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Degradation of Palm Oil Mill Effluent by TiO_2/Sonolysis Treatment

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Final Year Project Report ☑
Masters ☐
PhD ☐

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Degradation of palm oil mill effluent by TiO_2/sonolysis treatment

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ABSTRACT

Palm oil mill effluent (POME) is one of the main wastewater sources in Sarawak due to its large cultivation. POME is a colloidal suspension that contains water, oils, grease, total suspended solids and organic matter that contributes to severe environmental problems when disposed to nearby water bodies. The objective of this study was to investigate the efficiency of TiO_2/sonolysis on POME degradation by varying the operating parameters such as catalyst dosage, amplitude, dilution and contact time. The study utilized sonolysis as an alternative method to remove chemical oxygen demand (COD) in POME in the presence of TiO_2. Different dosage of TiO_2 (0.1 g/L, 0.2 g/L and 0.4 g/L) was used to investigate this efficiency towards COD reduction. POME was diluted with distilled water (1:1000 and 1:100) before underwent treatment with different dosage of TiO_2 and sonolysis conditions. The highest COD reduction of 96.1% for 1:1000 and 80% for 1:100 was obtained using 0.4 g/L of TiO_2 and 60% amplitude at 5 minutes of contact time. Thus, the optimum condition of TiO_2/sonolysis treatment was obtained using 0.4 g/L of TiO_2 with 60% amplitude for 1:1000 dilution at 5 minutes of contact time. Thus, this study has shown that TiO_2/sonolysis can be used as a possible tool to reduce COD in POME.

Keywords: Palm oil mill effluent, sonolysis, degradation, titanium dioxide, chemical oxygen demand

ABSTRAK

Efluen kilang kelapa sawit (POME) adalah salah satu sumber air sisa utama di Sarawak kerana penanamannya yang besar. POME adalah koloid yang mengandungi air, minyak, gris, pepejal terampai dan bahan organik yang menyumbang kepada pelbagai masalah kepada alam sekitar apa dilupuskan ke badan air berdekatan. Objektif kajian ini adalah untuk mengkaji kecekapan TiO_2*/sonolisis untuk degradasi POME dengan mengubah parameter operasi seperti dos pemangkin, amplitud, pencairan dan masa. Kajian ini menggunakan sonolysis sebagai kaedah alternatif untuk menghilangkan permintaan oksigen kimia (COD) dalam POME dengan menggunakan* TiO_2*. Dos yang berbeza* TiO_2 *(0.1 g/L, 0.2 g/L dan 0.4 g/L) digunakan untuk menyiasat kecekapan ini terhadap pengurangan COD. POME dicairkan dengan air suling (1:1000 dan 1:100) sebelum menjalani rawatan dengan dos* TiO_2 *yang berbeza dan sonolysis. Pengurangan COD tertinggi 96.1% untuk 1:1000 dan 80% untuk 1:100 diperoleh menggunakan 0.4 g/L* TiO_2 *dan amplitud 60% pada masa 5 minit. Oleh itu, keadaan optimum rawatan* TiO_2*/sonolysis menggunakan 0.4 g/L* TiO_2 *dengan amplitud 60% untuk pencairan 1:1000 pada masa 5 minit. Oleh itu, kajian ini menunjukkan bahawa* TiO_2*/sonolisis boleh digunakan sebagai alat yang untuk mengurangkan COD dalam POME.*

***Kata kunci**: Sisa kilang minyak sawit, sonolisis, degradasi, titanium dioksida, permintaan oksigen kimia*

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°C	Degree Celcius
POME	Palm Oil Mill Effluent
CPO	Crude Palm Oil
MPOB	Malaysian Palm Oil Board
COD	Chemical Oxygen Demands
BOD	Biological Oxygen Demands
C/N	Carbon to Nitrogen Ratio
DO	Dissolved Oxygen
L	Litre
mg/L	Milligram
EFB	Empty Fruit Bunch
FFB	Fresh Fruit Bunch
t	Tonnes
DoE	Department of Environment
AOP	Advanced Oxidation Processes
TSS	Total Suspended Solid
TiO_2	Titanium dioxide

