2$  with  $S_2O_8^{2-}$  is still poorly to be understood (Huling et al., 2011).

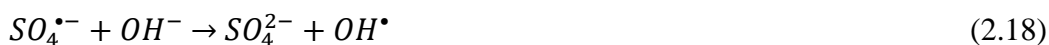
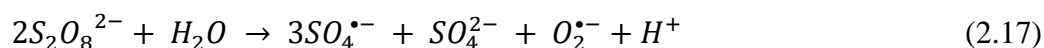
## 2.7 Factors Affecting Oxidation Process

Operational conditions such as pH, temperature, dosage of  $S_2O_8^{2-}$  and  $H_2O_2$  as well as contact time of BIOTPOME in oxidation process are crucial in determining the effectiveness of persulphate oxidation treatment. In past, there has been lack of study and research done on POME or BIOTPOME treatment using persulphate oxidation. The recent study was carried out using this oxidation method to treat landfill leachate wastewaters (Deng and Ezyske, 2011; Hilles et al., 2015). Landfill leachate and palm oil mill effluent are complicated wastewater which need to be treated. Parameters

such as BOD, COD, colour and NH<sub>3</sub>-N are required to be tested before discharged into river.

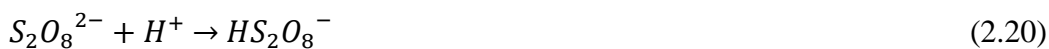
### 2.7.1 pH Adjustment

According to Block et al. (2004), persulphate oxidation reacts more efficient under acidic and alkali condition ( $3 < \text{pH} < 10$ ). Under favourable pH, persulphate is seem like to be ‘activated’. It is so called as base activation in persulphate oxidation. Some of studies using sodium hydroxide (NaOH) as activator in generation of sulphate radicals. There have two mechanisms involved in the activation process (Furman et al., 2010). Persulphate first reacted with NaOH through base-catalyzed hydrolysis and lead to generation of hydroperoxide anion (HO<sub>2</sub><sup>-</sup>). HO<sub>2</sub><sup>-</sup> produced will subsequently attack another persulphate molecule to form sulphate radical (SO<sub>4</sub><sup>•-</sup>) and sulphate ion (SO<sub>4</sub><sup>2-</sup>) as well as the HO<sub>2</sub><sup>-</sup> will also being oxidized into superoxide (O<sub>2</sub><sup>•-</sup>). The two mechanisms are summarized as shown in Eq. (2.17). SO<sub>4</sub><sup>•-</sup> then reacts with OH<sup>-</sup> and resulted in generation of hydroxyl radical (OH<sup>•</sup>) as shown in Eq. (2.18). Through the activated S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidation, the reactive oxygen species produced are hydroxyl radical (OH<sup>•</sup>), sulphate radical (SO<sub>4</sub><sup>•-</sup>) and superoxide (O<sub>2</sub><sup>•-</sup>) (Elloy, 2014). O<sub>2</sub><sup>•-</sup> has lower reactivity than OH<sup>•</sup> and will decompose in fast rate as it formed due to easily reacts with hydroperoxyl (HO<sub>2</sub><sup>•</sup>) and H<sup>+</sup> as shown in Eq. (2.19) (Sharma and Rokita, 2012).



Releasing of free radicals through breakdown of persulphate (acid-catalyzed) in acidic pH as in Equation (2.20) - (2.21) (Epold and Dulova, 2015). Hydrogen ion (H<sup>+</sup>) acts as catalyst during formation of sulphate radicals. SO<sub>4</sub><sup>•-</sup> or OH<sup>•</sup> which can act predominantly in degradation reaction actually depending on pH

(Lee et al., 2012). Liang et al. (2007) found that  $SO_4^{\bullet-}$  is predominant on low pH condition while  $OH^{\bullet}$  is predominant radical species on high pH conditions through radical scavenging test.



### 2.7.2 Temperature

Temperature is another important factor to determine the oxidation's performance. If the treatment under milder temperature, there will be more efficient in costing and environmentally sound (Lee et al., 2012). Ahmadi and other authors (in press) studied the decolourization of synthetic coloured wastewater (RY84) under different temperatures of 20, 30, 40 and 50 °C. The result showed the efficiency of colour removal has increased (69.3 % to 97.1 %) as the temperature was risen. By adjusting temperature to 50 °C, COD and ammonia nitrogen removal on mature landfill leachate were achieved 79 % and 100 % under acidic pH with suitable dosage of  $S_2O_8^{2-}$  (Deng and Ezyske, 2011).

### 2.7.3 Dosages of $S_2O_8^{2-}$ and $H_2O_2$

The initial concentration of  $S_2O_8^{2-}$ ,  $H_2O_2$  and COD are necessary to adjusted in order to obtain optimum concentrations used for treatment. The concentrations of  $S_2O_8^{2-}$ ,  $H_2O_2$  and COD normally are determined in term of molar ratio or weight ratio (Deng and Ezyske, 2011; Abu Amr et al., 2013). As increasing in concentration of  $S_2O_8^{2-}$ , better the performance of oxidation on treating contaminants.

However, if exceed  $S_2O_8^{2-}$  dosage is used, the efficiency of treatment will also be affected. There may have low in concentration of free radicals because many free

radical scavengers were produced and they compete with each other due to their reactivity properties is nonselective as Eq. (2.18). Thus, optimum dosage of  $S_2O_8^{2-}$  and  $H_2O_2$  are important to ensure the high removal efficiency of contaminant in wastewater. The optimum dosage of  $S_2O_8^{2-}$  were 4.2 g and 5.88 g in  $S_2O_8^{2-}$ -oxidation and  $S_2O_8^{2-}/H_2O_2$  oxidation accordingly on treating anaerobic stabilized landfill leachate (Hilles et al., 2015). While for  $H_2O_2$ , 8.63 g was determined as optimum dosage used to activate  $S_2O_8^{2-}$  in the landfill leachate oxidation treatment.

#### **2.7.4 Contact Time**

If the contact time between the contaminant with  $SO_4^{\cdot-}$  is long enough, the organics of wastewater can react completely with  $S_2O_8^{2-}$  or  $SO_4^{\cdot-}$ . A recent study shown 46 % and 81 % of COD removal on stabilized landfill leachate achieved through  $S_2O_8^{2-}$  oxidation within 60 min and  $S_2O_8^{2-}/H_2O_2$  oxidation within 120 min, respectively (Hilles et al., 2015).

Besides, the authors have also studied on raw textile wastewater treatment by using zeolite activated persulphate oxidation and the influence of reaction time is studied among 30-420 min (Kehinde and Aziz, 2015). The decolourization efficiency was increased from 74 % to 90 % when the contact time was also increased from 30 min to 240 min. After 30 min, the colour removal efficiency has increased gradually and this indicated that the oxidation of organics substances in the wastewater was carried out rapidly during first 30 min. Optimum contact time is required in order to enhance the effectiveness of treatment.

## CHAPTER 3

### RESEARCH METHODOLOGY

#### 3.1 Methodology Flow Chart



### 3.2 Sample Collection

The biologically treated POME sample was collected from Tian Siang Oil Mill (Air Kuning) Sdn. Bhd., Perak, Malaysia. Figure 3.1 shows the location of mill in the District of Batang Padang in Perak which departed from UTAR Perak campus. The samples collected were come from an outlet pipe of the maturation pond as shown in Figure 3.2 before releasing into nearby the river. The mill has started the commissioning since year 2000 and the daily capacity of processing FFB has increased to 120 tons/hr. 5.5 L of clean and empty polypropylene containers were used for the collection (Figure 3.3). After collection, the samples were directly transported to the environmental laboratory in immediate. The samples were preserved at temperature, 4 °C in order to minimize the possibility on biodegradation of sample and chemical reactions occurrence (APHA, 2005).

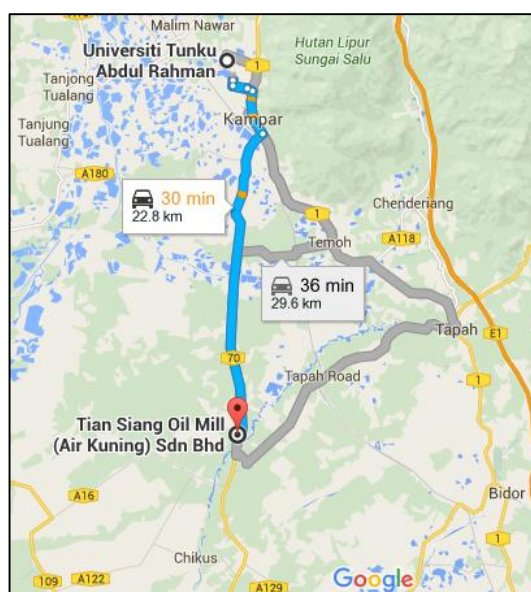


Figure 3.1 Location Map of Tian Siang Oil Mill (Air Kuning) Sdn. Bhd.



Figure 3.2 Maturation Pond no.2 in Tian Siang Oil Mill.



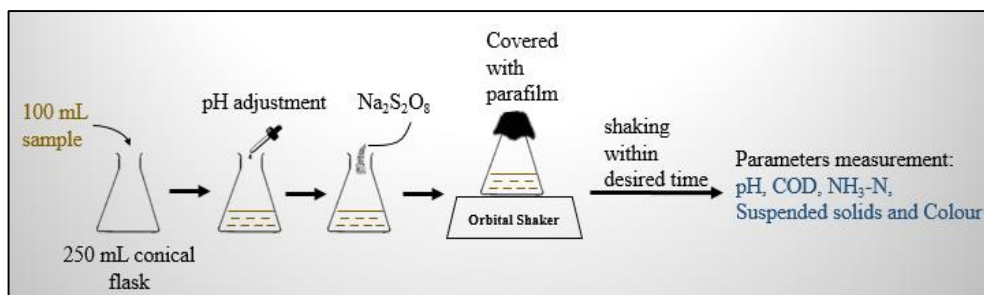
**Figure 3.3 Collected Biologically Treated POME Sample.**

### 3.3 Experimental Procedures

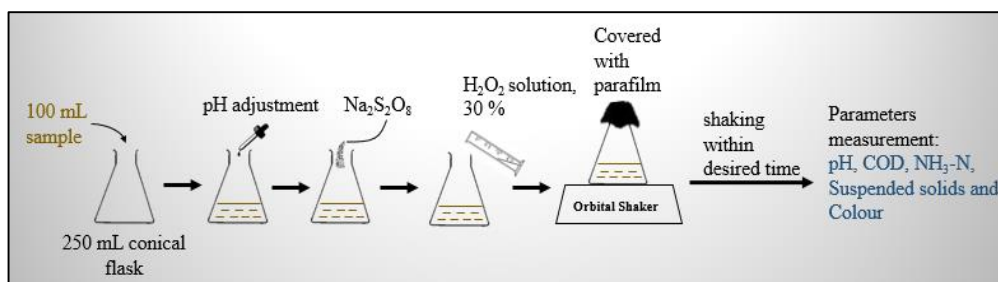
Deionized water produced from “Smart2Pure” Ultra-Pure Water System (TKA, Germany) was used to prepare 5M sodium hydroxide (NaOH) and 5M hydrochloric acid (HCl). The required sample preserved under 4 °C was taken out and thawed to ambient temperature (27 °C) before starting the experiment. All experiments were carried out in duplicate.  $S_2O_8^{2-}$  oxidation and  $S_2O_8^{2-}/H_2O_2$  oxidation were performed in batch mode and in non-buffered solutions.  $S_2O_8^{2-}$  was from crystallized formed sodium persulphate,  $Na_2S_2O_8$  ( $\geq 98\%$ , Sigma-Aldrich).  $S_2O_8^{2-}$  dosage was pre-determined in term of  $S_2O_8^{2-}/COD_i$  ratio.

