Advanced Treatment of Palm Oil Mill Effluent Using Thermally Activated Persulfate Oxidation

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Abstract: Advanced treatment of biologically processed palm oil mill effluent (BIOTPOME), which possesses a potential danger to the water sources is required to meet the Malaysian discharge standard, as BIOTPOME contains high level of chemical oxygen demand (COD), suspended solids and oil and grease even after going through conventional treatment process. The significant but insufficient treatment efficiency of ponding system in Malaysia urged an alternative method to treat the recalcitrant organic compounds. Thus, post-treatment of BIOTPOME using oxidation by thermally activated persulfate process was proposed to solve this issue. In order to maximize the removal of COD and color, the central composite design (CCD) module of the response surface approach was used to optimize the interactions of the process variables temperature, $S_2O_8^{2-}$/COD ratio, and reaction time. In order to identify the significant terms of interacting process factors, CCD performed a batch study from which statistical models of responses were created. All models were confirmed by analysis of variance (ANOVA) showing significances with Prob > F less than 0.1. The optimal performance was obtained at the temperature of 67.4 °C, $S_2O_8^{2-}$/COD ratio of 9.8 and reaction time of 120 min, rendering COD removal of 85.65% and color removal of 85.74%. The total cost for the treatment process was RM0.94 per liter.

Keywords: sulfate radical; advanced oxidation process; thermos-activation; treatment optimization; organic pollutants

1. Introduction

Elaeis guineensis, more commonly known as oil palm trees, has been established as an industrial crop since the 1960s when the plantation area was undergoing expansion from 54,674 hectares in 1960 to 5.9 million hectares in 2019. According to the report by the United States Department of Agriculture (USDA) in 2021, Malaysia accounted for 26.37% of the world’s palm oil production, falling behind Indonesia with 57.64% of the world’s palm oil production [1]. With government bodies such as MPOC and Malaysian Agricultural Research and Development Institute (MARDI), the palm oil industries in Malaysia are still flourishing nowadays. The process of palm oil extraction generates several types of waste in solid, liquid and gas forms during the milling process of the fresh fruit bunches. These by-products included but are not limited to: empty fruit bunches, oil palm shell and fuel ash, methane gas and palm oil mill effluent (POME), which can lead to serious environmental issues if it was directly discharged in the water streams [2,3]. Untreated POME is brown...
in color and full of colloidal suspension with an unpleasant and pungent smell, which consists of 95% water, 4% total solids and 0.7% oil [4]. As POME that is not treated properly will cause environmental pollution especially water pollution, it has to undergo treatment before being safely discharged. Since POME is rich in organic components, the industries mostly used anaerobic and aerobic lagoons to treat POME [2,5]. However, these methods did not achieve high efficiency in lowering the COD and total suspended solids (TSS) content, as well as removing the brownish color of the POME. In fact, the analysis of the POME from the ponds revealed that the removal of lignin along with other types of organic matters is significant but insufficient after going through the treatments of anaerobic ponds and anaerobic reactor. Therefore, the brownish color remains, and the biologically treated POME (BIOTPOME) is not appropriate to be safely discharged into water streams despite its non-toxic nature. Furthermore, the conventional open ponding system possess other disadvantages such as requirement of large land area (around 30–45 acres) and long hydraulic retention time (3 months) for the biological degradation process [6].