1.0 INTRODUCTION

Ultrasound is an alternative environmental friendly technology that plays an important role in chemical and physical activities in the process manufacturing industry as a non-polluting and effective activation method. Ultrasound has effects on rate of various processes effectively such as cleaning, homogenization, emulsification, extraction, diffusion, and chemical reactions (Mäntysalo et al., 1987; Sivakumar and Rao, 2001; Sivakumar and Rao, 2003). Recently, substantial amount of interest has emerged in the ultrasound application for the hazardous contaminants treatment in water. Destruction in aqueous phase usually happens due to the collapsing of cavitation bubbles that includes numerous reaction pathways and zones for instance pyrolysis inside the bubble and/or the bubble-liquid interface and hydroxyl radical-mediated reactions at the bubble-liquid interface and/or in bulk of liquid (Adewuyi, 2001). The effectiveness of the process has been reported to remove numerous target compounds such as phenol, polychlorinated biphenyls chloroaromatics, chlorophenols, nitrophenols, pesticides, polycyclic aromatic hydrocarbons, dyes, CFCs and surfactants from relatively dilute solutions (Adewuyi, 2001).

As one of the leading industries in Malaysia, the palm oil industry has produced 18.79 million tonnes of crude palm oil (CPO) which are from oil palm plated area of 5.08 million hectares in 2012 (MPOB, 2013). It has been estimated that production from the industry has caused a great amount of palm oil mill effluent (POME) at nearly three times the CPO quantity. POME is an extremely polluting wastewater due to high chemical oxygen demand (COD) and biological oxygen demand (BOD) levels if discharged directly towards the river (Nurul et al., 2013). According to Verla et al. (2014), a colloidal suspension that contains 95 – 96% of water, 0.6 – 0.7% of oil and grease and 4 – 5% of total solids can be found in POME. It is a thick, brown liquid with a discharge temperature of 80°C and 90°C where an enormous amount of water is needed to extract the crude oil. To process one tonne of fresh fruit bunch, it can take up to about 1.5 cubic meters of water. About 50% of the water results in POME whereas another 50% are lost as steam through the sterilizer exhaust, piping leakages as well as wash waters (Awotoye et al., 2011).

During the extraction of crude palm oil from fresh fruit bunches more than 50% of the water will be cleared to the environment as (POME), whereas some are lost as the steam in the boilers blow down, wash water and leakage (Ahmad et al., 2003). A tremendously great degradable organic matter content can be found in the raw partially treated POME, which is because of the existence of unrecovered palm oil part (Ahmad et al., 2003). According to Okwute and Isu (2007), high amounts of fatty acids, carbohydrates, proteins and other plant materials found in untreated POME, could potentially alter the parameters of environment such as BOD, C/N ratio, DO and COD level. Highly polluting POME causes oxygen depletion, use of land and other associated effects (Sridhar & AdeOluwa, 2011). In Malaysia, POME is being treated with anaerobic digestion which includes aerobic post treatment where palm oil mills used ponding system (Poh & Chong, 2009; Chaiprapat & Laklam, 2011; Zinatizadeh et al., 2007).

Previous studies showed applications on the usage of sonolysis on water treatment. Mason et al. (2003) state that there are possible usage of sonolysis in the decontamination of water under as well as with other treatments. Sonolysis also has been used as pretreatment for POME for the investigation on its biohydrogen production, bioelectricity generation and underlying microbial communities (Leaño et al., 2012). Sonolysis has been also applied as a pretreatment for anaerobic digestion of solid organic waste to improve its biodegradability sources on increasing the biogas manufacture and energy recovery (Cesaro & Berlgiorno, 2012). Treatments using sonolysis are used to degrade chemicals which can be found in effluents of agricultural origin.