There have few variables were examined in the experiment under ambient temperature such as pH, dosage of  $S_2O_8^{2-}$ , dosage ratio of  $H_2O_2 : S_2O_8^{2-}$ , dosage of  $H_2O_2$  and reaction time in order to obtain the optimum COD,  $NH_3-N$ , suspended solids (SS) and colour removal. The experiment can be divided into two main parts i.e.,  $S_2O_8^{2-}$  oxidation and  $S_2O_8^{2-}/H_2O_2$  oxidation. In  $S_2O_8^{2-}$  oxidation, pH adjustment, contact time and dosage of  $S_2O_8^{2-}$  were investigated. For  $S_2O_8^{2-}/H_2O_2$  oxidation, the factors such as pH adjustment, dosage ratio of  $H_2O_2 : S_2O_8^{2-}$  and varied dosage of  $H_2O_2$  with  $S_2O_8^{2-}$  were studied. Figure 3.4 and 3.5 show the overall experiment steps of both oxidations.





**Figure 3.4 Experiment Steps for  $S_2O_8^{2-}$  Oxidation.**



**Figure 3.5 Experiment Steps for  $S_2O_8^{2-}/H_2O_2$  Oxidation.**

### 3.3.1 pH Adjustment

The experiment was carried out at ambient temperature. 100 mL of sample was poured into each of 250 mL conical flask. Samples initially were adjusted to desired pH (3, 5, 7, 9, 10, 11 and 12) using 5 M hydrochloric acid (HCl) and 5 M sodium hydroxide (NaOH).  $S_2O_8^{2-}/COD_i$  ratio was initially set to 4. The dosage of  $S_2O_8^{2-}$  (g) was estimated according to initial COD ( $COD_i$ ) of BIOTPOME measured (mg/L). For instance,  $S_2O_8^{2-}: COD_i$  ratio was set to 4 : 1 and this indicated 1.32 g  $S_2O_8^{2-}$  was required for 100 mL sample per 0.329 g  $COD_i$ . Desired volumes of  $S_2O_8^{2-}$  dosages were then added into each of conical flasks respectively for initiating oxidation process purpose. The conical flasks were covered with parafilm. The conical flasks were placed on the NB-101M Orbital Shaker (N-biotek, South Korea) as shown in Figure 3.6 at 200 rpm and shaken for 1 hr. COD,  $NH_3-N$ , SS, colour and pH of samples were measured once the shaker was stopped shaking. If not, the treated samples would be preserved in refrigerator (4 °C) for measurement within 24 hr. Optimum pH was determined according to the result obtained.



**Figure 3.6 Orbital Shaker (NB-101M, South Korea).**

### 3.3.2 Contact Time

The experiment was carried out through different contact times (5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min and 240 min) at ambient temperature. 100 mL of sample was poured into each of 250 mL conical flask. Samples initially were adjusted to desired pH using prepared HCl or NaOH.  $S_2O_8^{2-}/COD_i$  ratio was obtained according to previous experiment. Prepared volumes of  $S_2O_8^{2-}$  were then added into the each of conical flasks correspondingly. The conical flasks were placed on the orbital shaker at 200 rpm and shaken for well mixing purpose. The samples were measured in term of COD,  $NH_3-N$ , SS, colour and pH once the shaker was stopped shaking. If not, the samples would be preserved in refrigerator (4 °C) for measurement within 24 hr. Optimum contact time was determined according to the result obtained.

### 3.3.3 Dosage Ratio of $S_2O_8^{2-}$ : $COD_i$

The experiment was carried out at ambient temperature. 100 mL of sample was poured into each of 250 mL conical flask. Samples initially were adjusted to desired pH using prepared HCl or NaOH.  $S_2O_8^{2-}$  :  $COD_i$  ratio was set randomly as 0.5 : 1.0, 1.0 : 1.0, 2.0 : 1.0, 3.0 : 1.0, 4.0 : 1.0, 5.0 : 1.0 and 6.0 : 1.0. Prepared amounts of  $Na_2S_2O_8$  were added into the each of conical flasks respectively for initiating

oxidation process. The conical flasks were covered with parafilm. The conical flasks were placed on the orbital shaker at 200 rpm and shaken within the optimum contact time obtained from previous experiment. The samples were measured in term of COD, colour,  $\text{NH}_3\text{-N}$ , SS and pH once the shaker was stopped shaking. If not, the samples would be preserved in refrigerator (4 °C) for measurement within 24 hr. Optimum dosage ratio of  $\text{S}_2\text{O}_8^{2-}$ : COD<sub>i</sub> ratio was determined according to the result obtained.

### 3.3.4 Dosage Ratio of $\text{H}_2\text{O}_2$ : $\text{S}_2\text{O}_8^{2-}$

The experiment was carried out within 20 min at initial pH of original sample. 100 mL of sample was poured into each of 250 mL conical flask. The optimum  $\text{S}_2\text{O}_8^{2-}$  : COD<sub>i</sub> ratio obtained from  $\text{S}_2\text{O}_8^{2-}$  oxidation was used and fixed in this experiment. Desired volumes of  $\text{H}_2\text{O}_2$  stock solution (30 %, Fisher Chemical, ACS grade) were prepared in millilitre. The dosage ratios of  $\text{H}_2\text{O}_2$  :  $\text{S}_2\text{O}_8^{2-}$  were also predetermined based on the dosage of  $\text{S}_2\text{O}_8^{2-}$  from the optimum  $\text{S}_2\text{O}_8^{2-}$  : COD<sub>i</sub> ratio. The dosage ratios of  $\text{H}_2\text{O}_2$  :  $\text{S}_2\text{O}_8^{2-}$  were set in 0.5 : 1.0, 1.0 : 1.0, 2.0 : 1.0, 2.5 : 1.0 and 3.0 : 1.0 by fixing the optimum  $\text{S}_2\text{O}_8^{2-}$  dosage obtained. Dosages of  $\text{S}_2\text{O}_8^{2-}$  were first added into the each of conical flasks respectively. Then,  $\text{H}_2\text{O}_2$  were added into the conical flasks. The conical flasks were placed on the orbital shaker at 200 rpm and shaken for well mixing purpose. The samples were measured in term of COD,  $\text{NH}_3\text{-N}$ , SS, colour and pH once the shaker was stopped shaking. Optimum dosage ratio of  $\text{H}_2\text{O}_2$  :  $\text{S}_2\text{O}_8^{2-}$  was determined according to the result obtained.

### 3.3.5 Dosages of $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$

Different dosages of  $\text{H}_2\text{O}_2$  /  $\text{S}_2\text{O}_8^{2-}$  were varied (0.61 g / 0.41 g, 1.22 g / 0.82 g, 2.45 g / 1.63 g, 3.67 g / 2.45 g, 4.89 g / 3.26 g and 6.12 g / 4.08 g) based on optimum dosage ratio of  $\text{H}_2\text{O}_2$  :  $\text{S}_2\text{O}_8^{2-}$  determined. The  $\text{S}_2\text{O}_8^{2-}$ : COD<sub>i</sub> ratio was fixed in this experiment which obtained from previous  $\text{S}_2\text{O}_8^{2-}$  oxidation. The experiment was

carried out within 20 min at pH of original sample. 100 mL of sample was poured into each of 250 mL conical flask. Dosages of  $S_2O_8^{2-}$  were first added into the each of conical flasks respectively. Then,  $H_2O_2$  were added into the conical flasks. The conical flasks were placed on the orbital shaker at 200 rpm and shaken for well mixing purpose. The samples were measured in term of COD,  $NH_3-N$ , SS, colour and pH once the shaker was stopped shaking.

### **3.4 Analytical Procedures**

The following parameters such as  $BOD_5$ , COD, turbidity, pH, colour, SS and  $NH_3-N$  were measured on sample before oxidation treatment according to standard method provided. After oxidation treatment, COD,  $NH_3-N$ , SS, pH and colour of sample were also measured. All the analysis methods were adapted from Standard Methods for the Examination of Water and Wastewater (APHA, 2005) and Hach Water Analysis Book (Hach, 2005).

#### **3.4.1 Biochemical Oxygen Demand (BOD)**

BOD measurement was carried out for 5 d (APHA, 2005). Five BOD bottles are prepared before starting the experiment. The sample was initially diluted with dilution factor of 100. 30 mL sample was added into first 300 mL BOD bottle with 270 mL of distilled water. Series dilutions were done by transferring 30 mL from each bottle to another bottle. Additional distilled water should be added into BOD bottles until top of bottles if necessary. Initial dissolved oxygen level (DO) was measured by DO 2700 Dissolved Oxygen (DO) Meter (Eutech, United Kingdom) as shown in Figure 3.7 within 30 min after dilution. The BOD bottles were closed and sealed with parafilm to prevent air disturbance. The bottles were incubated at 20 °C for 5 d. Final DO were measured after 5 d of incubation.

$$\text{BOD}_5 \text{ (mg/L)} = (\text{DO}_i - \text{DO}_f) / P \quad (3.1)$$

where

$\text{DO}_i$  = Initial DO concentration, mg/L

$\text{DO}_f$  = Final DO concentration, mg/L

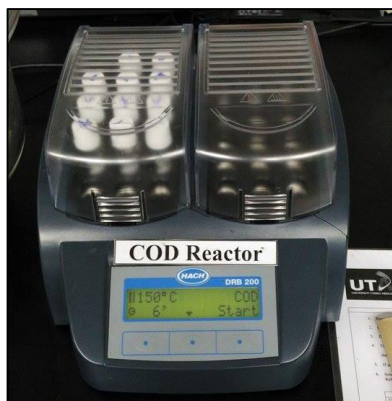
P = decimal volumetric fraction of sample determined



**Figure 3.7 Dissolved Oxygen Meter (DO 2700, UK).**

### 3.4.2 Chemical Oxygen Demand (COD)

COD measurements of samples were using the Dichromate Reactor Digestion Method (HACH Method 8000) (Hach, 2005). The samples were first diluted with dilution factor of 10. 2 mL of diluted sample was added into vial with an angle of 45° and mixed gently. The vial then rinsed with deionised water and wiped with a clean towel. For blank preparation, 2 mL of deionized water was added into vial and mixed gently. DRB 200 Digital Reactor Block (Hach, Germany) as shown in Figure 3.8 was turned on and preheated to 150 °C. The vials were then heated for 2 hr. The vials were cooled down to room temperature. For colorimetric measurement, DR 6000 UV-Vis spectrophotometer (Hach, Germany) was used. After selecting program ‘COD HR 1500 mg/L’ in Stored Program, the blank was put in and set zero. The samples were put instead of blank vial and pressed ‘Read’ button. The reading was shown in mg/L unit. The samples were measured in duplicate in order to obtain accurate result.