Due to the limitations experienced by ponding system, it can be observed that the current trend on POME studies had shifted towards investigating and exploring various polishing technologies of POME to expel the color and remaining organic compounds before being discharged into water bodies. Advanced oxidation process (AOP) mechanisms in the industries mainly utilize hydroxyl radical to destruct the structure of organic compounds [7]. Sulfate radical-based AOPs have gained attention in recent years to replace hydroxyl radical due to: higher redox potential, reaction in wider pH range and higher efficiency in oxidizing persistent organic pollutants with unsaturated bonds or aromatic rings that are difficult to be treated during microbial degradation [8]. The process of AOPs takes place in two steps: on-site generation of radicals, then proceeds with the reaction of radicals with organic or biological pollutants. Persulfate activation to form sulphate radicals can be achieved through several methods such as thermal, ultraviolet, ultrasound or heterogeneous and homogeneous catalysis [9]. Although sulfate radical-based research has been increasing, there is limited information on the thermally activated persulfate and its performance in treating treatment POME. Typically, thermal activation is one of the most effective methods for persulfate activation to generate reactive species. Since the bond energy of peroxide (O–O) in persulfate is 140–213.3 kJ mol$^{-1}$, a thermal activation at >30 °C is enough to break the O–O bond for the generation of sulfate anion radicals ($\text{SO}_4^{\cdot-}$). These $\text{SO}_4^{\cdot-}$ radicals can be further converted to hydroxyl radicals (•OH), which are also an effective species in degrading organic contaminants.

In order to fulfil the discharge limit established by the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977, this study focused on using an advanced oxidation process using a thermally activated sulfate radical (SR-AOP) for further polishing of biologically treated POME. The central composite design (CCD) module was used to statistically optimize this supplementary post treatment. To maximize COD and color treatment efficacy, POME temperature, $\text{S}_2\text{O}_8^{2-}$/COD ratio, and reaction duration were adjusted.

2. Materials and Methods

2.1. Treated POME Characteristics

The POME used in this study originated from a palm oil factory that is based in the state of Perak. The final treatment pond of the ponding system, from which water would eventually be pumped into the nearby water bodies, was where the POME samples were taken. To reduce biological and chemical alterations, the collected samples were delivered to an environmental laboratory and kept at 4 °C. Based on an analysis of the Standard Methods for the Examination of Water and Wastewater handbook [10], the characteristics of partially treated POME from ponding systems are shown in Table 1.
Table 1. Characterization of biologically treated POME.

| Parameter | Unit   | Average Value |
|-----------|--------|---------------|
| COD       | mg/L   | 4020.0        |
| N-NH₃     | mg/L   | 4810.0        |
| Color     | PtCo   | 5400.0        |
| Turbidity | NTU    | 1280          |
| BOD₅      | mg/L   | 444.5         |
| pH        | -      | 7.6           |
| Temperature | °C     | 32.9          |

2.2. Setup of Laboratory-Scale Thermally Activated AOP System

Batch experiments were conducted for all via Schott bottle containing 100 mL of POME. Respective dosage of Na₂S₂O₈ in crystalized powder form and a magnetic stirrer were added to the bottle, then the bottle was capped. The temperature of the stirring water bath with lid was set, and the bottle was placed in the water bath, making sure the water bath level exceeded the solution level, and the solution was heated for a designated duration of time. Following the completion of each batch experiment, the COD and color concentrations were analyzed, and the respective removal efficiencies were determined using Equation (1):

\[
\text{Removal efficiency (\%) = } \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \tag{1}
\]

where \(C_i\) and \(C_f\) refer to the initial and final concentrations of COD and color.

2.3. Experimental Design and Statistical Analysis

In this work, RSM was used to analyze and optimize the treatment of POME from ponding system using the Design-Expert® Version 7.0 software (Stat-Ease, Inc., Minneapolis, MN 55413, USA). The correlation between the process variable and the answer was assessed using the CCD module of RSM, which is the most often used module of RSM. According to Guven et al. [11], CCD is a useful design tool for sequential experimentation since it allows for a reasonable amount of information to be tested for lack of fit when there are enough experimental values available. Temperature (A), \(S_2O_8^{2-}/COD\) ratio (B), and reaction time (C) were the three important process factors in this study that needed to be adjusted. Each process variable was numerically altered from \(-1\) to \(+1\) coded value. The corresponding real value ranges, which were derived from early studies and supported by the literature, were 25 to 80 °C, 0.2 to 10.0 ratio, and 10.0 to 120.0 min [12–14] Six repeated batches were run at the midpoint of each process variable as part of the design by CCD, which resulted in a total of 20 batch tests for the purpose of determining the random error (Table 2). The simultaneous percentage reductions of COD and color at the end of each run were the monitored reactions. As shown in Equation (2), each response was then statistically modeled using a quadratic model via correlation with process variable terms.