1.1 Problem Statement

Anaerobic digestion which has been commonly applied in most palm oil mills in Malaysia possess several disadvantages such as longer recovery time as the system takes a long time to return to operating conditions to normal and removal of pathogens and nutrients are low and bad odour may occur. Open pond system also is another POME treatment method employed in most palm oil mills and this system requires large land application and has long retention time. Thus, an alternative method, TiO_2/sonolysis treatment is investigated as a possible mean for degradation of organic matter in POME. Sonolysis is a simple application and produces no toxic by-products making the system effective for wastewater treatment. In this study, TiO_2/sonolysis treatment is applied as possible tool due to its ability in degrading organic matter, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in POME.

1.2 Objectives

The objectives of this study are to:

i. characterize commercial TiO_2 for their surface morphology and functional groups
ii. investigate the efficiency of TiO_2/sonolysis on POME degradation by varying the operating parameters such as catalyst dosage, amplitude, dilution and contact time.

2.0 LITERATURE REVIEW

2.1 Palm Oil Mill Effluent

The world's most organised national agricultural division is the Malaysian palm oil industry (Oswal et al., 2002; Yacob et al., 2006). POME is a wastewater produced during palm oil processing that is acidic, viscous and non-toxic in nature (Wu et al., 2009). POME contains high concentration of chemical oxygen demand (COD) (65000 mg/L) and biochemical oxygen demand (BOD) (25000 mg/L) which made it prone to environmental pollution if this wastewater is left untreated (Lam and Lee, 2011). In the year 2008, 17.73 million tonnes of palm oil production resulted in about 44.33 million tonnes of POME.

According to Seyed and Mazlan (2014), palm oil mills produced palm oil EFB, a solid waste residue. In order to loosen the fruits from bunches and deactivate pericarp enzymes, the harvested fresh fruit bunches (FFB) are pasteurised in a horizontal steam sterilizer. To remove the sterilized fruit from bunches, the rotary drum thresher is used. Feedstock for oil production received sterilized fruits in palm oil extraction process and the EFB are transported to the warehouse. Several cyclones are employed to isolate fibres and nuts in palm oil production chain from the effluent produced by screw type press, subsequently kernels and shells are generated from nuts. According to Mahlia (2001), the previous is applied in kernel oil mills and the latter is solid waste. 100 t of FFB can generate 5 t of shell, 20-22 t EFB and around 14 t oil-rich fiber as stated by Perez (1997).

POME is treated with anaerobic digestion that includes aerobic post treatment where most palm oil mills use ponding system due to simpler operational control and cheaper equipment cost (Poh and Chong, 2009; Chaiprapat and Laklam, 2011; Zinatizadeh et al., 2007). The disadvantages of this biological treatment are long hydraulic retention time, investment in land for ponds and digesters for anaerobic treatment are expensive as well as production of methane gas which is known to be a greenhouse effect for the environment (Bhatia et al., 2007). Ahmad (2009) stated that many mills are unable to achieve the discharge limits as outlined by Department of Environment of Malaysia even after aerobic ponding treatment.

2.2 Sonolysis

Due to the chemical and physical effects of development in numerous progresses, ultrasound has significantly attained considerations. Park and Taylor (1956) have reported hydroxyl radical development in aqueous solution as the first evidence of this experiment. Hydrogen and hydroxyl radicals formation from the sonication of water are shown via spin trapping techniques (Makino et al., 1982). The "hot spot" theory was introduced to describe the phenomena of thermal and radical that are based on the ultrasound. According to Thompson and Doraiswamy (1999), the application of ultrasound on the organic contaminants elimination from water has increased significantly. Ultrasound is capable to create radical species mainly hydroxyl radicals, ●OH. Compared to other advanced oxidation process (AOP)s, ultrasound has unique benefits as it can be handle effortlessly, does not require addition of reagents to the pollutants nature (Xiao et al., 2017). High frequency sound (ultrasound) will be produced at sufficiently high alternating potential. It is possible to generate chemical changes as a result of acoustically generated cavitation when more a powerful ultrasound at a lower frequency is applied to a system. Frequencies about 18 kHz are usually considered to be ultrasonic. For ultrasonic cleaning, the frequency used range from 20 kHz to over 100 kHz and most commonly used for industrial cleaning are between 20 and 50 kHz. Moreover, ultrasound has wavelength between successive compression waves measuring roughly 10 to 10^{-3} cm (Mahvi, 2009). The compression and expansion cycled of ultrasound is shown in Figure 2.1:

