Post-treatment of palm oil mill effluent (POME) using combined persulphate with hydrogen peroxide ($S_2O_8^{2-}$/H_2O_2) oxidation

Chia Ken Lin, Mohammed J. K. Bashir, Salem S. Abu Amr and Lan Ching Sim

ABSTRACT

The aim of the current study is to evaluate the effectiveness of combined persulphate with hydrogen peroxide ($S_2O_8^{2-}$/H_2O_2) oxidation as a post-treatment of biologically treated palm oil mill effluent (POME) for the first time in the literature. The removal efficiencies of chemical oxygen demand (COD), ammoniacal nitrogen (NH_3-N), and suspended solids (SS) were 36.8%, 47.6%, and 90.6%, respectively, by $S_2O_8^{2-}$ oxidation alone under certain operation conditions (i.e., $S_2O_8^{2-}$ = 0.82 g, pH 11, and contact time 20 min). Nevertheless, the combined process ($S_2O_8^{2-}$/H_2O_2) achieved 75.8% and 87.1% removals of NH_3-N and SS, respectively, under 2.45/1.63 g/g H_2O_2/$S_2O_8^{2-}$, pH 11, and 20 min oxidation. Moreover, 56.9% of COD was removed at pH 8.4.

Key words | hydrogen peroxide, industrial wastewater, persulphate oxidation, POME, post-treatment

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INTRODUCTION

Oil palm plantations have been well developed in Malaysia since the 1870s. Malaysia so far has the second largest palm oil production globally (Green Palm 2015). In 2014, Malaysia generated around 20 million tonnes of crude palm oil, while for Indonesia around 30 million tonnes of crude palm oil was produced (SGS 2015). The oil palm species planted in Malaysia is called *Elaeis guineensis* Jacq. or African oil palm; each hectare of oil palm results in 10–35 tonnes of fresh fruit annually, and the economic life of an oil palm tree is around 20–25 years (Singh *et al.* 2010). During palm oil processing, biomass wastes such as palm press fibres, palm kernel shells, empty fruit bunches, and palm oil mill effluent (POME) are generated (Hassan *et al.* 2013). POME is the largest portion of waste generated from the palm oil industry: 28% by weight in relation to fresh fruit bunches (FFB) (Abdullah & Sulaiman 2013). POME is an intractable wastewater which is thick brown in appearance and has an unpleasant odour from palm oil extraction. POME discharge is normally as hot as 80–90 °C an consists of water, oil and fine suspended solids (SS) (Liew *et al.* 2015). It is a form of colloidal suspension which is mainly yielded from hydrocyclone wastewater (4%), sterilizer

wastewater (36%) and clarification wastewater (60%), accordingly (DOE 1999; Wu *et al.* 2010; Liew *et al.* 2015). POME is a non-toxic wastewater (Rupani *et al.* 2010) but it comprises nutrients such as nitrogen and phosphorous as well as other insignificant mineral constituents (Mohammed & Chong 2014) which can cause environmental problems and endanger aquatic life. Thus, around 85% of effluent treatment facilities in the oil palm industry have installed the ponding system (Ahmad & Krimly 2014). A series arrangement of anaerobic, facultative and aerobic open ponding is one of the conventional biological treatment systems for POME in Malaysia (Aris *et al.* 2008). However, the biologically treated POME (BIOTPOME) requires a post-treatment due to insufficient removal of colour and chemical oxygen demand (COD) prior to discharge into watercourses (Fadzil *et al.* 2013; Bashir *et al.* 2016). Successive amounts of organic and nutrient contents in term of COD will introduce eutrophication problems and further increase the amount of oxygen depleted in water (Fadzil *et al.* 2013). Advanced oxidation processes have recently been used to treat recalcitrant pollutant contained in water and soil. It involves the generation of highly reactive radicals and degradation of contaminants by

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the oxidants. Persulphate ($S_2O_8^{2-}$) oxidation is an advanced chemical oxidation which utilizes $S_2O_8^{2-}$ anions as an oxidant. The oxidation-reduction potential for $S_2O_8^{2-}$ oxidation is shown as Equation (1) (Block *et al.* 2004).

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad (1)$$

$S_2O_8^{2-}$ can also produce highly reactive sulphate radical ($SO_4^{\bullet-}$) with 2.6 V redox potential through $S_2O_8^{2-}$ activation (Deng *et al.* 2014). $S_2O_8^{2-}$ can be activated by different agents such as heat, UV light and metal. Hydrogen peroxide (H_2O_2) is an oxidant which potentially functions as activator of $S_2O_8^{2-}$. In this dual oxidant system, the reactivity of peroxide in reduction of targeted organic substances collaborates with the improved stability of persulphate (Block *et al.* 2004). In the mechanism of $S_2O_8^{2-}$ activation, $SO_4^{\bullet-}$ and hydroxyl radical ($OH^{\bullet}$) are released and consumed through the initiation, propagation and termination reactions as shown in Equations (2)–(5) (Cronk 2008). The end product of oxidation, sulphate ion (SO_4^{2-}), is an inert salt and not harmful to the environment as it is not considered as a pollutant (Ahmadi *et al.* in press). However, the residual of sulphate ions can be removed following further aerobic and anaerobic treatment processes. Thabet *et al.* (2009) removed 91% of sulphate from leachate using anaerobic treatment reactor processes.