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} \beta_{ij} x_i x_j + \epsilon \tag{2}
\]

where the response is \(Y\); the process variables are \(x_i\) and \(x_j\); the constant coefficient is \(\beta_0\); \(\beta_i\), the interaction coefficients of linear are \(\beta_{ii}\) and \(\beta_{ij}\) quadratic and second order terms, respectively; the number of process variables is \(k\) and the random error component is \(\epsilon\).

The coefficient of determination (\(R^2\)) value and F-test from analysis of variance (ANOVA) based on probability (\(p\)-value) of 95% confidence level were used to confirm the accuracy of the fitted model [15]. The best conditions for process variables focused on maximum removal efficiencies of COD and color of post-treated POME for discharge were then predicted using the models that represented their respective responses’ interaction.
Table 2. Summary of CCD batch experiments and their response values.

| Run | Temperature (°C) | S$_2$O$_8^{2-}$/COD Ratio | Reaction Time (min) | COD (%) | Color (%) |
|-----|-----------------|--------------------------|---------------------|---------|-----------|
| 1   | 25.0            | 0.20                     | 10.0                | 10.90   | 27.96     |
| 2   | 25.0            | 0.20                     | 120.0               | 16.19   | 40.37     |
| 3   | 25.0            | 10.00                    | 10.0                | 25.75   | 38.89     |
| 4   | 25.0            | 10.00                    | 120.0               | 7.24    | 49.81     |
| 5   | 80.0            | 10.00                    | 10.0                | 31.84   | 31.85     |
| 6   | 80.0            | 10.00                    | 120.0               | 86.62   | 89.63     |
| 7   | 80.0            | 0.20                     | 10.0                | 13.56   | 36.11     |
| 8   | 80.0            | 0.20                     | 120.0               | 29.15   | 55.93     |
| 9   | 52.5            | 2.65                     | 65.0                | 54.35   | 60.74     |
| 10  | 52.5            | 5.10                     | 65.0                | 46.62   | 68.52     |
| 11  | 52.5            | 5.10                     | 65.0                | 46.19   | 64.26     |
| 12  | 52.5            | 5.10                     | 65.0                | 52.09   | 65.19     |
| 13  | 52.5            | 5.10                     | 65.0                | 49.38   | 65.37     |
| 14  | 52.5            | 5.10                     | 92.5                | 49.90   | 77.04     |
| 15  | 52.5            | 7.55                     | 65.0                | 65.35   | 66.67     |
| 16  | 66.3            | 5.10                     | 65.0                | 47.74   | 70.37     |
| 17  | 38.8            | 5.10                     | 65.0                | 37.39   | 67.04     |
| 18  | 52.5            | 5.10                     | 37.5                | 43.51   | 75.74     |
| 19  | 52.5            | 5.10                     | 65.0                | 46.79   | 64.07     |

3. Results and Discussion

In particular, Table 1 presents the ponding system’s treatment of POME performance. The Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977 of Malaysia was violated by the POME discharged to the nearby water sources since it still included excessive levels of COD, color, turbidity, suspended particles, and ammonia-nitrogen. This suggests that post-treatment of POME from ponding systems is essential, both to comply with the decree and to safeguard the environment’s health while receiving the discharged POME.