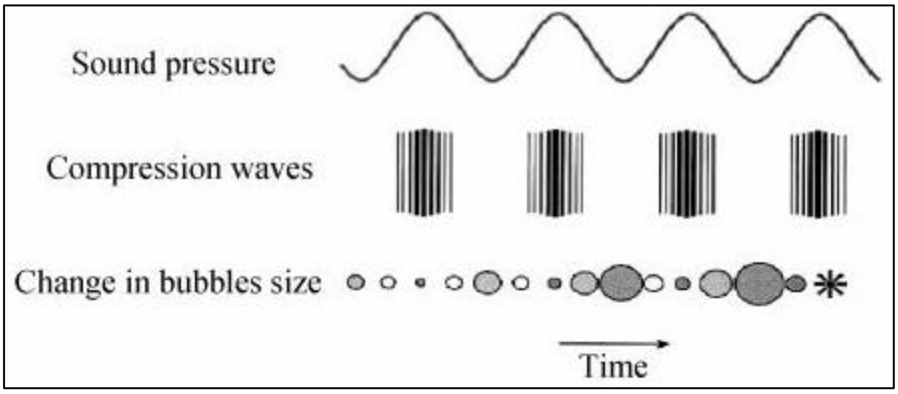

Figure 2.1: Compression and expansion cycle of ultrasound (Gong and Hart, 1998).

2.2.1 Mechanism of Sonolysis

Acoustic version cavitation such as the formation, growth and implosive bubbles collapse is used when high – intensity ultrasound waves interrelate with dissolved gases in the liquid medium (Suslick & Fang, 1999). Compression and expansion cycles are components of ultrasound waves. Waves have adequate concentration to surpass molecular forces of liquid in generating bubbles during the expansion. Alternating compression and expansion ultrasound cycles continually absorb by these bubbles. Hence, the bubbles grow via the vapour diffusion or gas from liquid medium till they achieve a critical size and thus, collapse. Cavitation bubble compression in aqueous solutions that leads to chemical reactions is shown in Figure 2.2:

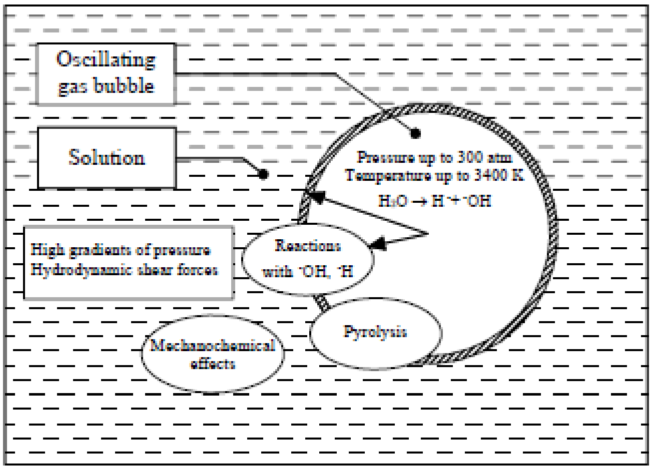

Figure 2.2: Cavitation bubble compression in aqueous solutions that leads to chemical reactions (Rokita et al., 2014).

The bubble collapse are localized “hotspot” with a temperature of ~5000K, pressure of ~1000 atm, and short-life. Thus, chemical processes or bond cleavage occur such as water molecules and gases are broken (Torres-Palma & Serna-Galvis, 2018).