NH_3-N would be oxidized into nitrogen compounds as shown in Equations (6) and (7) under presence of silver ions (Ali 2005).

Initiation:

$$Na_2S_2O_8 + Activator \rightarrow 2SO_4^{\bullet-} + 2Na^+ \qquad (2)$$

Propagation:

$$SO_4^{\bullet-} + H_2O \rightarrow OH^{\bullet} + HSO_4^- \qquad (3)$$

Termination I:

$$SO_4^{\bullet-} + RH \rightarrow R^{\bullet} + HSO_4^- \qquad (4)$$

Termination II:

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \qquad (5)$$

where RH and $R^{\bullet}$ represent an organic matter and oxidized organic matter.

$$3S_2O_8^{2-} + 2NH_3 \rightarrow N_2 + 6SO_4^- + H^+ \qquad (6)$$

$$4S_2O_8^{2-} + NH_4^+ + 3H_2O \rightarrow NO_3^- + 8SO_4^- + 10H^+ \qquad (7)$$

In this study, $S_2O_8^{2-}$ oxidation alone and H_2O_2 activated persulphate ($S_2O_8^{2-}$/H_2O_2) oxidation were investigated for the removals of COD, NH_3-N and SS from BIOTPOME for the first time. The pH, contact time and dosage of $S_2O_8^{2-}$ and H_2O_2 were the operational parameters used to achieve better removal efficiency of BIOTPOME.

MATERIALS AND METHODS

BIOTPOME sampling and sample characterization

The BIOTPOME sample was collected from Tian Siang Oil Mill (Air Kuning) Sdn. Bhd., Perak, Malaysia. The mill has been in commission since 2000 and the daily capacity of processing FFB has increased to 120 tons/hr. The samples were collected using 5.5 L clean and empty polypropylene containers and transported instantly to the environmental laboratory. The samples were preserved at 4 °C in order to minimize the possibility of biodegradation of sample and chemical reaction occurrence (APHA 2005). The initial characteristics of BIOTPOME were analysed and are presented in Table 1.

Experimental setup of $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation system

Sample preserved under 4 °C was warmed to ambient temperature (27 °C) before starting the experiment. A 250 mL conical flask filled with 100 mL of sample was prepared

Table 1 | Characteristics of BIOTPOME sample

Parameters	Unit	Range	Average
BOD_5	mg/L	110–191	151
COD	mg/L	2,990–3,590	3,290
Total dissolved solids	mg/L	5,880–5,980	5,930
SS	mg/L	340–361	351
NH_3-N	mg/L	116–130	123
Turbidity	NTU	640–689	665
Colour	PtCo	5,410–6,250	5,830
pH	–	8.0–8.7	8.4
Temperature	°C	25	25
Conductivity	mS/cm	11.75–11.96	11.86

for each experiment. The sample was placed on an orbital shaker (NB-101M) at shaking speed of 200 rpm under ambient temperature. The crystallized form of sodium persulphate ($Na_2S_2O_8$, ≥98%, Sigma-Aldrich) was utilized for $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation. A 30% H_2O_2 solution was employed after adding $S_2O_8^{2-}$ into sample in $S_2O_8^{2-}$/H_2O_2 oxidation. For $S_2O_8^{2-}$ oxidation, operational conditions involved were $S_2O_8^{2-}$ dosage, pH and contact time. For $S_2O_8^{2-}$/H_2O_2 oxidation, the operational conditions were dosage ratios of H_2O_2:$S_2O_8^{2-}$, dosage concentration of H_2O_2:$S_2O_8^{2-}$ and pH.

$S_2O_8^{2-}$ dosage was pre-determined in term of $S_2O_8^{2-}$: COD_0 ratio (g/g). The $S_2O_8^{2-}$:COD_0 ratio was set to 4:1 and 1.32 g $S_2O_8^{2-}$ was required for 100 mL sample per 0.329 g initial COD (COD_0). The desired actual amount of powdered $S_2O_8^{2-}$ ($Na_2S_2O_8$) was 1.67 g with considering its purity by using Equation (8).

$$Na^{2+} + S_2O_8^{2-} \rightarrow Na_2S_2O_8 \tag{8}$$

In $S_2O_8^{2-}$/H_2O_2 oxidation, the optimum dosage of $S_2O_8^{2-}$ found from $S_2O_8^{2-}$ oxidation, 0.82 g, was applied constantly to find out the optimum ratio of H_2O_2:$S_2O_8^{2-}$ among 0.5:1.0–3.0:1.0. Based on the ratios, dosages of H_2O_2 used ranged between 0.41 g and 2.45 g. For the experiment of varying dosages, the optimum dosage ratio of 1.5:1.0 was fixed for varying dosages of H_2O_2 and $S_2O_8^{2-}$, and the dosages were adjusted in terms of H_2O_2/$S_2O_8^{2-}$ (0.61 g/0.41 g to 6.12 g/4.08 g).