**Figure 3.8 Digital Reactor Block (DRB 200, Germany).**

### 3.4.3 Colour

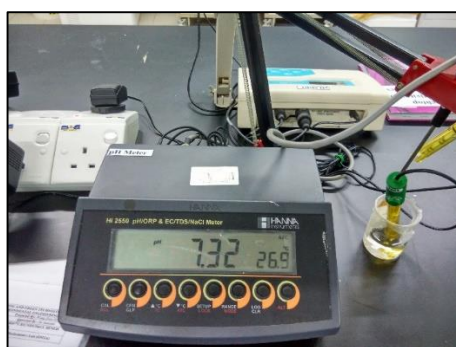
Spectrophotometric Method-Single Wavelength Method (APHA, 2005) was used as colour measurement of sample. The samples were first diluted with dilution factor of 10. 1 mL of sample and 9 mL of distilled water were pipetted into a clean beaker for each sample. The empty glass vials were filled with diluted samples until half of vials. For blank preparation, the vial was filled with distilled water until half of vial. The blank was inserted and set in DR 6000 UV-Vis Spectrophotometer (Hach, Germany) after selecting program 'Colour 465nm' in Stored Program. 'Read' button was pressed when the samples were measured in PtCo unit. The samples were measured in duplicate in order to obtain accurate result. Figure 3.9 shows the Spectrophotometer used for colour measurement.



**Figure 3.9 UV-Vis Spectrophotometer (DR 6000, Germany).**

### 3.4.4 pH

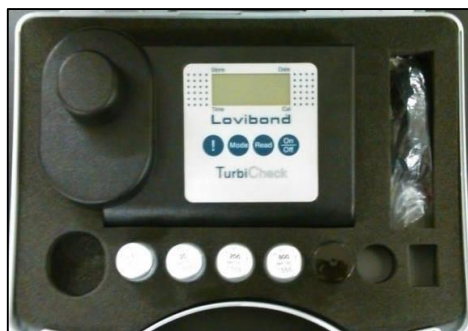
pH of samples was measured using HI 2550 pH meter (Hanna, USA) through Electrometric Method (APHA, 2005). Calibration of pH meter was done using buffer solution of pH 4, 7 and 10. For measurement, pH probe was firstly inserted into the sample and waited until obtained stable reading. The electrodes were rinsed with distilled water before next measurement. The samples were measured in duplicate in order to obtain accurate result. Figure 3.10 shows the pH meter used in the study.



**Figure 3.10 pH Meter (Hanna HI 2550, USA).**

### 3.4.5 Turbidity

Turbidity of sample was measured using TB 210 IR Turbidity Meter (Lovibond, Germany) as shown in Figure 3.11. Nephelometric Method (APHA, 2005) was used for the turbidity measurement. The sample first was filled in sample test tube until marked line. The test tube was shaken for proper mixing and wiped with clean towel before inserted into turbidity meter. The reading was obtained within seconds after pressed 'Read' button. The samples were measured twice in term of Nephelometric Turbidity Units (NTU) to obtain accurate result.



**Figure 3.11 Turbidity Meter (TB 210 IR, Germany).**

#### **3.4.6 Ammoniacal Nitrogen (NH<sub>3</sub>-N)**

NH<sub>3</sub>-N was measured using Nessler Method (APHA, 2005). 25 mL blank was prepared from deionized water. The samples were first diluted with deionized water in dilution factor of 200. 25 mL samples were pipetted out and prepared for adding the Ammonia Nitrogen Reagent set. Ammonia Nitrogen Reagent set includes Nessler Reagent, Mineral Stabilizer and Polyvinyl Alcohol Dispersing Agent. 3 drops of Mineral Stabilizer were firstly added into each samples and blank and then shaken. 3 drops of Polyvinyl Alcohol Dispersing Agent were also added into blank and each samples and shaken. 1 mL of Nessler Reagent then added into blank and each samples and shaken again. The samples and blank were pipetted into the empty glass vials. DR 6000 UV-Vis spectrophotometer (Hach, Germany) (Figure 3.9) was used in measurement. The blank was firstly inserted into the spectrophotometer and set zero reading after selecting 'Ammonia Nitrogen Nessler 2.5mg/L' in Favourite Program. The samples were then measured in term of mg/L. The samples were analysed in duplicate.



### **3.4.7 Suspended Solids (SS)**

Photometric method was used for suspended solids measurement (Hach, 2005). Samples were pipetted in the glass vials. For blank, distilled water was also pipetted in the empty glass vial. The blank was placed in DR 6000 UV-Vis spectrophotometer (Hach, Germany) as Figure 3.9 and set zero reading after selecting 'suspended solids 750 mg/L' in Stored Program. The samples were measured in mg/L and measurements were repeated twice for accuracy of readings.

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Initial Characteristics of BIOTPOME

The sample was thawed to room temperature before starting the parameter tests. The initial characteristics of sample were presented in Table 4.1. Average values of biological oxygen demand (BOD) and chemical oxygen demand (COD) of sample were  $151 \pm 41$  mg/L and  $3290 \pm 300$  mg/L, respectively. This was indicated more non-biodegradable organic or inorganic compounds contained than biodegradable organic matters in the sample. The parameters like suspended solids (SS) and ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ) were  $351 \pm 41$  mg/L and  $123 \pm 7$  mg/L in average value. The sample was in neutral pH condition, pH 8.4. Total dissolved solids (TDS), turbidity and conductivity were also being characterized and the average values were  $5930 \pm 50$  mg/L,  $665 \pm 25$  NTU and  $11.86 \pm 0.11$  mS/cm, respectively.

**Table 4.1 Characteristics of BIOTPOME Sample.**

Parameters	Unit	Range	Average	Discharge Limit
BOD	mg/L	110 – 191	151	100
COD	mg/L	2990 – 3590	3290	1000
TDS	mg/L	5880 – 5980	5930	-
SS	mg/L	340 – 361	351	400
$\text{NH}_3\text{-N}$	mg/L	116 – 130	123	150
Turbidity	NTU	640 – 689	665	-
Colour	PtCo	5410 – 6250	5830	-
pH	-	8.0 - 8.7	8.4	5.0 - 9.0
Temperature	°C	25	25	45
Conductivity	mS/cm	11.75 - 11.96	11.86	-

## 4.2 $S_2O_8^{2-}$ Oxidation on BIOTPOME

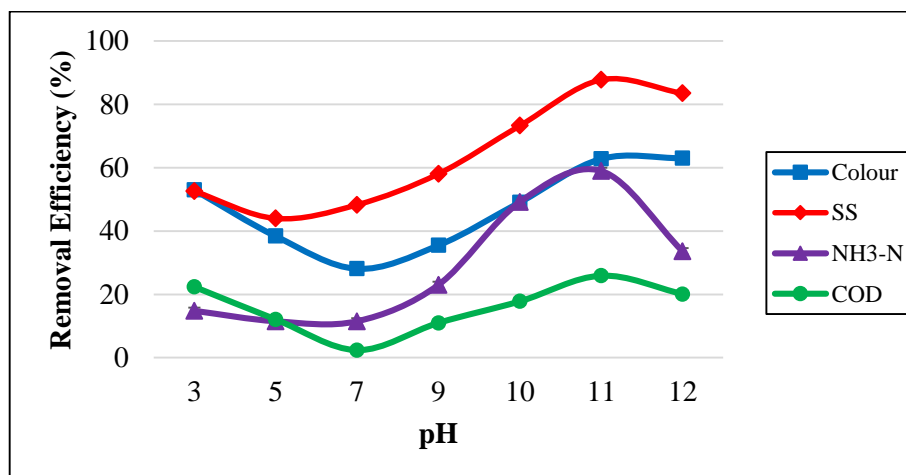
In  $S_2O_8^{2-}$  oxidation, the operational conditions such as pH, contact time and  $S_2O_8^{2-}$  dosage were studied for their effect in removing the parameters of BIOTPOME such as COD,  $NH_3-N$ , colour and SS. The oxidation processes were carried out under ambient temperature.

### 4.2.1 Effect of pH Adjustment

Different initial pHs (3, 5, 7, 9, 10, 11 and 12) were adjusted accordingly by fixing the dosage of  $S_2O_8^{2-}$  ( $S_2O_8^{2-} : COD_i = 4.0 : 1.0$ ) before  $S_2O_8^{2-}$  oxidation process was initiated. The oxidation process was carried out for 1 hour under ambient temperature. Figure 4.1 shows the removal efficiencies of COD,  $NH_3-N$ , colour and SS of BIOTPOME on different pH values. The highest removal efficiency of  $S_2O_8^{2-}$  oxidation was achieved under alkali condition, pH 11 with 21.9 % COD, 59.0 %  $NH_3-N$ , 62.8 % colour and 87.8 % SS. For trend of the graph, in terms of COD and colour, the percentage removals were decreased from pH 3 to pH 7 and rose again after pH 7 until pH 11, however removal in pH 12 were lower compared to pH 11. For the parameters like  $NH_3-N$  and SS, the removals were dropped slightly from pH 3 and started rising after pH 5, and the removal condition at pH 12 eventually were also reduced compared to pH 11. It seems like alkali and acidic condition led to high removals on the parameters but less removal efficiencies under neutral pH like 7.

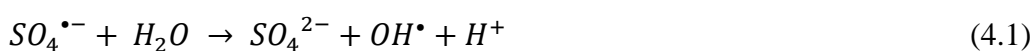
As shown in Figure 4.1, 22.4 % of COD, 14.8 % of  $NH_3-N$ , 53.0 % of colour and 52.6 % of SS removals were achieved at low pH value. Compared to removal efficiency at high pH value like pH 11, COD removal is 21.9 % which almost same with the COD removal at low pH. It is suggested that pH adjustment has no major effect on degradation of organic matters. However, for removal on  $NH_3-N$ , 59.0 % of  $NH_3-N$  was being removed at pH 11 which higher than  $NH_3-N$  removal at pH 3. This represents  $S_2O_8^{2-}$  oxidation is effective on  $NH_3-N$  removal under alkali condition. For pH 12, the parameters' removals were lowered than pH 11 may due to consumption of  $OH^\bullet$  by  $SO_4^{2-}$  anions at higher pH. The amount of  $OH^\bullet$  was

increased as higher the pH (Liang et al., 2007). Thus, existence of  $\text{OH}^\bullet$  as main radical would be affected and consumed by  $\text{SO}_4^{2-}$  anions in oxidation if the amount of  $\text{SO}_4^{2-}$  anions is excessive (Abu Amr et al., 2013; Liang et al., 2007).  $\text{SO}_4^{2-}$  is the final product of oxidation (Maurino et al., 1997) which causes large amount of salts produced in the effluent of treatment.