Water is broken into hydrogen atom and hydroxyl radical (Eq. 1).

$$H_2O +))) \rightarrow H^\bullet + {}^\bullet OH \qquad (1)$$

Oxygen and nitrogen create atomic species (Eqs. 2 and 3), and volatile organic substances in the system are pyrolyzed.

$$O_2 +))) \rightarrow 2O^\bullet \qquad (2)$$

$$N_2 +))) \rightarrow 2N^\bullet \qquad (3)$$

Furthermore, some radicals reaction occur (Eqs 4-11). (Adewuyi, 2011).

$$H^\bullet + O_2 \rightarrow HOO^\bullet \qquad (4)$$

$$O^\bullet + H_2O \rightarrow 2{}^\bullet OH \qquad (5)$$

$$H^\bullet + H^\bullet \rightarrow H_2 \qquad (6)$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \qquad (7)$$

$$N^\bullet + {}^\bullet OH \rightarrow NO + H^\bullet \qquad (8)$$

$$NO + {}^\bullet OH \rightarrow HNO_2 \qquad (9)$$

$$2HOO^\bullet \rightarrow H_2O_2 + O_2 \qquad (10)$$

$$H^\bullet + HOO^\bullet \rightarrow H_2O_2 \qquad (11)$$

The three zones systems that has been restructured in the process of sonochemical are solution bulk, cavitation bubble interface and inner of bubble (Gogate, 2008). The hydrophilic substances are located in bulk solution, whereas the hydrophobic non-volatile compounds can be found in the interfacial zone and the volatile substances are stored in the cavitation bubble (Gogate, 2008). Hence, a pollutant’s nature defines the direction of degradation in the process of sonochemical. The hydrophilic compounds are removed by promoting from hydroxyl radicals that influence the bulk of solution after the collapse of the bubbles. In the interfacial zone, the hydrophobic non-volatile compounds are removed by radical attacks or/and reactions of thermal. Petrier and Francony (1997) has stated that the pollutants inside the bubbles are pyrolyzed.

When ultrasound is irradiated, the formation of many microbubbles arises in the first stage. Then, the bubble violently collapses during the irradiation and localised hot spots of super critical conditions are produced when high pressure and temperature are involved. Generally, there are three different regions of bubbles where degradation may occur. The first region which is the bubble’s inner region has higher pressure and temperature; the interface in the second region is between the bulk liquid and bubble, whereas the bulk solution will be in the final region. Generally, free radical attack and pyrolysis are responsible in the first two regions while the predominant reaction is where the hydroxyl radical attack at the bulk liquid (Gogate, 2002).

2.3 Factors Affecting Sonolysis

There are few factors that affects sonolysis such as catalysts concentration, amplitude, concentration of dilution and contact time.

2.3.1 Effect of Catalyst Dosage

The cost of water treatment process is affected by the optimum amount of catalyst dosage. The degradation rate increases with the increasing amount of TiO_2 catalyst until a certain optimum dosage is reached (Tang et al., 2012). The increase in sonocatalyst intensifies the nucleation sites for formation of cavity to take place. Moreover, the sonocatalyst acts as a catalyst to promote the dissociation of water reaction to generate ·OH radicals (Tang et al., 2012). Other studies showed a further increase in catalyst dosage after the optimum point will lead to mutual screening effects that will slow down the rate of degradation to prevent the pollutant molevules from receiving energy from the ultrasound wave (Wang, et al., 2007).

2.3.2 Effect of Amplitude

The degradation rate increases amplitude of ultrasound energy in the effluents. Hydroxyl radicals' generation on the surface of the catalyst can be enhanced when the amount of ultrasound energy increased. The catalytic performance increases as ultrasound has the capacity to clean the surface of the catalyst from aggregated particles (Yetim & Tekin, 2016). Sivakumar et al. (2002) stated that the organic compounds are degraded when energy concentration decreased as the generated bubble cavities collapsed violently. Hence, the greater the size of the bubble, the higher the organic compounds of rate of degradation. When the number of bubble cavities per unit liquid volume is higher, the formation of bubble cloud arises and the sound waves transmitted between the vessel walls and transducer tip are disturbed where there could be a possibility of larger bubble formation. Due to the interference, less concentration of cavitation energy disperses into the system to encourage the POME degradation. Hence, the resultant energy is predicted to disperse lower when 50% amplitude power is used than 80% (Parthasarathy et al., 2016).