For pH adjustment 5 M sodium hydroxide and 5 M hydrochloric acid were used. Different pH values (3–12) were examined in both $S_2O_8^{2-}$ (60 min; 200 rpm) and $S_2O_8^{2-}$/H_2O_2 oxidations (20 min; 200 rpm). For $S_2O_8^{2-}$/ H_2O_2 oxidation, 2.45 g/1.63 g of H_2O_2/$S_2O_8^{2-}$ dosage obtained as optimum from the previous oxidation was fixed for the pH variation of $S_2O_8^{2-}$/H_2O_2 oxidation. The filtered samples were analysed after each run of experiment. All experiments were carried out in duplicate. Effectiveness of $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation of BIOTPOME were studied in term of removal efficiencies of pH, COD, NH_3-N, colour and SS.

Analytical method

COD, NH_3-N, colour, SS and pH parameters were analysed before and after the oxidation treatment using *Standard Methods for the Examination of Water and Wastewater* (APHA 2005) and *Hach Water Analysis Book* (Hach 2005).

NH_3-N concentration was determined by the Nessler method. Colour was examined by the spectrophotometric method – single wavelength method. The pH was measured using a digital pH meter. COD measurement of samples was carried out using the dichromate reactor digestion method (Hach Method 8000) while SS was tested by photometric method. Removal efficiencies of COD, NH_3-N, colour and SS were calculated as Equation (9):

$$Removal\ percentage(\%) = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \tag{9}$$

where C_i and C_f represent the initial and final COD, NH_3-N or SS concentrations.

RESULTS AND DISCUSSION

BIOTPOME treatment: $S_2O_8^{2-}$ oxidation

In $S_2O_8^{2-}$ oxidation, the operational conditions of pH, contact time and $S_2O_8^{2-}$ dosage were investigated in removing the contaminants of BIOTPOME such as COD, NH_3-N, colour and SS. All oxidation processes were carried out at shaking speed 200 rpm under ambient temperature.

Effect of pH adjustment

Different initial pHs (3, 5, 7, 9, 10, 11 and 12) were adjusted accordingly while $S_2O_8^{2-}$ concentration was fixed at 1.32 g ($S_2O_8^{2-}$:COD_0 = 4.0:1.0) before initiating the oxidation. Figure 1 shows the removal efficiencies of COD, NH_3-N, colour and SS in BIOTPOME under pH influence. 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, and 87.8% SS. In terms of COD and colour, the
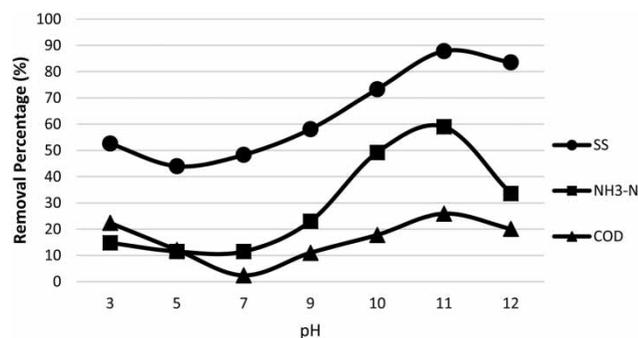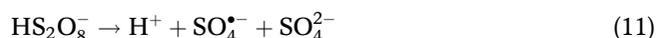

Figure 1 │ Effect of Initial pH on removals of SS, NH_3-N and COD by $S_2O_8^{2-}$ oxidation (1 h contact time; $S_2O_8^{2-}$:COD_0 = 4.0:1.0; shaking speed, 200 rpm).

removal percentages were decreased from pH 3 to pH 7 and rose again after pH 7 until pH 11; however, removal percentages of parameters at pH 12 were lowered compared to pH 11. For the parameters NH_3-N and SS, the removals dropped slightly from pH 3 and started rising after pH 5, and the removal efficiencies at pH 12 eventually were also reduced compared to pH 11. It seems that alkali and acidic condition led to high removals on the parameters but lower removal efficiencies under neutral pH.