**Figure 4.1 Effect of Initial pHs on Removals of Colour, SS,  $\text{NH}_3\text{-N}$  and COD by  $\text{S}_2\text{O}_8^{2-}$  Oxidation (1 hr contact time;  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i$  ratio = 4.0 : 1.0 at 200 rpm).**

Hydrogen ( $\text{H}^+$ ) ions were released under acidic condition like pH 3 and acted as catalyst to react with  $\text{S}_2\text{O}_8^{2-}$  anions, inducing the generation of sulphate radical ( $\text{SO}_4^{\bullet-}$ ) as Equation (2.20) and (2.21). At alkali pH, hydroxyl radical ( $\text{OH}^\bullet$ ) may formed as Equation (2.17) and (2.18). Hydroxide ( $\text{OH}^-$ ) ions could be consumed for activation of  $\text{S}_2\text{O}_8^{2-}$  under alkaline condition in order to generate  $\text{OH}^\bullet$ . This represents the effect of pH has significant influence on  $\text{S}_2\text{O}_8^{2-}$  oxidation. According to Lee et al. (2012) and Liang et al. (2007), another possible mechanism of formation of  $\text{OH}^\bullet$  is it could be formed under all pHs as Equation (4.1) but smaller reaction rate constant compared to Equation (2.16). Among the radical formations,  $\text{SO}_4^{\bullet-}$  is predominate radical at acidic pH while  $\text{OH}^\bullet$  is main radical at alkali pH (Zhao et al., 2013).

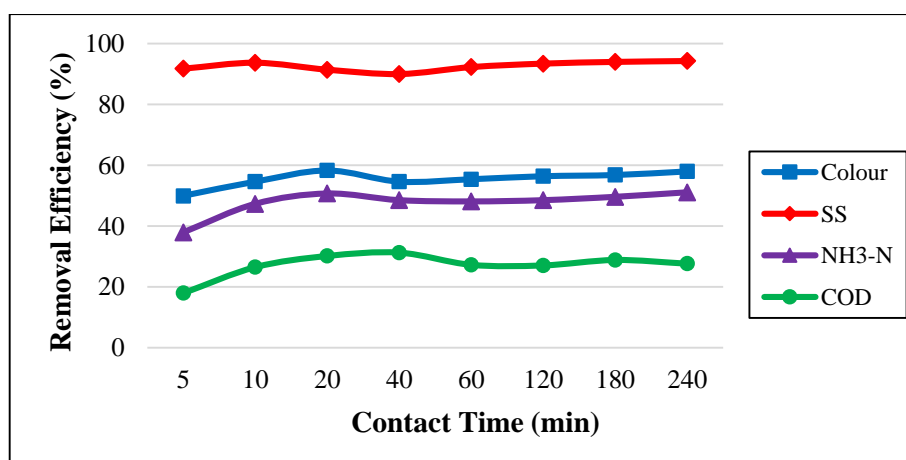


$\text{OH}^\bullet$  is one of highly reactive oxygen species (ROS) generated from reaction of  $\text{SO}_4^{\bullet-}$  as Equation (4.1) and ROS is involved in chain initiation, radical

propagation and chain termination as indicated in Eqs. (2.3) - (2.6) (Huie et al., 1991 cited in Deng and Ezeyske, 2011). These chain reactions may result in complete or part degradation on organic compounds too (Berlin, 1986 cited in Deng and Ezeyske, 2011). According to graph obtained, the highest removal of COD achieved was 22.4 % at pH 3 only. It indicates the  $S_2O_8^{2-}$  oxidation conducted in acidic pH has caused limited elimination of organic compounds.

#### 4.2.2 Effect of Contact Times

For the experiment which is varied in different contact times, the fixed dosage of  $S_2O_8^{2-}$  ( $S_2O_8^{2-} : COD_i = 4.0 : 1.0$ ) and pH 11 were applied. The contact times of 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min and 240 min were being conducted accordingly. As shown in Figure 4.2, optimum removal rate for colour, SS,  $NH_3-N$  and COD were 58.3 %, 91.4 %, 50.7 % and 30.2 %, respectively at 20 min. The COD removed was slightly higher compared with 21.9 % of COD eliminated from previous operational condition, pH adjustment at 60 min. However, removal of  $NH_3-N$  at 20 min was lower compared to  $NH_3-N$  removed of last pH adjustment study at 60 min, 59.0 %. Suspended solids were also greatly removed from the range of 89.9 % to 94.3%. While for colour, 49.9 % - 58.3 % of removal efficiencies were observed between the contact times of 5 min to 240 min.

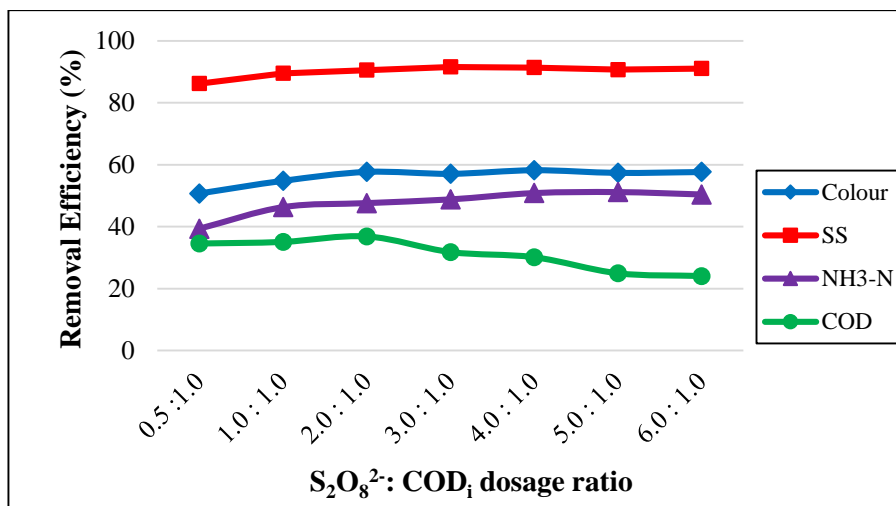


**Figure 4.2 Effect of Contact Time on Removals of Colour, SS,  $NH_3-N$  and COD by  $S_2O_8^{2-}$  Oxidation (pH 11;  $S_2O_8^{2-} : COD_i$  ratio = 4.0 : 1.0 at 200 rpm).**

For the trend of Figure 4.2, the colour,  $\text{NH}_3\text{-N}$  and COD removals were increased when the contact times were in 5 min to 20 min while colour,  $\text{NH}_3\text{-N}$  removal efficiencies decreased after 20 minutes. COD reduction was slightly decreased after 40 min. The removals of pollutants were not significant change after 40 min. This may represent  $\text{S}_2\text{O}_8^{2-}$  or radicals attacked rapidly on those parameters and rapid decomposition of  $\text{S}_2\text{O}_8^{2-}$  so time taken for oxidation was short. The rapid decomposition of  $\text{S}_2\text{O}_8^{2-}$  can be caused by water and heat so acidic condition would be resulted from the oxidation as indicated in Equation (2.1) (Hernandez, 2005). Equation (2.1) is applied to  $\text{S}_2\text{O}_8^{2-}$  oxidation which is in mild acid, neutral and base aqueous solutions (Kolthoff and Miller, 1951). Sulphate ions ( $\text{SO}_4^{2-}$ ) and  $\text{H}^+$  ions may produce from dissociation of hydrogen sulphate ion ( $\text{HSO}_4^-$ ) as shown in Equation (2.2).  $\text{HSO}_4^-$  is a weak acid. The formation of  $\text{H}^+$  ions has caused pH reduction (Romero et al., 2010; Huang et al., 2005) so it may explain why all the pH values of BIOTPOME were slightly decreased after oxidation process in this study.

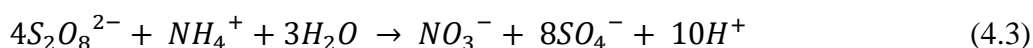
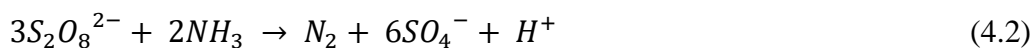
#### 4.2.3 Effect of $\text{S}_2\text{O}_8^{2-}$ Dosages

Figure 4.3 demonstrates the removal percentages of pollutant parameters of BIOTPOME with varied dosages of  $\text{S}_2\text{O}_8^{2-}$  in relation to  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i$  (0.5 : 1.0, 1.0 : 1.0, 2.0 : 1.0, 3.0 : 1.0, 4.0 : 1.0, 5.0 : 1.0 and 6.0 : 1.0). In the oxidation system, the operational condition such as pH was fixed at 11 and contact time taken was 20 min. The optimum removal of parameters like colour, SS,  $\text{NH}_3\text{-N}$  and COD were 90.6 %, 57.7 %, 47.6 % and 36.8 %, respectively when  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i = 2.0 : 1.0$ . After  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i = 2.0 : 1.0$ , a significant decreasing was obtained in COD removal. The COD reduction was ranged in 24.0 % to 31.8 % at  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i = 3.0 : 1.0$  to  $6.0 : 1.0$ . As discussed in subchapter 2.7.3, excessive amount of  $\text{S}_2\text{O}_8^{2-}$  would affect the treatment efficiency.  $\text{SO}_4^{2-}$  can act as scavenger to attack  $\text{OH}^\bullet$  and reduce the decomposition rate of COD as in similar study of degradation of trichloroethylene by  $\text{S}_2\text{O}_8^{2-}$  oxidation (Liang et al., 2007).



**Figure 4.3 Effect of Dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> on Removals of Colour, SS, NH<sub>3</sub>-N and COD by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation (20 min contact time; pH 11 at 200 rpm).**

The removal efficiency of colour was increased from 50.7 % to 57.7 % between S<sub>2</sub>O<sub>8</sub><sup>2-</sup> : COD<sub>i</sub> = 0.5 : 1.0 and 2.0 : 1.0 while the removal was not obvious change at S<sub>2</sub>O<sub>8</sub><sup>2-</sup> : COD<sub>i</sub> = 3.0 to 6.0 (57.1 % - 57.5 %). Colour was not definitely influenced by dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. NH<sub>3</sub>-N removals were increased gradually from 39.3 % to 51.2 % and slight dropped to 50.4 % at S<sub>2</sub>O<sub>8</sub><sup>2-</sup> : COD<sub>i</sub> = 6.0 : 1.0. The result indicated NH<sub>3</sub>-N could be degraded as the dosage of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> increased. Strong oxidizing agents are favour in attracting electron from components of NH<sub>3</sub>-N such as ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>) (Deng and Ezyske, 2011). If silver compounds existed within BIOTPOME, NH<sub>3</sub>-N would be oxidized to nitrogen compounds by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as Equations (4.2) and (4.3) (Ali, 2005). The researchers have also reported that OH<sup>•</sup> produced through advanced oxidation was low in rate constant with NH<sub>3</sub> (Huang et al., 2008; Zhang et al., 2005 cited in Deng and Ezyske, 2011) and it indicates low removal efficiency would be occurred in NH<sub>3</sub>-N. It is suggested that S<sub>2</sub>O<sub>8</sub><sup>2-</sup> may directly reacts NH<sub>3</sub>-N compounds and less amount of OH<sup>•</sup> is produced from chain initiation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.