2.3.3 Effect of Dilution

The concentration of pollutants varies depending on the water source. The increasing initial concentration of dilution decreases the degradation rate for volatile substance (Goel et al., 2004). Meanwhile, the removal of hydrophilic and hydrophobic nonvolatile compounds is increased at higher initial concentrations in the aqueous media (Villegas-Guzman et al., 2015). The cavitation bubble influenced the decreasing rate of degradation at higher initial concentrations of volatile compounds. More molecules have opportunity to diffuse into cavitation bubble as concentration of the volatile substances increases. The temperature and pressure in the cavitation bubbles increase and strengthens the cavitation collapse that results in higher efficiency of degradation (Jiang et al., 2002). On the contrary, when concentration of non-volatile pollutants is lower, less molecules are close to the cavitation bubble interface and the reactions with radicals and thermal processes are less favoured, thus, decreasing the rate of degradation of these compounds (Serna- Galvis et al., 2015).

2.3.4 Effect of Contact Time

The rate of degradation increases as the times increase as well. Studies have shown that 50% amplitude and 90 minutes of cavitation time were able to degrade the chemical oxygen demand (COD) and total suspended solid (TSS) on wastewaters (Parthasarathy et al., 2016). Degradation on secondary effluent organics in POME showed better degradation with high frequency compared to lower frequency. Formation of H_2O_2 at 130 kHz frequency was about

2.5 times higher than at the frequency of 35 kHz. The effect of frequency shows efficiency in removing suspended COD at 35 kHz due to finer bubbles formation and therefore more intensive collapse of theses bubbles at lower frequencies (Nasseri et al., 2006).

2.4 Application of Sonolysis on POME and other wastewaters

Currently, there have been a number of studies that have applied ultrasound for dyes and pesticides treatments (Tiehm & Neis, 2005) and biological pollutants removal (Mason, 2003). According to Lifka et al. (2003), in technical scales, water irradiation with ultrasonic waves appears to be practicable without the addition of oxidizing chemicals. By activating the catalytic surfaces, the ultrasound can improve the catalytic oxidation process. Synergetic effects can be used for water purification in combination with other AOPs (Lifka et al., 2003).

The usage of sonolysis has been used to improve bioavailability for bioelectricity and hydrogen production for POME pre-treatment (Leaño et al., 2012). The increased of substrate surface area are related to the advanced bioavailability as a result of cavitation and acoustic streaming that are cause from the ultrasound propagation in a aqueous milieu. Leaño et al. (2012) stated that bioH_2 possibility and the generation of bioelectricity via the utilization of ultrasonicated POME and substrate. Previous study have suggested that the increasing doses of ultrasound demonstrated positive effect on the rate of hydrogen production and the efficiency of COD removal (Leaño et al., 2012). With an exposure to ultrasound and a slight polluted systems can be used to kill the algae and as a slight polluted system provides a decrease to transmission of sound, there is likelihood to use high frequency ultrasound (emission of power and consumption low) (Leaño et al., 2012). The algal population of 8.55, 35.22, 67.22, 90.67 and 100% were destroyed by 30, 60, 90, 120 and 150 seconds of sonication. The results determined that increasing sonication time has considerable effect on algal removal.

Phenol is one of the most abundant pollutants in industrial wastewater (Alnaizy & Akgerman, 2000). Treatments using sonolysis are used to degrade *p*-coumaric acid and *p*-hydroxylbenzaldehyde which are found in effluents of agricultural origin. It showed that low frequency is capable to degrade *p*-coumaric acid and *p*-hydroxylbenzaldehyde in dilute synthetic solution. This showed that ultrasonic treatment could be possibly used with biological post-treatment to treat refractory wastes.

Other studies showed a photocatalytic process, anatase TiO_2 powder improved degradation results. Wang et al. (2017) stated that Methyl Orange degraded by 96.5% when transitional TiO_2 is used with 3.6% anatase phase. Chitosan degradation using ultrasound irradiation and its combination with heterogeneous TiO_2 was also investigated. The sonolytic degradation increased with increasing ultrasound power and TiO_2 sono-photocatalysis degraded chitosan completely (Taghizadeh and Abdollahi, 2010).