3.1. Statistical Significance of Responses’ Models

In this work, CCD of RSM optimized the use of thermally activated sulfate radical-based AOP process as a post-treatment technique of POME. Table 2 displays the response outcomes of batch trials created by CCD using statistically varying process factors. Based on the prediction of a parameter, the CCD module can provide an empirical design for associating response to a process variable [15]. Polynomial equations might be used to determine the relationship between responses and process factors by using factorial regression analysis to the experimental data in Table 2. Equations (3) and (4) illustrate the quadratic models that were obtained for each response after the statistically unimportant model terms were removed:

\[
\text{COD removal (\%)} = 49.093 + 12.50A + 10.25B + 7.10C - 35.48A^2 + 33.66B^2 - 18.90C^2 + 8.73AB + 10.45AC \quad (3)
\]

\[
\text{Color removal (\%)} = 66.987 + 6.84A + 6.21B + 11.95C + 1.13AB + 6.78AC + 4.56BC \quad (4)
\]

The model terms A, B, and C, respectively, stand in for the process variables temperature, S$_2$O$_8^{2-}$/COD ratio, and reaction time. The ANOVA study of two response quadratic models is explained in Tables 3 and 4.
Table 3. ANOVA results for validating response surface quadratic models for COD removal.

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | Remarks |
|--------|----------------|----|-------------|---------|----------|---------|
| COD Removal Efficiency | | | | | | |
| Model | 5638.00 | 9 | 626.44 | 41.83 | <0.0001 | significant |
| A | 1328.37 | 1 | 1328.37 | 88.70 | <0.0001 |
| B | 893.44 | 1 | 893.44 | 59.65 | <0.0001 |
| C | 428.41 | 1 | 428.41 | 28.60 | 0.0006 |
| $A^2$ | 234.20 | 1 | 234.20 | 15.63 | 0.0042 |
| $B^2$ | 210.80 | 1 | 210.80 | 14.07 | 0.0056 |
| $C^2$ | 66.45 | 1 | 66.45 | 4.43 | 0.0682 |
| AB | 609.87 | 1 | 609.87 | 40.72 | 0.0002 |
| AC | 873.41 | 1 | 873.41 | 58.32 | <0.0001 |
| BC | 29.60 | 1 | 29.60 | 1.97 | 0.1971 |
| Residual | 119.80 | 8 | 14.97 | | | |
| Lack of Fit | 115.51 | 5 | 23.10 | 16.16118 | 0.0222 |
| Pure Error | 4.28 | 3 | 1.42 | | | |

$R^2 = 0.9792$, Adjusted $R^2 = 0.9559$, Predicted $R^2 = -0.2774$, C.V. = 9.5745%, Adequate Precision = 25.1211

Final equation in terms of coded factors:

$$\text{COD removal efficiency} = 49.093 + 12.50A + 10.25B + 7.10C - 35.48A^2 + 33.66B^2 - 18.90C^2 + 8.73AB + 10.45AC$$

The Prob > F of less than 0.01 consistently indicated that the response quadratic models were adequate and significant. The coefficient of determination ($R^2$) for each model showed that the quadratic models satisfactorily accounted for the experimental data. According to Myers et al. [16], a good fit model should have $R^2 > 0.8$, which was demonstrated in
this investigation. Myers et al. [16] claim that an $R^2$ value that is closer to 1.0 is statistically preferable. Next, all of the models’ coefficients of variance were under 10%, indicating high model repeatability [12]. All models showed appropriate precisions of higher than 4.0, indicating that the models’ signals may be utilized to guide the design space [17]. As a result, the models that were created were sufficient for navigating the design space described by CCD and for predicting reactions [13]. On the other hand, the estimated standard deviation values of all below 10%, a normally acceptable variance, revealed the dispersion of data values around their respective means. In this regard, the resulting models’ anticipated responses could be seen scattering about the actual values of the responses, as shown in Figure 1, demonstrating that the variances were small in every case.