As shown in Table 4.2, using  $S_2O_8^{2-}$  oxidation alone under different operational conditions, the removal efficiencies were ranged from 21.9 to 36.8 % for COD, 47.6 % to 59.0 % for  $NH_3-N$ , 57.7 % to 62.8 % for colour and 87.8 % to 91.4 % for SS. The pH values of samples were risen to 10.5 - 10.6 after oxidation treatment process. By adjusting the operational conditions in optimum as  $S_2O_8^{2-} : COD_i = 2.0 : 1.0$ , pH 11 and 20 min contact time, 36.8 % COD, 47.6 %  $NH_3-N$ , 57.7 % colour and 90.6 % SS were achieved in removal efficiency.

**Table 4.2 Removals of COD,  $NH_3-N$ , Colour and SS of BIOTPOME in Different Operational Conditions Using  $S_2O_8^{2-}$  Oxidation.**

Operational Conditions	Final pH	COD Removal (%)	$NH_3-N$ Removal (%)	Colour Removal (%)	SS Removal (%)
<b>pH 11</b> (CT = 1 hr ; $S_2O_8^{2-} : COD_i$ ratio = 4.0 : 1.0)	10.5	21.9	59.0	62.8	87.8
<b>CT = 20 min</b> (pH 11 ; $S_2O_8^{2-} : COD_i$ ratio = 4.0 : 1.0)	10.5	30.2	50.7	58.3	91.4
<b><math>S_2O_8^{2-} : COD_i</math> ratio = 2.0 : 1.0</b> (pH 11 ; CT = 20 min)	10.6	36.8	47.6	57.7	90.6

\*Contact Time, CT

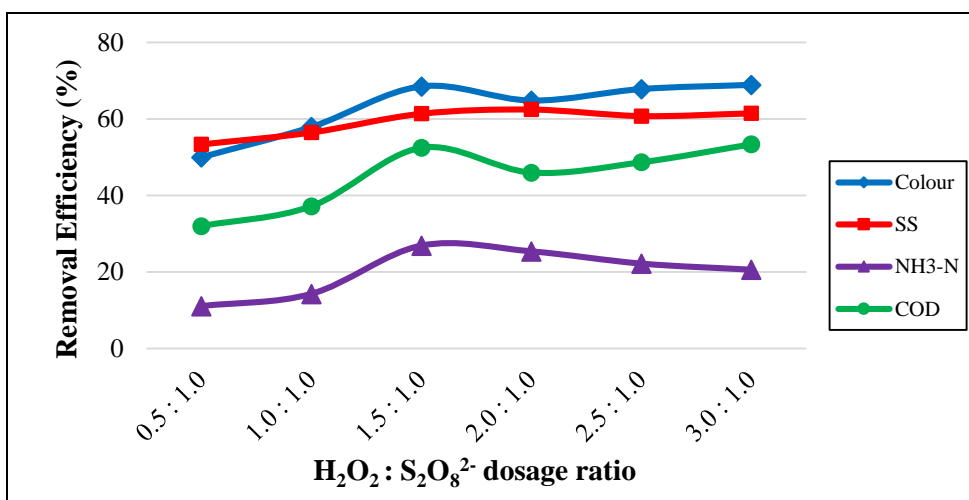
### 4.3 $S_2O_8^{2-}/H_2O_2$ Oxidation on BIOTPOME

Hydrogen peroxide ( $H_2O_2$ ) was investigated and played an enhancement role in  $S_2O_8^{2-}$  oxidation on treating BIOTPOME. In the study, COD,  $NH_3-N$ , colour and SS parameters were analysed before and after each experiment accordingly. The operational conditions such as pH and dosages of  $S_2O_8^{2-}$  and  $H_2O_2$  were also controlled in the oxidation process under ambient temperature.



### 4.3.1 Effect of Dosage Ratios of $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$

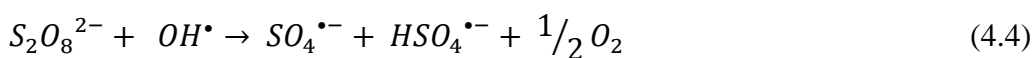
By varying the dosage ratios of  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  (0.5 : 1.0, 1.0 : 1.0, 1.5 : 1.0, 2.0 : 1.0, 2.5 : 1.0 and 3.0 : 1.0), the oxidation on BIOTPOME was performed under pH 8.4 within 20 min. The result is demonstrated in Figure 4.4. The optimum removal of colour, SS,  $\text{NH}_3\text{-N}$  and COD by using  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  dosage ratio of 1.5 : 1.0 were 68.5 %, 61.4 %, 26.9 % and 52.5 %. When the smallest dosage ratio ( $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-} = 0.5 : 1.0$ ) was applied, 50.0 % colour, 53.4 % SS, 11.1 %  $\text{NH}_3\text{-N}$  and 32 % COD removals were already being achieved. As dosage ratio increased, removal percentage on parameters were also increased. However, the removals of COD,  $\text{NH}_3\text{-N}$  and colour were decreased after dosage ratio was 1.5 : 1.0. The removals of colour (64.8 %),  $\text{NH}_3\text{-N}$  (25.4 %) and COD (46 %) were decreased at  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-} = 2.0 : 1.0$  but degradation in colour and COD were increased to 68.9 % and 53.4 % at  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  dosage ratio = 3.0 : 1.0.



**Figure 4.4 Effect of Dosage Ratios of  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  on Removals of Colour, SS,  $\text{NH}_3\text{-N}$  and COD by  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  Oxidation (20 min contact time;  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i$  ratio = 2.0 : 1.0; pH 8.4 at 200 rpm).**

Removal of SS was slightly increased to 62.5 % at  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-} = 2.0 : 1.0$  may due to human error as the percentage of SS reduced at  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-} = 1.5 : 1.0$  was almost same as the removal percentages of SS at  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-} = 2.5$  and 3.0. Besides, overall removal of  $\text{NH}_3\text{-N}$  was low if compared with removals of colour, SS

and COD. There is slow reaction rate between  $\text{NH}_3\text{-N}$  and  $\text{OH}^\bullet$  as discussed in sub-chapter 4.2.3. and would lead to fewer  $\text{NH}_3\text{-N}$  being attacked by  $\text{OH}^\bullet$  produced. In  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  oxidation, there is also possible for  $\text{H}_2\text{O}_2$  produces  $\text{OH}^\bullet$  and  $\text{OH}^\bullet$  then reacted with  $\text{SO}_4^{\bullet-}$  according to the mechanism of chain initiation as shown in Equations (2.9) - (2.16).  $\text{S}_2\text{O}_8^{2-}$  could also be activated by  $\text{OH}^\bullet$  to produce  $\text{SO}_4^{\bullet-}$  as indicated in Equation (4.4) (Abu Amr et al., 2013). Therefore, the oxidant or radicals would be in less amount to eliminate the contaminants of BIOTPOME. These mechanisms have been suggested in studies but the actual function of  $\text{H}_2\text{O}_2$  in  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  oxidation was not clearly defined.

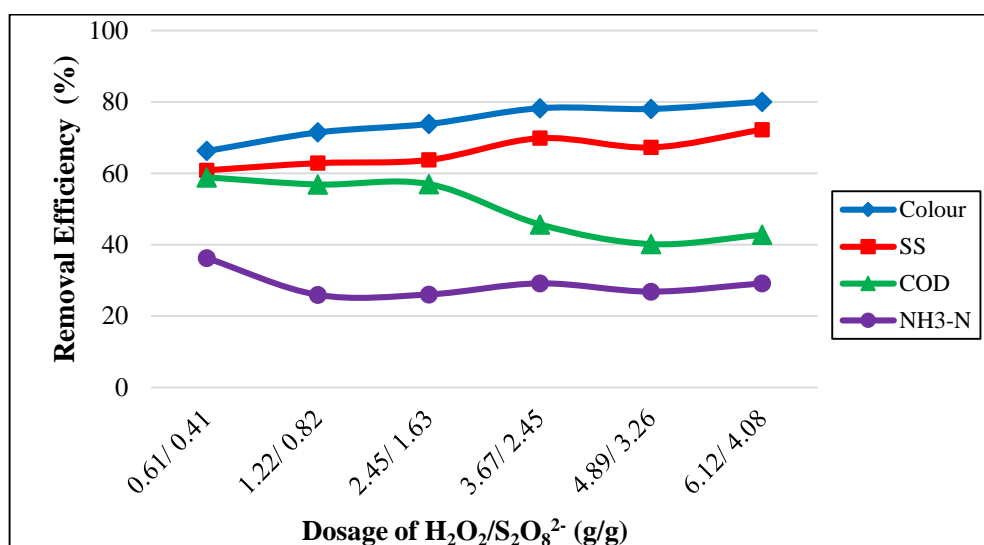


### 4.3.2 Effect of Dosages of $\text{H}_2\text{O}_2 / \text{S}_2\text{O}_8^{2-}$

After the optimum dosage ratio of  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  (1.5 : 1.0) was determined, different dosages of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$  were studied with fixed in order to enhance the effectiveness of treatment. The dosages of  $\text{H}_2\text{O}_2 / \text{S}_2\text{O}_8^{2-}$  were varied among 0.61 g / 0.41 g, 1.22 g / 0.82 g, 2.45 g / 1.63 g, 3.67 g / 2.45 g, 4.89 g / 3.26 g and 6.12 g / 4.08 g. The oxidation was conducted under original pH, pH 8.4 and 20 min contact time. The optimum result was obtained based on overall removals of parameters. The optimum dosage of  $\text{H}_2\text{O}_2 / \text{S}_2\text{O}_8^{2-}$  acquired through the experiment was 2.45 g / 1.63 g and the removal efficiencies, 73.8 %, 63.7 %, 56.9 % and 26 % were achieved in term of colour, SS,  $\text{NH}_3\text{-N}$  and COD, respectively. By fixing the dosage ratio and varied the dosages of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , the removals of colour,  $\text{NH}_3\text{-N}$  and SS were increased gradually in overall. When the dosage of  $\text{H}_2\text{O}_2 : \text{S}_2\text{O}_8^{2-}$  was increased from 0.61 g / 0.41 g to 2.45 g / 1.63 g, 58.8 % - 56.9 % COD removal were achieved. However, the COD removal was decreased afterward when additional dosages of  $\text{H}_2\text{O}_2 / \text{S}_2\text{O}_8^{2-}$  (g/g) was added.