3.0 METHODOLOGY

3.1 POME Sampling

5 L of POME sample was collected from the cooling pond at Felcra Berhad Wilayah Sarawak in Kota Samarahan. The POME sample was collected and stored into polyethylene bottles. The air-tight bottles was transported to the laboratory and kept refrigerated at 4°C until further analysis.

3.2 Characterization of POME

Diluted pre-treated POME was used for water quality analysis. The levels of biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and dissolved oxygen (DO) and pH were determined. All analyses were performed according to the Standard Methods of Water and Wastewater Treatment (APHA, 1999).

3.2.1 Chemical Oxygen Demand (COD) Analysis

The COD concentration of the treated sample was analysed using DR 5000 spectrophotometer as described by APHA (2005). The treated sample was pipetted 2.5 mL into vial with 3.5 mL of concentrated $Ag_2SO_4.H_2SO_4$ acid solution and 1.5 mL of potassium dichromate, $K_2Cr_2O_7$ digestion solution. The solution was heated at 150°C in reactor box for 2 hours. The procedures were repeated by replacing the solution with blank sample with purified water. The samples were cooled down at room temperature before being transferred and titrated with $Fe(NH_2)_2(SO_4).6H_2O$, 0.0125 N FAS solution. Ferroin indicator was used to indicate the colour change to reddish brown. The COD in the sample was calculated according to Eq. 3.1:

$$COD\ (mgL^{-1}) = \frac{(Average\ blank - average\ sample)\ x\ normality\ x\ 8000}{Volume\ of\ sample\ (mL)} \tag{3.1}$$

3.2.2 Biochemical Oxygen Demand (BOD)

POME sample was pipetted into BOD bottle containing aerated dilution water and the dissolve oxygen (DO) content is determined and recorded by using DO meter. The bottle was incubated for five days. At the end of five days, the final DO content is determined. The difference between initial DO reading and the final DO reading was calculated. The sample was diffused to correct due to DO decrease as this will represent the BOD's sample. The BOD value was calculated according to Eq. 3.2:

$$BOD = \frac{mg}{L} = \frac{(D_1 - D_2)}{P} \tag{3.2}$$

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L,

D_2 = DO of diluted sample after 5 d incubation at 20°C, mg/L,

P = fraction of w/w sample to total combined volume

3.2.3 Total Suspended Solid (TSS) Analysis

To determine the amount of TSS in sample, a set of Buchner flask was used. Filter paper was weighted and recorded. Using the pump through Buchner flask, 500 mL of sample was used to suck. The suction was continued until the sample solution was filtered completely. The filter paper was cooled in a room temperature. Then it was weighted again and recorded. TSS in the sample was calculated according to Eq. 3.3:

$$mg\ total \frac{solids}{L} = \frac{(A-B)\ X\ 1000}{sample\ volume, mL} \tag{3.3}$$

Where:

A = weight of dried residue + dish, mg

B = weight of dish, mg

3.2.4 pH Analysis

The pH value for POME was determined using a pH meter (model H19024 series). To get an accurate reading, the pH meter was calibrated using buffer solutions of pH 4, 7 and 8.

3.3 TiO_2/sonolysis treatment of POME

All TiO_2/sonolysis treatments were conducted using sonic dismembrator ultrasonic processor (FisherBrand Model 505). A beaker containing 250 mL POME dilution of 1:100 and 1:1000 were added with 0.1 g, 0.2 g and 0.4 g of TiO_2 in beaker. The samples were treated with 30% and 60% (32.36 W and 55.03 W) amplitude of ultrasound energy and the pH values were determined during each contact time (t_0, t_5, t_{10} and t_{20}). All the samples were analyzed for COD content. The percentage of COD reduction was calculated according to Eq. 3.4:

$$\%\ of\ COD\ reduction = \left(1 - \frac{C_A}{C_o}\right) X100 \tag{3.4}$$

C_O is the initial value of COD and C_A is the COD value at time, t.