3.2. The Effect of Variable Interactions on Responses

The interactions of process factors (namely temperature, $S_2O_8^{2−}$/COD ratio, and reaction time) effecting the removal of color and COD of post-treated POME by thermally activated sulfate radical-based AOP method were then accessed using the fitted models (Equations (3) and (4)). In a 3D surface plot, steep curvature indicates an obvious interaction of process factors that results in a synergistic impact, and vice versa. The results of the interactions between the process variables are shown in Figures 2 and 3 of this study for the various statistically expected responses of treated POME using the thermally activated sulfate radical-based AOP method. From 25.0 to 60.0 $°$C, the elimination of color and COD typically increased with temperature. The elimination of color (Figure 2) showed the biggest changes among them, going from 40% at 25.0 $°$C to 80% at 60.0 $°$C and then increasing to 100% at 80.0 $°$C, at the minimum temperature and the highest $S_2O_8^{2−}$/COD ratio. Likewise, Yabalak [18] found that the elevated temperatures supply sufficient energy to rupture the peroxide bonds in persulfate molecules, as well as produce $SO_4^{−}$ radicals for faster degradation of organic compounds. Other than that, the heat energy provided from the high temperature in the solutions can break the $\pi$ bonds in the structure of the components that contributed the dark color of the BIOTPOME. This causes the structure to undergo changes and a decrease in color density.

![Figure 1. Cont.](image-url)
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In thermally activated SR-AOP process, the sulfate radical is activated when the heat supplied provides energy for the O–O bond to experience fission, as shown below.

$$S_2O_8^{2−} \stackrel{heat}{\rightarrow} 2SO_4^{•−}$$

$$HSO_5^{−} \stackrel{heat}{\rightarrow} SO_4^{•−} + OH^{•}$$

As the heating temperature increases, the radical generation rate becomes higher, thus increasing the rate of removal of the targeted pollutants [19], which fits the Arrhenius equation as shown in Equation (5). However, extreme high temperature can contribute to high concentration of radicals which may result in reactions to occur among the radicals instead of the intended reactions of the radicals with the contaminants. Ultimately, an improved micropollutant degradation may not be achieved.

$$\ln(k) = \ln A - \frac{E_a}{RT} - \frac{d[contaminant]}{dt} = k \times [contaminant]$$

(5)

The red color of surface graph at a $S_2O_8^{2−}$/COD ratio of 5.10 has a wider spread as compared to that of higher $S_2O_8^{2−}$/COD ratio of 10. This may be due to the reason that $S_2O_8^{2−}$ can act as a $SO_4^{•−}$ radical scavenger after exceeding a certain concentration, therefore lowering the removal efficiency when the radical concentration in the high. This observation is similar to that of furfural degradation [20], agrochemical wastewater treatment [18] and penicillin G degradation [21] by heat activated persulfate oxidation. Under low ratio, the addition of time and temperature did not result in a major change in COD removal efficiency. This shows that a low temperature is unable to lower the COD level when there is an absence of persulfate radicals being added, as similar to bitumen effluents treatment [22]. The effect of temperature is just as significant as the time increment.

$$SO_4^{•−} + S_2O_8^{2−} \rightarrow SO_4^{2−} + S_2O_8^{•−}$$
Figure 2. The 3D response surface plots showing the effect of temperature vs. persulfate on (a) color removal and (b) COD removal (reaction time = 120 min).
Figure 3. The 3D response surface plots showing the effect of temperature vs. time on (a) color removal and (b) COD removal (S$_2$O$_8^{2−}$/COD Ratio: 10.00).

3.3. Optimizing the Interactions between Process Variables in the Electrocoagulation Process

The interactions between the process variables that were covered in the previous section provided some guidance for reducing the ranges of the variables while identifying the optimal conditions for the process to occur. As a result, the S$_2$O$_8^{2−}$/COD ratio and reaction time set in the RSM’s CCD were both limited to ranges of 0.2–10.0 and 20–120 min, respectively. On the other hand, a minimal temperature was intended to provide an economically viable post-treatment for POME without affecting the process’s viability. In the case of the replies, the COD and color removal were maximized in order to meet the
discharge requirement and simultaneously minimize the adverse environmental effect of the POME discharge. At a temperature of 67.4 °C, an $S_2O_8^{2−}$/COD ratio of 9.8, and a reaction duration of 120 min, the ideal conditions were discovered. In this ideal situation, 85.65 percent of COD and 85.74 percent of color would be removed. According to the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977 [23], the COD and color of post-treated POME were anticipated to be 598 mg/L and 560 Pt/Co, respectively, which are acceptable for discharge to the natural environment. The procedure was adjusted to attain optimal conditions and put into practice to validate the accuracy of expected outputs. The actual outcomes are displayed in Table 5. The reliability of the CCD tool in improving the thermally activated SR-AOP process was afterwards discovered by the calculation of the standard deviations between anticipated and actual values for each response.