As dosage of  $\text{H}_2\text{O}_2$  increases,  $\text{H}_2\text{O}_2$  and  $\text{SO}_4^{\bullet-}$  may non-productively degrade and scavenged, respectively then result in fasten the termination mechanism due to

the free radicals will scavenge oxidants and oxidants may scavenge radicals too (Ko et al., 2012) as Eqs. (4.5) and (4.6). Ko et al. (2012) has also mentioned  $S_2O_8^{2-}$  and  $OH^\bullet$  may react with each other although the reaction rate is slow.

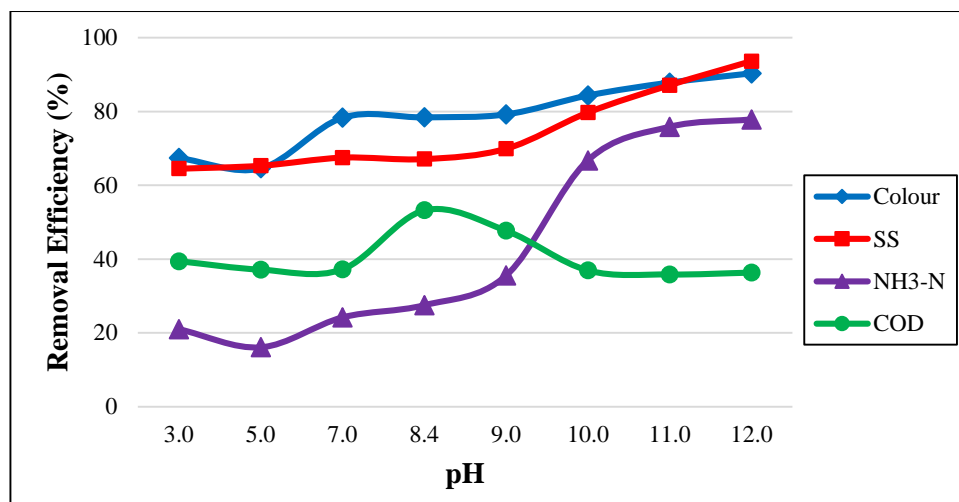


**Figure 4.5** Effect of Dosages of  $H_2O_2 / S_2O_8^{2-}$  on Removals of Colour, SS, NH<sub>3</sub>-N and COD by  $S_2O_8^{2-}/H_2O_2$  Oxidation (20 min contact time;  $S_2O_8^{2-} : COD_i$  ratio = 2.0 : 1.0;  $H_2O_2 : S_2O_8^{2-}$  dosage ratio = 1.5 : 1.0; pH 8.4 at 200 rpm).

### 4.3.3 Effect of pH Adjustment

Different initial pHs (3, 5, 7, 8.4, 9, 10, 11 and 12) were also studied in  $S_2O_8^{2-}/H_2O_2$  oxidation on BIOTPOME. Fixed variables such as  $S_2O_8^{2-} : COD_i = 2.0 : 1.0$ , dosage of  $H_2O_2 : S_2O_8^{2-} = 2.45 \text{ g} / 1.63 \text{ g}$  and 20 min contact time were employed in the oxidation system. In Figure 4.6, the optimum pH for overall removals on parameters was 11. 87.8 % colour, 87.1 % SS, 75.8 % NH<sub>3</sub>-N and 35.8 % COD were eliminated under pH 11. Removals of colour and SS were increased steeply as pH increased. The removal efficiencies of colour and SS obtained were 67.4 % and 64.5 % under

acidic condition, pH 3. 90.3 % colour removal and 93.6 % SS removal were also gained as initial pH was 12. While the removal of  $\text{NH}_3\text{-N}$  was improved from 21.0 % to 77.8 % as pH increased from 3 to 11.



**Figure 4.6 Effect of Initial pHs on Removals of Colour, SS,  $\text{NH}_3\text{-N}$  and COD by  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  Oxidation (20 min contact time;  $\text{S}_2\text{O}_8^{2-} : \text{COD}_i = 2.0 : 1.0$ ; dosage of  $\text{H}_2\text{O}_2 / \text{S}_2\text{O}_8^{2-} = 2.45 \text{ g} / 1.63 \text{ g}$  at 200 rpm).**

Comparing to the study of varied dosages of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , the overall removal percentage on the parameters were increased except COD. As increasing in pH by adding sodium hydroxide (NaOH),  $\text{S}_2\text{O}_8^{2-}$  could be decomposed in faster rate (Watts, 2011) and this may cause generation of immediate species and radicals as shown in the mechanisms of Equations (2.17) and (2.18). In the performance of oxidation illustrated in Figure 4.6, alkali pH has great influence in degradation of  $\text{NH}_3\text{-N}$ . This indicates effect of pH adjustment has tendency on elimination of inorganic compounds in  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  oxidation. Regarding the mechanism to degrade the target compounds such as organic pollutants,  $\text{OH}^\bullet$  would be involved in hydrogen abstraction or hydroxylation under alkali condition while  $\text{SO}_4^{\bullet-}$  prefers involved in electron transfer (Minisci and Citterio, 1983; Peyton, 1993 cited in Liang et al., 2007).

In summary of  $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$  oxidation, through adjustment of the dosage ratios and dosages of  $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$  (g/g), removal efficiencies of COD,  $\text{NH}_3\text{-N}$ , colour

and SS were 52.5 % - 56.9 %, 26 % - 26.9 %, 68.5 % - 73.8 % and 61.4 % - 63.7 %, correspondingly with the final pH values of 8.2. However, under adjustment of pH, COD removal was decreased and NH<sub>3</sub>-N removal was increased sharply compared with COD and NH<sub>3</sub>-N removals under varied dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub>. In the studied conditions (S<sub>2</sub>O<sub>8</sub><sup>2-</sup> : COD<sub>i</sub> = 2.0 : 1.0, pH 11, 20 min contact time and H<sub>2</sub>O<sub>2</sub> / S<sub>2</sub>O<sub>8</sub><sup>2-</sup> dosage = 2.45 g / 1.63 g), the highest removal efficiencies of COD, NH<sub>3</sub>-N, colour and SS achieved 35.8 %, 75.8 %, 87.8 % and 87.1 %, respectively at final pH, 10.1.

**Table 4.3 Removals of COD, NH<sub>3</sub>-N, Colour and SS of BIOTPOME in Different Operational Conditions Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation.**

Operational Conditions	Final pH	COD Removal (%)	NH <sub>3</sub> -N Removal (%)	Colour Removal (%)	SS Removal (%)
<b>Dosage ratio of H<sub>2</sub>O<sub>2</sub> : S<sub>2</sub>O<sub>8</sub><sup>2-</sup> = 1.5 : 1.0</b> (Contact Time = 20 min; S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> : COD <sub>i</sub> = 2.0 : 1.0; pH 8.4)	8.2	52.5	26.9	68.5	61.4
<b>Dosage of H<sub>2</sub>O<sub>2</sub> / S<sub>2</sub>O<sub>8</sub><sup>2-</sup> = 2.45 g / 1.63 g</b> (Contact Time = 20 min; S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> : COD <sub>i</sub> = 2.0 : 1.0; Dosage ratio of H <sub>2</sub> O <sub>2</sub> : S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> = 1.5 : 1.0 ; pH 8.4)	8.2	56.9	26	73.8	63.7
<b>pH = 11</b> (Contact Time = 20 min; S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> : COD <sub>i</sub> = 2.0 : 1.0; Dosage of H <sub>2</sub> O <sub>2</sub> / S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> = 2.45 g / 1.63 g)	10.1	35.8	75.8	87.8	87.1

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

Based on this study,  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidation are applicable in removing colour, SS,  $NH_3-N$  and COD of BIOTPOME. To the best of our knowledge, this research is the first experimental study of  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidations in BIOTPOME treatment. For  $S_2O_8^{2-}$  oxidation, 36.8 % COD, 47.6 %  $NH_3-N$ , 57.7 % colour and 90.6 % suspended solids were removed at the optimum operation conditions ( $S_2O_8^{2-} : COD_i = 2.0 : 1.0$  at pH 11 in 20 min contact time). In  $S_2O_8^{2-}/H_2O_2$  oxidation, 35.8 % COD, 75.8 %  $NH_3-N$ , 87.8 % colour and 87.1 % suspended solids were achieved when operation condition were  $S_2O_8^{2-} : COD_i = 2.0 : 1.0$ ,  $H_2O_2 / S_2O_8^{2-}$  dosage = 2.45 g / 1.63 g, pH 11 and 20 min contact time. The highest removal of COD was 56.9 % when  $S_2O_8^{2-} : COD_i = 2.0 : 1.0$  and dosage of  $H_2O_2 / S_2O_8^{2-} = 2.45$  g / 1.63 g at pH 8.4 and 20 min contact time. High removal of COD could be obtained without adjusting pH while  $NH_3-N$  was effectively removed at alkaline condition.

The effluent of treatment was not allowed to discharge to the environment yet due to unable to reach the discharge standard limits of a few parameters especially COD under certain operational conditions although  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidation were good in treating BIOTPOME. Final values of pH for  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidation which have more than pH 9 were also not suitable to release into environment according to discharge standard of POME wastewater in Table 2.2. This study concluded that  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidation were efficient to reduce certain parameters of BIOTPOME under certain operational conditions.

Through the research, there are few improvements and recommendations should be done. Firstly, the detailed activation and degradation mechanism of persulphate ( $S_2O_8^{2-}$ ) with hydrogen peroxide ( $H_2O_2$ ) on composition of BIOTPOME are required to be investigated so can understand more on the interaction of oxidants and radicals with those organic matters,  $NH_3-N$ , colour and SS. Kinetic study of  $S_2O_8^{2-}$  and  $S_2O_8^{2-}/H_2O_2$  oxidation on BIOTPOME using electron spin resonance (ESR) techniques (Zhao et al., 2013) is suggested. In order to gain higher removal in parameters of BIOTPOME, other operational condition such as temperature has potential for further investigation in future.

The end product of oxidation, sulphate ion ( $SO_4^{2-}$ ) is inert salt and not harmful to environment as it is not considered as pollutant (Ahmadi et al., in press). Production of  $SO_4^{2-}$  from the oxidation process was undesirable and it is not sound environmentally if discharge into river stream. It is recommended that the amount of  $SO_4^{2-}$  generated should be determined after treatment. The effluent of treatment is also suggested to be further processed through adsorption treatment since the effluent has exceeded the standard discharge limit.