In $S_2O_8^{2-}$ oxidation, releasing of free radicals through breakdown of persulphate (acid-catalysation) in acidic condition are shown in Equations (10) and (11) (Epold & Dulova 2015). Proton acts as catalyst to react with $S_2O_8^{2-}$ anions and leads to the generation of sulphate radical ($SO_4^{\bullet-}$). Under alkali condition, hydroxide (OH^-) ions could be decomposed when $S_2O_8^{2-}$ is activated under alkaline condition in order to generate $OH^\bullet$ as Equation (12), resulting in a slight decrease in pH. This shows pH has significant influence on $S_2O_8^{2-}$ oxidation. Another possible mechanism of formation of $OH^\bullet$ according to Liang *et al.* (2007) is shown in Equation (13) but this reaction has a smaller reaction rate constant of $< 60\ M^{-1}\,s^{-1}$ compared to Equation (12), $7 \times 10^7\ M^{-1}\,s^{-1}$. Among the radical formations, $SO_4^{\bullet-}$ is the predominant radical at acidic pH while $OH^\bullet$ is the main radical at alkali pH (Zhao *et al.* 2013).

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{10}$$

$$HS_2O_8^- \rightarrow H^+ + SO_4^{\bullet-} + SO_4^{2-} \tag{11}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^\bullet \tag{12}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^\bullet + H^+ \tag{13}$$

Effect of contact time

The concentration removals of COD, NH_3-N, SS and colour were studied in different contact times (5, 10, 20, 40, 60, 120, 180 and 240 min) in $S_2O_8^{2-}$ oxidation. The $S_2O_8^{2-}$ dosage (1.32 g) was fixed by the ratio of $S_2O_8^{2-}:COD_0 = 4.0:1.0$ as in the oxidation with previous pH adjustment. As shown in Figure 2, the optimum removal for SS, NH_3-N and COD were 91.4%, 50.7% and 30.2% at 20 min. This may represent the free radicals attacking rapidly on BIOTPOME due to fast kinetic of those radicals (Cronk 2008). The
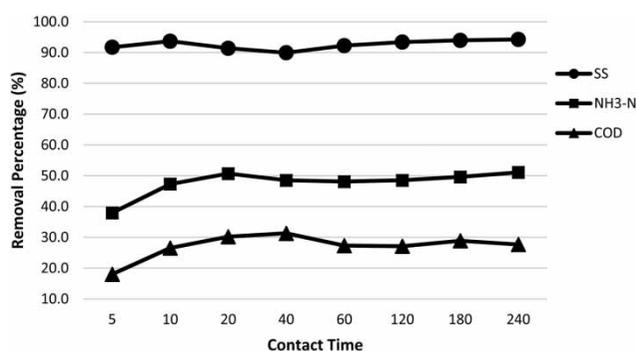

Figure 2 │ Effect of contact time on removals of SS, NH_3-N and COD by $S_2O_8^{2-}$ oxidation (pH 11; $S_2O_8^{2-}:COD_0 = 4.0:1.0$; shaking speed, 200 rpm).

COD removed was higher compared with the 221.9% of COD eliminated from previous operational condition, pH adjustment at 60 min. However, the removal of NH_3-N at 20 min, 50.7%, was lower than NH_3-N removed at 60 min, 59.0%, in the previous study of pH adjustment. In these conditions, $S_2O_8^{2-}$ or radicals possibly attacked the organic compound rather than NH_3-N. SS was also greatly removed with a range of 89.9% to 94.3%.

Effect of dosages of $S_2O_8^{2-}$

Figure 3 demonstrates the removal percentage of parameters of BIOTPOME with varied dosages of $S_2O_8^{2-}$ (0.20–2.45 g) in relation to ratio of $S_2O_8^{2-}:COD_0$ (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). The optimum removal of parameters like SS, NH_3-N and COD was 57.7%, 47.6% and 36.8% when ratio of $S_2O_8^{2-}:COD_0 = 2.0:1.0$. By increasing $S_2O_8^{2-}$ dosage higher than 2.0:1.0 of $S_2O_8^{2-}:COD_0$ ratio, there was significant decrease on COD removal. COD removal ranged from 24.0% to 31.8% for $S_2O_8^{2-}:COD_0 = 3.0:1.0$ to 6.0:1.0. Excessive amount of $S_2O_8^{2-}$ may affect the treatment efficiency.
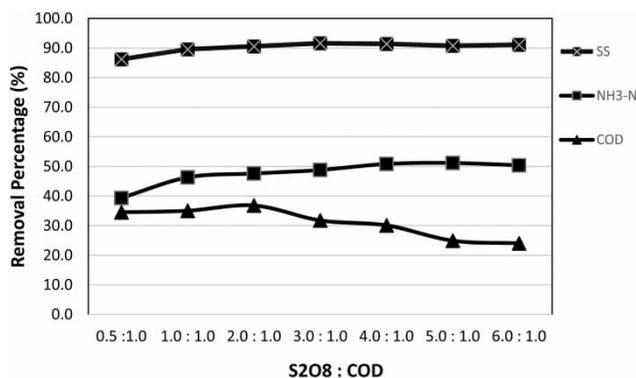

Figure 3 │ Effect of dosages of $S_2O_8^{2-}$ on removal of SS, NH_3-N and COD by $S_2O_8^{2-}$ oxidation (20 min contact time; pH 11; shaking speed, 200 rpm).

Sulphate ion, SO_4^{2-}, formed from $S_2O_8^{2-}$ can act as scavenger to attack oxidant and intermittently reduce the decomposition rate of COD as in the study of degradation of trichloroethylene by $S_2O_8^{2-}$ oxidation (Liang *et al.* 2007).

Table 2 shows the removal efficiencies for $S_2O_8^{2-}$ oxidation of BIOTPOME. The removal efficiencies ranged from 21.9% to 36.8% for COD, 47.6% to 59.0% for NH_3-N, and 87.8% to 91.4% for SS. The pH values of samples rose to 10.5–10.6 after oxidation treatment. By adjusting the operational conditions to optimum, as $S_2O_8^{2-}$:$COD_0 = 2$, pH 11 and 20 min contact time, 36.8% COD, 47.6% NH_3-N, 57.7% colour and 90.6% SS removal efficiencies were achieved.

$S_2O_8^{2-}$/H_2O_2 oxidation

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

Effect of dosage ratio of H_2O_2:$S_2O_8^{2-}$

By fixing the optimum ratio of $S_2O_8^{2-}$:$COD_0 = 2.0:1.0$, the dosage ratios of H_2O_2:$S_2O_8^{2-}$ were varied (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) for the oxidation of BIOTPOME under pH 8.4 within 20 minutes and the
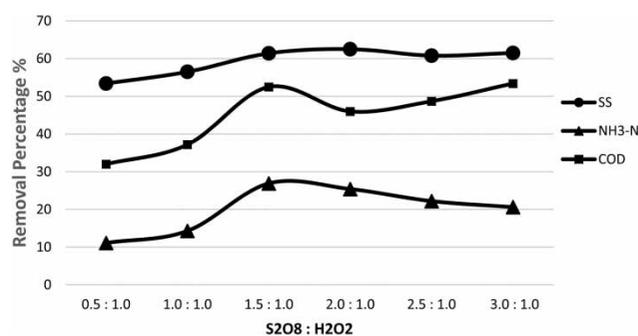

Figure 4 │ Effect of dosage ratios of H_2O_2:$S_2O_8^{2-}$ on removals of SS, NH_3-N and COD by $S_2O_8^{2-}$/H_2O_2 oxidation (20 min contact time; $S_2O_8^{2-}$:$COD_0 = 2.0:1.0$; pH 8.4 at 200 rpm).

result is shown in Figure 4. The optimum removals of SS, NH_3-N and COD were 61.4%, 26.9% and 52.5% by using H_2O_2:$S_2O_8^{2-}$ dosage ratio of 1.5:1.0. When the lowest dosage ratio (0.5:1.0) was applied 53.4% SS, 11.1% NH_3-N and 32% COD removals were achieved. As dosage ratio increased, removal percentage of parameters were also increased. However, the removals of COD, NH_3-N and colour were decreased as the dosage ratio was increased over 1.5:1.0.

Effect of dosage of H_2O_2/$S_2O_8^{2-}$

The dosages of H_2O_2/$S_2O_8^{2-}$ (g/g) were varied based on the optimum ratio of H_2O_2:$S_2O_8^{2-}$ (1.5:1.0), as shown in Figure 5. Different dosages of H_2O_2/$S_2O_8^{2-}$ (g/g: 0.61/0.41, 1.22/0.82, 2.45/1.63, 3.67/2.45, 4.89/3.26 and 6.12/4.08) in order to enhance the performance of $S_2O_8^{2-}$/H_2O_2 oxidation. The optimum parameter was obtained based on overall removals of parameters and the optimum dosage of H_2O_2/$S_2O_8^{2-}$ determined was 2.45 g/1.63 g. SS, NH_3-N and COD removals were as high as 63.7%, 56.9% and 26%, respectively. By fixing the dosage ratio and varying the dosages of $S_2O_8^{2-}$ and H_2O_2, the SS removal was increased gradually overall. When the dosage of H_2O_2/$S_2O_8^{2-}$ was increased from 0.61 g/0.41 g to 2.45 g/1.63 g, COD removal was between 58.8% and 56.9%. The removal was decreased afterward when additional dosage of H_2O_2/$S_2O_8^{2-}$ (g/g) was added. Removal efficiencies of SS and NH_3-N were increased gradually as dosages of $S_2O_8^{2-}$ and H_2O_2 were increased.