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## APPENDICES

## APPENDIX A TABLES OF EXPERIMENTAL RESULTS

**Table A1 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation at Different Initial pHs.**

pH		Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
3	2.5	5900	2760	344.0	163.0	122.0	104.0	3310	2570
	2.5	5860	2770	344.0	163.0	122.0	104.0	3310	2570
	<b>2.5</b>	<b>5880</b>	<b>2765</b>	<b>344.0</b>	<b>163.0</b>	<b>122.0</b>	<b>104.0</b>	<b>3310</b>	<b>2570</b>
5	3.6	5900	3620	344.0	193.0	122.0	108.0	3310	2910
	3.6	5860	3620	344.0	192.0	122.0	108.0	3310	2910
	<b>3.6</b>	<b>5880</b>	<b>3620</b>	<b>344.0</b>	<b>192.5</b>	<b>122.0</b>	<b>108.0</b>	<b>3310</b>	<b>2910</b>
7	7.4	5900	4220	344.0	178.0	122.0	108.0	3310	3230
	7.4	5860	4230	344.0	178.0	122.0	108.0	3310	3230
	<b>7.4</b>	<b>5880</b>	<b>4225</b>	<b>344.0</b>	<b>178.0</b>	<b>122.0</b>	<b>108.0</b>	<b>3310</b>	<b>3230</b>
9	8.7	5900	3790	344.0	144.0	122.0	94.0	3310	2940
	8.8	5860	3800	344.0	144.0	122.0	94.0	3310	2950
	<b>8.8</b>	<b>5880</b>	<b>3795</b>	<b>344.0</b>	<b>144.0</b>	<b>122.0</b>	<b>94.0</b>	<b>3310</b>	<b>2945</b>
10	9.7	5900	2990	344.0	92.0	122.0	62.0	3310	2720
	9.7	5860	2990	344.0	92.0	122.0	62.0	3310	2720
	<b>9.7</b>	<b>5880</b>	<b>2990</b>	<b>344.0</b>	<b>92.0</b>	<b>122.0</b>	<b>62.0</b>	<b>3310</b>	<b>2720</b>
11	10.5	5900	2190	344.0	42.0	122.0	50.0	3310	2590
	10.5	5860	2190	344.0	42.0	122.0	50.0	3310	2580
	<b>10.5</b>	<b>5880</b>	<b>2190</b>	<b>344.0</b>	<b>42.0</b>	<b>122.0</b>	<b>50.0</b>	<b>3310</b>	<b>2585</b>
12	11.1	6240	2310	361.0	59.0	122.0	81.0	3340	2909
	11.1	6240	2310	361.0	60.0	122.0	81.0	3320	2909
	<b>11.1</b>	<b>6240</b>	<b>2310</b>	<b>361.0</b>	<b>59.5</b>	<b>122.0</b>	<b>81.0</b>	<b>3330</b>	<b>2909</b>



**Table A2 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME at Different Initial pHs by Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation.**

pH	Colour Removal (%)	SS Removal (%)	NH <sub>3</sub> -N Removal (%)	COD Removal (%)
3	53.0	52.6	14.8	22.4
5	38.4	44.0	11.5	12.1
7	28.1	48.3	11.5	2.4
9	35.5	58.1	23.0	11.0
10	49.1	73.3	49.2	17.8
11	62.8	87.8	59.0	21.9
12	63.0	83.5	33.6	12.6

**Table A3 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation with Different Contact Times at pH 11.**

Contact Time (min)	pH	Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
5	10.4	5420	2710	350.0	29.0	116.0	72.0	3330	2730
	10.4	5400	2710	350.0	29.0	116.0	72.0	3330	2730
	<b>10.4</b>	<b>5410</b>	<b>2710</b>	<b>350.0</b>	<b>29.0</b>	<b>116.0</b>	<b>72.0</b>	<b>3330</b>	<b>2730</b>
10	10.5	6250	2835	348.0	22.0	130.0	68.0	3430	2520
	10.5	6250	2834	348.0	22.0	130.0	68.0	3430	2520
	<b>10.5</b>	<b>6250</b>	<b>2835</b>	<b>348.0</b>	<b>22.0</b>	<b>130.0</b>	<b>68.0</b>	<b>3430</b>	<b>2520</b>
20	10.5	6250	2609	348.0	30.0	130.0	64.0	3430	2410
	10.5	6250	2608	348.0	30.0	130.0	64.0	3430	2380
	<b>10.5</b>	<b>6250</b>	<b>2609</b>	<b>348.0</b>	<b>30.0</b>	<b>130.0</b>	<b>64.0</b>	<b>3430</b>	<b>2395</b>
40	10.5	6250	2836	348.0	35.0	130.0	67.0	3430	2350
	10.4	6250	2836	348.0	35.0	130.0	67.0	3430	2360
	<b>10.5</b>	<b>6250</b>	<b>2836</b>	<b>348.0</b>	<b>35.0</b>	<b>130.0</b>	<b>67.0</b>	<b>3430</b>	<b>2355</b>
60	10.5	6250	2785	348.0	27.0	130.0	67.0	3430	2500
	10.5	6250	2785	348.0	27.0	130.0	68.0	3430	2490
	<b>10.5</b>	<b>6250</b>	<b>2785</b>	<b>348.0</b>	<b>27.0</b>	<b>130.0</b>	<b>67.5</b>	<b>3430</b>	<b>2495</b>
120	10.5	6250	2725	348.0	23.0	130.0	67.0	3430	2500
	10.5	6250	2725	348.0	23.0	130.0	67.0	3430	2500
	<b>10.5</b>	<b>6250</b>	<b>2725</b>	<b>348.0</b>	<b>23.0</b>	<b>130.0</b>	<b>67.0</b>	<b>3430</b>	<b>2500</b>
180	10.4	6250	2700	348.0	21.0	130.0	66.0	3430	2460
	10.4	6250	2699	348.0	21.0	130.0	65.0	3430	2420
	<b>10.4</b>	<b>6250</b>	<b>2700</b>	<b>348.0</b>	<b>21.0</b>	<b>130.0</b>	<b>65.5</b>	<b>3430</b>	<b>2440</b>
240	10.4	6250	2625	348.0	20.0	130.0	64.0	3430	2480
	10.4	6250	2625	348.0	20.0	130.0	63.0	3430	2480
	<b>10.4</b>	<b>6250</b>	<b>2625</b>	<b>348.0</b>	<b>20.0</b>	<b>130.0</b>	<b>63.5</b>	<b>3430</b>	<b>2480</b>

**Table A4 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME at pH 11 by Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation in Different Contact Times.**

Contact Time (min)	Colour Removal (%)	SS Removal (%)	NH <sub>3</sub> -N Removal (%)	COD Removal (%)
5	49.9	91.7	37.9	18.0
10	54.6	93.7	47.7	26.5
20	58.3	91.4	50.7	30.2
40	54.6	89.9	48.5	31.3
60	55.4	92.2	48.1	27.3
120	56.4	93.4	48.5	27.1
180	56.8	94.0	49.6	28.9
240	58.0	94.3	51.1	27.7

**Table A5 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation in Different Dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> within 20 min at pH 11.**

S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> :COD <sub>i</sub>	pH	Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
0.5 : 1.0	10.8	5550	2730	347.0	48.0	122.0	74.0	3320	2170
	10.8	5530	2730	349.0	48.0	122.0	74.0	3310	2170
	<b>10.8</b>	<b>5540</b>	<b>2730</b>	<b>348.0</b>	<b>48.0</b>	<b>122.0</b>	<b>74.0</b>	<b>3315</b>	<b>2170</b>
1.0 : 1.0	10.6	5550	2500	348.0	36.0	122.0	65.0	3310	2150
	10.7	5530	2510	347.0	36.0	122.0	66.0	3310	2150
	<b>10.7</b>	<b>5540</b>	<b>2505</b>	<b>347.5</b>	<b>36.0</b>	<b>122.0</b>	<b>65.5</b>	<b>3310</b>	<b>2150</b>
2.0 : 1.0	10.6	5900	2490	348.0	33.0	128.0	67.0	3310	2060
	10.6	5880	2490	347.0	33.0	128.0	67.0	3310	2060
	<b>10.6</b>	<b>5890</b>	<b>2490</b>	<b>347.5</b>	<b>33.0</b>	<b>128.0</b>	<b>67.0</b>	<b>3310</b>	<b>2060</b>
3.0 : 1.0	10.6	5900	2510	348.0	29.0	128.0	65.0	3310	2260
	10.6	5880	2540	347.0	29.0	128.0	66.0	3310	2250
	<b>10.6</b>	<b>5890</b>	<b>2525</b>	<b>347.5</b>	<b>29.0</b>	<b>128.0</b>	<b>65.5</b>	<b>3310</b>	<b>2255</b>
4.0 : 1.0	10.5	5900	2460	348.0	30.0	128.0	63.0	3310	2310
	10.5	5880	2450	347.0	30.0	128.0	63.0	3310	2320
	<b>10.5</b>	<b>5890</b>	<b>2455</b>	<b>347.5</b>	<b>30.0</b>	<b>128.0</b>	<b>63.0</b>	<b>3310</b>	<b>2315</b>
5.0 : 1.0	10.5	5900	2510	348.0	32.0	128.0	62.0	3310	2490
	10.5	5880	2510	347.0	32.0	128.0	63.0	3310	2480
	<b>10.5</b>	<b>5890</b>	<b>2510</b>	<b>347.5</b>	<b>32.0</b>	<b>128.0</b>	<b>62.5</b>	<b>3310</b>	<b>2485</b>
6.0 : 1.0	10.4	5900	2490	348.0	31.0	128.0	64.0	3310	2530
	10.5	5880	2490	347.0	31.0	128.0	63.0	3310	2500
	<b>10.5</b>	<b>5890</b>	<b>2490</b>	<b>347.5</b>	<b>31.0</b>	<b>128.0</b>	<b>63.5</b>	<b>3310</b>	<b>2515</b>

**Table A6 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Oxidation in Different Dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> within 20 min at pH 11.**

S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> : COD <sub>i</sub>	Colour Removal (%)	SS Removal (%)	NH <sub>3</sub> -N Removal (%)	COD Removal (%)
0.5 : 1.0	50.7	86.2	39.3	34.5
1.0 : 1.0	54.8	89.6	46.3	35.0
2.0 : 1.0	57.7	90.5	47.6	36.8
3.0 : 1.0	57.1	91.6	48.8	31.8
4.0 : 1.0	58.3	91.4	50.8	30.1
5.0 : 1.0	57.4	90.8	51.2	24.9
6.0 : 1.0	57.7	91.1	50.4	24.0

**Table A7 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation in Different Dosages of H<sub>2</sub>O<sub>2</sub> within 20 min at pH 8.2 (Fixed S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Dosage).**