As dosage of H_2O_2 increases, H_2O_2 and $SO_4^{\bullet-}$ may non-productively degrade and scavenge, respectively, and result in a quicker termination reaction because the free radicals will scavenge oxidants and oxidants may scavenge radicals too (Ko *et al.* 2012) as in Equations (14) and (15). Ko *et al.*
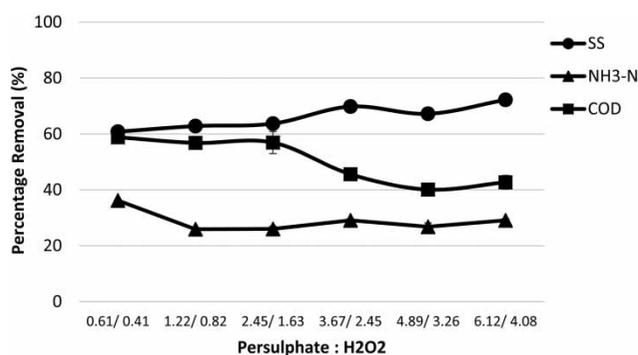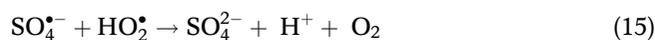
Table 2 │ Removals of COD, NH_3-N and SS of BIOTPOME in different operational conditions using $S_2O_8^{2-}$ oxidation

Operational conditions	Final pH	COD removal (%)	NH3-N removal (%)	SS removal (%)
pH 11 (Contact time = 1 hr; $S_2O_8^{2-}$:COD_0 = 4.0:1.0)	10.5	21.9	59.0	87.8
Contact time = 20 min (pH 11; $S_2O_8^{2-}$:COD_0 = 4.0:1.0)	10.5	30.2	50.7	91.4
$S_2O_8^{2-}$:COD_0 = 2.0:1.0 (pH 11; Contact time = 20 min)	10.6	36.8	47.6	90.6

Figure 5 | Effect of dosage of $S_2O_8^{2-}$:H_2O_2 on removals of SS, NH3-N and COD by $S_2O_8^{2-}$/H_2O_2 oxidation (20 min contact time; $S_2O_8^{2-}$:COD_0 = 2.0:1.0; H_2O_2:$S_2O_8^{2-}$ ratio = 1.5:1.0; pH 8.4 at 200 rpm).

(2012) have also mentioned $S_2O_8^{2-}$ and $OH^{\bullet}$ may react with each other although the reaction rate is slow.

$$H_2O_2 + SO_4^{\bullet-} \rightarrow SO_4^{2-} + HO_2^{\bullet} + H^+ \tag{14}$$

$$SO_4^{\bullet-} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^+ + O_2 \tag{15}$$

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 of BIOTPOME. Fixed variables of $S_2O_8^{2-}$:COD_0 = 2.0:1.0, dosage of H_2O_2/$S_2O_8^{2-}$ of 2.45 g/1.63 g and 20 minutes contact time were employed in the oxidation system. In Figure 6, the optimum pH for overall removals of parameters was 11; 87.1% SS, 75.8% NH$_3$-N and 35.8% COD were eliminated under pH 11. SS removal increased steeply as pH increased. The removal efficiencies of SS were 64.5% under acidic condition, pH 3. Colour removal of 90.3% and SS removal of 93.6% were also gained with initial pH of 12. The removal of NH$_3$-N was improved from 21% to 77.8% as pH increased, while the maximum removal of COD (53.2%) was achieved at pH 8.4.

Table 3 shows a summary of $S_2O_8^{2-}$/H_2O_2 oxidation. Through adjustment of the dosage ratios and dosages of H_2O_2/$S_2O_8^{2-}$ (g/g), removal efficiencies of COD, NH$_3$-N and SS were 52.5%–56.9%, 26%–26.9%, 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$_3$-N removal was increased sharply compared with COD and NH$_3$-N removals under varied dosages of $S_2O_8^{2-}$ and H_2O_2. In the studied conditions ($S_2O_8^{2-}$:COD_0 = 2.0:1.0, pH 11, 20 min contact time and H_2O_2/$S_2O_8^{2-}$
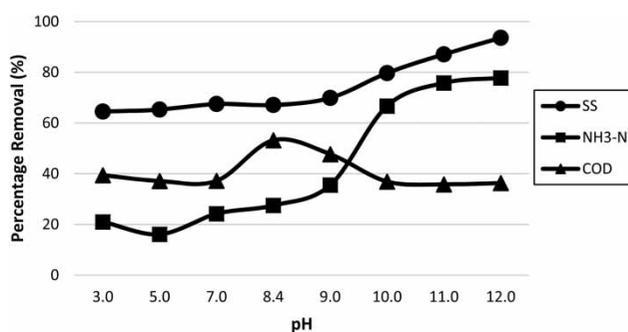

Figure 6 | Effect of initial pH on removals of SS, NH3-N and COD by $S_2O_8^{2-}$/H_2O_2 oxidation (20 min contact time; $S_2O_8^{2-}$:COD_0 = 2.0:1.0; H_2O_2/$S_2O_8^{2-}$ = 2.45 g/1.63 g at 200 rpm).

Table 3 | Removals of COD, NH$_3$-N and SS of BIOTPOME in different operational conditions using $S_2O_8^{2-}$/H_2O_2 oxidation

Optimum operational conditions	Final pH	COD removal (%)	NH$_3$-N removal (%)	SS removal (%)
Dosage ratio of H_2O_2:$S_2O_8^{2-}$ =1.5:1.0 (Contact time = 20 min; $S_2O_8^{2-}$:COD_0 = 2.0:1.0; pH 8.4)	8.2	52.5	26.9	61.4
Dosage of H_2O_2/$S_2O_8^{2-}$ = 2.45 g/1.63 g (Contact time = 20 min; $S_2O_8^{2-}$:COD_0 = 2.0:1.0; H_2O_2:$S_2O_8^{2-}$ dosage ratio =1.5:1.0; pH 8.4)	8.2	56.9	26	63.7
pH = 11 (Contact time = 20 min; $S_2O_8^{2-}$:COD_0 = 2.0:1.0; H_2O_2/$S_2O_8^{2-}$ = 2.45 g/1.63 g)	10.1	35.8	75.8	87.1

dosage of 2.45 g/1.63 g), the highest removal efficiencies of COD, NH$_3$-N and SS were 35.8%, 75.8% and 87.1%, respectively, at final pH of 10.1.

Although the optimum removal for ammonia and SS was achieved at pH 11, significant removal for COD was also achieved at pH 8.4. This findings is in agreement with Hilles et al. (2016a, 2016b) using $S_2O_8^{2-}$/H_2O_2 for concentrated landfill leachate treatments.

In the light of the above, operational cost for using $S_2O_8^{2-}$/H_2O_2 was calculated for kg COD removal. As the major cost of the treatment process is related to chemicals used, the operational costs were USD0.4/L 37% H_2O_2 and USD0.8/kg sodium persulfate (Na$S_2O_8^{2-}$), and about 4.98 kg

of persulfate and 5.2 L of 37% H_2O_2 are required to remove 1 kg COD (in 303 L of POME). Around USD6 is required to treat 303 L of POME using $S_2O_8^{2-}$/H_2O_2 oxidation process. Hilles *et al.* (2016a) reported USD10.7/kg COD removal using the same treatment process for landfill leachate.

CONCLUSIONS

In this study, $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation were used for removing SS, NH_3-N and COD from BIOTPOME. To the best of our knowledge, this is the first experimental study conducted to treat BIOTPOME via $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation. For $S_2O_8^{2-}$ oxidation, 36.8% COD, 47.6% NH_3-N and 90.6% SS were removed at the optimum operation conditions ($S_2O_8^{2-}$ = 0.82 g, pH 11, and 20 min contact time). In $S_2O_8^{2}$/H_2O_2 oxidation, 35.8% COD, 75.8% NH_3-N and 87.1% SS were achieved when operation conditions were $S_2O_8^{2-}$:COD_0 = 2.0:1.0, H_2O_2/$S_2O_8^{2-}$ = 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_0 = 2.0:1.0 and 2.45 g/1.63 g of H_2O_2/$S_2O_8^{2-}$ 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. Values of final COD and pH of $S_2O_8^{2-}$ and $S_2O_8^{2-}$/H_2O_2 oxidation above the standard discharge limit and not suitable for release into the environment according to the industrial discharge standard for POME (DOE 1999). 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.

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REFERENCES

Abdullah, N. & Sulaiman, F. 2013 The oil palm wastes in Malaysia. In: *Biomass Now-Sustainable Growth and Use* (M. D. Matovic, ed.). Intech, Canada, pp. 75–100.

Ahmad, A. & Krimly, M. Z. 2014 Palm oil mill effluent treatment process evaluation and fate of priority components in an open and closed digestion system. *Current World Environment* **9** (2), 321–330.

Ahmadi, M., Behin, J. & Mahnam, A. R. in press Kinetics and thermodynamics of peroxydisulphate oxidation of Reactive Yellow 84. *Journal of Saudi Chemical Society*. doi.org/10.1016/j.jscs.2013.07.004.

Ali, I. H. 2005 *Kinetic Study of Oxidation of Three Simple Sugars by Peroxydisulphate*. MSc Thesis, University of Khartoum, Khartoum, Sudan.

APHA (American Public Health Association) 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Aris, A., Ooi, B. S., Kon, S. K. & Ujang, Z. 2008 Tertiary treatment of palm oil mill effluent using Fenton oxidation. *Malaysia Journal of Civil Engineering* **20** (1), 12–25.

Bashir, M. J. K., Tham, M. H., Lim, J. W., Ng, C. A. & Abu Amr, S. S. 2016 Polishing of treated palm oil mill effluent (POME) from ponding system by electro-oxidation process. *Water Science and Technology* **73**, 2704–2712.

Block, P. A., Brown, R. A. & Robinson, D. 2004 Novel activation technologies for sodium persulfate *in situ* chemical oxidation. In: *Proceedings of the Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, May 2004, Monterey, CA*. Battelle Press, Columbus, OH, USA.