H <sub>2</sub> O <sub>2</sub> : S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	pH	Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
0.5 : 1.0	8.1	4940	2470	352.0	163.0	126.0	112.0	3590.0	2142.5
	8.1	4940	2470	352.0	165.0	126.0	112.0	3590.0	2737.5
	<b>8.1</b>	<b>4940</b>	<b>2470</b>	<b>352.0</b>	<b>164.0</b>	<b>126.0</b>	<b>112.0</b>	<b>3590.0</b>	<b>2440.0</b>
1.0 : 1.0	8.2	4940	2090	352.0	152.0	126.0	108.0	3590.0	2177.5
	8.2	4940	2070	352.0	153.0	126.0	108.0	3590.0	2332.5
	<b>8.2</b>	<b>4940</b>	<b>2080</b>	<b>352.0</b>	<b>152.5</b>	<b>126.0</b>	<b>108.0</b>	<b>3590.0</b>	<b>2255.0</b>
1.5 : 1.0	8.2	4940	1560	352.0	136.0	126.0	92.0	3590.0	1737.5
	8.2	4940	1550	352.0	136.0	126.0	92.0	3590.0	1675.0
	<b>8.2</b>	<b>4940</b>	<b>1555</b>	<b>352.0</b>	<b>136.0</b>	<b>126.0</b>	<b>92.0</b>	<b>3590.0</b>	<b>1706.3</b>
2.0 : 1.0	8.3	4940	1740	352.0	131.0	126.0	94.0	3590.0	1737.5
	8.3	4940	1740	352.0	132.0	126.0	94.0	3590.0	2142.5
	<b>8.3</b>	<b>4940</b>	<b>1740</b>	<b>352.0</b>	<b>131.5</b>	<b>126.0</b>	<b>94.0</b>	<b>3590.0</b>	<b>1940.0</b>
2.5 : 1.0	8.3	4940	1590	352.0	138.0	126.0	98.0	3590.0	1902.5
	8.3	4940	1590	352.0	138.0	126.0	98.0	3590.0	1777.5
	<b>8.3</b>	<b>4940</b>	<b>1590</b>	<b>352.0</b>	<b>138.0</b>	<b>126.0</b>	<b>98.0</b>	<b>3590.0</b>	<b>1840.0</b>
3.0 : 1.0	8.3	4940	1530	352.0	136.0	126.0	100.0	3590.0	1747.5
	8.3	4940	1540	352.0	135.0	126.0	100.0	3590.0	1597.5
	<b>8.3</b>	<b>4940</b>	<b>1535</b>	<b>352.0</b>	<b>135.5</b>	<b>126.0</b>	<b>100.0</b>	<b>3590.0</b>	<b>1672.5</b>

**Table A8 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation in Different Dosages of H<sub>2</sub>O<sub>2</sub> within 20 min at pH 8.4 (Fixed S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Dosage).**

H <sub>2</sub> O <sub>2</sub> : S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Colour Removal (%)	SS Removal (%)	NH <sub>3</sub> -N Removal (%)	COD Removal (%)
0.5 : 1.0	50.0	53.4	11.1	32.0
1.0 : 1.0	57.9	56.5	14.3	37.2
1.5 : 1.0	68.5	61.4	26.9	52.5
2.0 : 1.0	64.8	62.5	25.4	46.0
2.5 : 1.0	67.8	60.8	22.2	48.7
3.0 : 1.0	68.9	61.5	20.6	53.4

**Table A9 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation in Different Dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub> within 20 min at pH 8.4 (Fixed Dosage Ratio of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> : H<sub>2</sub>O<sub>2</sub> = 1.5 : 1.0).**

H <sub>2</sub> O <sub>2</sub> / S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (g/g)	pH	Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
0.61 / 0.41	8.0	5580	1880	343.0	134.0	126.0	80.0	2990.0	1240.0
	8.0	5580	1890	340.0	134.0	128.0	82.0	2990.0	1226.0
	<b>8.0</b>	<b>5580</b>	<b>1885</b>	<b>341.5</b>	<b>134.0</b>	<b>127.0</b>	<b>81.0</b>	<b>2990.0</b>	<b>1233.0</b>
1.22 / 0.82	8.0	5580	1590	343.0	127.0	126.0	94.0	2990.0	1242.0
	8.0	5580	1600	340.0	127.0	128.0	94.0	2990.0	1341.0
	<b>8.0</b>	<b>5580</b>	<b>1595</b>	<b>341.5</b>	<b>127.0</b>	<b>127.0</b>	<b>94.0</b>	<b>2990.0</b>	<b>1291.0</b>
2.45 / 1.63	8.2	5580	1460	343.0	124.0	126.0	94.0	2990.0	1404.0
	8.2	5580	1460	340.0	124.0	128.0	93.0	2990.0	1168.0
	<b>8.2</b>	<b>5580</b>	<b>1460</b>	<b>341.5</b>	<b>124.0</b>	<b>127.0</b>	<b>93.5</b>	<b>2990.0</b>	<b>1286.0</b>
3.67 / 2.45	8.2	5580	1210	343.0	103.0	126.0	90.0	2990.0	1644.0
	8.2	5580	1220	340.0	103.0	128.0	90.0	2990.0	1611.0
	<b>8.2</b>	<b>5580</b>	<b>1215</b>	<b>341.5</b>	<b>103.0</b>	<b>127.0</b>	<b>90.0</b>	<b>2990.0</b>	<b>1627.5</b>
4.89 / 3.26	8.2	5580	1230	343.0	112.0	126.0	94.0	2990.0	1789.0
	8.2	5580	1230	340.0	112.0	128.0	92.0	2990.0	1793.0
	<b>8.2</b>	<b>5580</b>	<b>1230</b>	<b>341.5</b>	<b>112.0</b>	<b>127.0</b>	<b>93.0</b>	<b>2990.0</b>	<b>1791.0</b>
6.12 / 4.08	8.2	5580	1120	343.0	95.0	126.0	90.0	2990.0	1785.0
	8.2	5580	1110	340.0	95.0	128.0	90.0	2990.0	1638.0
	<b>8.2</b>	<b>5580</b>	<b>1115</b>	<b>341.5</b>	<b>95.0</b>	<b>127.0</b>	<b>90.0</b>	<b>2990.0</b>	<b>1711.5</b>

**Table A10 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation in Different Dosages of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub> within 20 min at pH 8.4 (Fixed Dosage Ratio of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub>).**

H <sub>2</sub> O <sub>2</sub> / S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (g/g)	Colour Removal (%)	SS Removal (%)	NH <sub>3</sub> -N Removal (%)	COD Removal (%)
0.61 / 0.41	66.2	60.8	36.2	58.8
1.22 / 0.82	71.4	62.8	25.9	56.8
2.45 / 1.63	73.8	63.7	26.0	56.9
3.67 / 2.45	78.2	69.8	29.1	45.6
4.89 / 3.26	78.0	67.2	26.8	40.1
6.12 / 4.08	80.0	72.2	29.1	42.7

**Table A11 Result for Colour, SS NH<sub>3</sub>-N and COD Removals of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation at pH 11 within 20 min (Fixed Dosage of H<sub>2</sub>O<sub>2</sub> / S<sub>2</sub>O<sub>8</sub><sup>2-</sup> = 2.45 g / 1.63 g).**

pH		Colour (PtCo)		SS (mg/L)		NH <sub>3</sub> -N (mg/L)		COD (mg/L)	
Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
3.0	2.4	5620	1840	348.0	123.0	124.0	98.0	3090.0	1874.0
	2.4	5640	1830	350.0	124.0	124.0	98.0	3090.0	1871.0
	<b>2.4</b>	<b>5630</b>	<b>1835</b>	<b>349.0</b>	<b>123.5</b>	<b>124.0</b>	<b>98.0</b>	<b>3090.0</b>	<b>1872.5</b>
5.0	4.8	5620	1970	348.0	121.0	124.0	104.0	3090.0	1935.0
	4.8	5640	2010	350.0	120.0	124.0	104.0	3090.0	1952.0
	<b>4.8</b>	<b>5630</b>	<b>1990</b>	<b>349.0</b>	<b>120.5</b>	<b>124.0</b>	<b>104.0</b>	<b>3090.0</b>	<b>1943.5</b>
7.0	7.9	5620	1220	348.0	113.0	124.0	94.0	3090.0	1939.0
	7.9	5640	1220	350.0	114.0	124.0	94.0	3090.0	1942.0
	<b>7.9</b>	<b>5630</b>	<b>1220</b>	<b>349.0</b>	<b>113.5</b>	<b>124.0</b>	<b>94.0</b>	<b>3090.0</b>	<b>1940.5</b>
8.4	8.2	5620	1217	348.0	115.0	124.0	90.0	3090.0	1444.0
	8.2	5640	1215	350.0	114.0	124.0	90.0	3090.0	1448.0
	<b>8.2</b>	<b>5630</b>	<b>1216</b>	<b>349.0</b>	<b>114.5</b>	<b>124.0</b>	<b>90.0</b>	<b>3090.0</b>	<b>1446.0</b>
9.0	8.7	5620	1160	348.0	105.0	124.0	80.0	3090.0	1611.0
	8.7	5640	1180	350.0	105.0	124.0	80.0	3090.0	1621.0
	<b>8.7</b>	<b>5630</b>	<b>1170</b>	<b>349.0</b>	<b>105.0</b>	<b>124.0</b>	<b>80.0</b>	<b>3090.0</b>	<b>1616.0</b>
10.0	9.7	5700	910	348.0	71.0	126.0	42.0	3090.0	1949.0
	9.7	5740	890	350.0	71.0	126.0	42.0	3090.0	1950.0
	<b>9.7</b>	<b>5720</b>	<b>900</b>	<b>349.0</b>	<b>71.0</b>	<b>126.0</b>	<b>42.0</b>	<b>3090.0</b>	<b>1950.0</b>
11.0	10.1	5700	680	348.0	44.0	126.0	38.0	3090.0	1986.0
	10.1	5740	690	350.0	45.0	126.0	38.0	3090.0	1982.0
	<b>10.1</b>	<b>5720</b>	<b>685</b>	<b>349.0</b>	<b>44.5</b>	<b>126.0</b>	<b>38.0</b>	<b>3090.0</b>	<b>1984.0</b>

12.0	10.3	5700	550	348.0	22.0	126.0	28.0	3090.0	1968.0
	10.3	5740	560	350.0	23.0	126.0	28.0	3090.0	1969.0
	<b>10.3</b>	<b>5720</b>	<b>555</b>	<b>349.0</b>	<b>22.5</b>	<b>126.0</b>	<b>28.0</b>	<b>3090.0</b>	<b>1968.5</b>

**Table A12 Removal Percentages of Colour, SS, NH<sub>3</sub>-N and COD of BIOTPOME Using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub> Oxidation at pH 11 within 20 min (Fixed Dosage of H<sub>2</sub>O<sub>2</sub> / S<sub>2</sub>O<sub>8</sub><sup>2-</sup> = 2.45 g / 1.63 g).**

<b>pH</b>	<b>Colour Removal (%)</b>	<b>SS Removal (%)</b>	<b>NH<sub>3</sub>-N Removal (%)</b>	<b>COD Removal (%)</b>
3.0	67.4	64.5	21.0	39.4
5.0	64.6	65.3	16.1	37.1
7.0	78.3	67.5	24.2	37.2
8.4	78.4	67.1	27.5	53.2
9.0	79.2	69.9	35.5	47.7
10.0	84.3	79.7	66.7	36.9
11.0	87.8	87.1	75.8	35.8
12.0	90.3	93.6	77.8	36.3