Cronk, G. 2008 Case study comparison of multiple activation methods for sodium persulfate ISCO treatment. In: *Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, 19–22 May, 2008*. JAG Consulting Group, USA.

Deng, D., Peng, L., Guan, M. & Kang, Y. 2014 Impact of activation methods on persulfate oxidation of methyl tert-butyl ether. *Journal of Hazardous Materials* **264**, 521–528.

DOE (Department of Environment) 1999 *Industrial Processes and the Environment: Crude Palm Oil Industry, Handbook No. 3*. DOE, Kuala Lumpur, Malaysia.

Epold, I. & Dulova, N. 2015 Oxidative degradation of levofloxacin in aqueous solution by $S_2O_8^{2-}$/Fe^{2+}, $S_2O_8^{2-}$/H_2O_2 and $S_2O_8^{2-}$/OH^- processes: a comparative study. *Journal of Environmental Chemical Engineering* **3** (2), 1207–1214.

Fadzil, N. A. M., Zainal, Z. & Abdullah, A. H. 2013 COD removal for palm oil mill secondary effluent by using UV/ferrioxalate/TiO_2/O_3 system. *International Journal of Emerging Technology and Advanced Engineering* **3** (7), 237–243.

Green Palm 2015 *Where is Palm Oil Grown?* Roundtable on Sustainable Palm Oil. Available from: http://greenpalm.org/about-palm-oil/where-is-palm-oil-grown-2 (accessed 16 August 2015).

Hach 2005 *Water Analysis Handbook*, 4th edn. Hach Company, USA.

Hassan, S., Kee, L. S. & Al-Kayiem, H. H. 2013 Experimental study of palm oil mill effluent and oil palm frond waste mixture as an alternative biomass fuel. *Journal of Engineering Science and Technology* **8** (6), 703–712.

Hilles, A. H., Abu Amr, S. S., Hussein, R. A., Arafa, A. I. & El-Sebaie, O. D. 2016a Performance of combined sodium

persulfate/H_2O_2 based advanced oxidation process in stabilized landfill leachate treatment. *Journal of Environmental Management* **66**, 493–498.

Hilles, A. H., Abu Amr, S. S., Hussein, R. A., Arafa, A. I. & El-Sebaie, O. D. 2016b Optimization of leachate treatment using persulfate/H_2O_2 based advanced oxidation process: case study: Deir El-Balah Landfill Site, Gaza Strip, Palestine. *Water Sciences and Technology* **73**(1), 102–112.

Ko, S., Crimi, M., Marvin, B. K., Holmes, V. & Huling, S. G. 2012 Comparative study on oxidative treatments of NAPL containing chlorinated ethanes and ethenes using hydrogen peroxide and persulphate in soils. *Journal of Environmental Management* **108**, 42–48.

Liang, C., Wang, Z. S. & Bruell, C. J. 2007 Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere* **66** (1), 106–113.

Liew, W. L., Kassim, M. A., Muda, K., Loh, S. K. & Affam, A. C. 2015 Conventional methods and emerging wastewater polishing technologies for palm oil mill effluent treatment: a review. *Journal of Environmental Management* **149**, 222–235.

Mohammed, R. R. & Chong, M. F. 2014 Treatment and decolorization of biologically treated palm oil mill effluent (POME) using banana peel as novel biosorbent. *Journal of Environmental Management* **132**, 237–249.

Rupani, P. F., Singh, R. P., Ibrahim, M. H. & Esa, N. 2010 Review of current palm oil mill effluent (POME) treatment methods: vermicomposting as a sustainable practice. *World Applied Sciences Journal* **10** (10), 1190–1201.

SGS 2015 *Global Palm Oil Market Update*. Available from: http://www.sgs.com/en/news/2015/04/global-palm-oil-market-update (accessed 1 April 2016).

Singh, R. P., Ibrahim, M. H., Esa, N. & Iliyana, M. S. 2010 Composting waste from palm oil mill: sustainable waste management practice. *Reviews in Environmental Science and Bio/Technology* **9** (4), 331–344.

Thabet, O. D., Bouallaguia, H. B., Cayol, J., Ollivier, B., Fardeaub, M. & Hamdi, M. 2009 Anaerobic degradation of landfill leachate using an upflow anaerobic fixed-bed 662 reactor with microbial sulfate reduction. *Journal of Hazardous Materials* **167**, 1133–1140.

Wu, T. Y., Mohammad, A. W., Jahim, J. M. & Anuar, N. 2010 Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *Journal of Environmental Management* **91** (7), 1467–1490.

Zhao, D., Liao, X., Yan, X., Huling, S. G., Chai, T. & Tao, H. 2013 Effect and mechanism of persulfate activated by different methods for PAHs removal in soil. *Journal of Hazardous Materials* **254–255**, 228–235.