| Response | Predicted Value | Actual Value | Percentage of Error (%) |
|----------|-----------------|--------------|--------------------------|
| COD (%)  | 86.62           | 85.65        | 1.2                      |
| Color (%)| 87.39           | 85.74        | 1.9                      |

Researchers had laboriously contributed to the literature vis-à-vis the use of thermally activated SR-AOP process for treatments other than POME. Ghauch et.al. [24] reported that with an initial ibuprofen concentration of 20.36 μM, $S_2O_8^{2−}$ concentration of 2.0 mM, temperature of 60 °C, pH 7.0 at 60 min of reaction time had resulted in complete removal of ibuprofen concentration. Future attempts were planned under different conditions such as lower temperature of less than 40 °C in order to lower the operational cost. In the treatment of agrochemical wastewater, which had been reported containing chemical compounds possessing numerous health risks, Yabalak [18] confirmed that 70.2% and 100% of total organic carbon and color removal was achieved with 90 °C temperature, 100 min reaction time and $S_2O_8^{2−}$ concentration of 80 mM. For the treatment of post oxidative effluents from production of petroleum bitumen under alkaline pH by Fernandes et al. [22], persulfate with a ratio of oxygen from oxidant and COD in the effluent ($r_{ox}$) of 1.28 at 60 °C achieved 33% COD reduction and 55% BOD reduction, respectively. This method was revealed to be effective for pre-treatment in terms of VOC degradation, and a secondary treatment was necessary for a cleaner production of petroleum bitumen.

3.4. Analysis of the Operational Cost

Cost analysis of biologically treated POME via thermally activated SR-AOP was carried out. Energy consumption and material cost is the main concern of thermally activated SR-AOP treatment. In this study, the operation costs were estimated for an applied temperature of 67.4 °C, 9.8 $S_2O_8^{2−}$/COD ratio and 120 min reaction time, which were the optimal operational conditions. Therefore, the sodium persulfate cost per liter of biologically treated POME was calculated by Equation (6), while the electricity cost was calculated by Equation (7). The cost of sodium persulfate was referred to the wholesale price of RM4.14 per kg, while the Malaysia electricity tariff was RM0.67 per kWh.

\[
\text{Sodium persulfate cost} = \text{cost per kg} \times \text{ratio} \times \text{COD} \times \text{molecular weight conversion} \\
= \text{RM4.14} \times 9.8 \times \frac{5400 \text{ mg}}{L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{238.12 \text{ g} S_2O_8^{2−}}{192 \text{ g} S_2O_8^{2−}} \times \frac{1}{98 \text{ purity}} \\
= \text{RM0.28/L} \tag{6}
\]

\[
\text{Electricity cost} = \text{cost} \times \text{power} \times (\text{heating time} + \text{reaction time}) \\
= \text{RM0.365} \times 0.8 \text{ kW} \times (15 \text{ min} + 120 \text{ min}) \times \frac{1 \text{ h}}{60 \text{ min}} \\
= \text{RM0.66/L} \tag{7}
\]
Per liter of POME, the computed total cost for heat activation of persulfate oxidation was RM0.94. The real dosage and electrical usage may vary depending on the POME influent quality.

4. Conclusions

Thermally activated persulphate was optimized for post-treatment of POME from ponding systems using the CCD of RSM. Temperature, $S_2O_8^{2-}$/COD ratio, and reaction time were three process factors that interacted and were simultaneously adjusted. The answers in the CCD module were programmed to remove COD and color as much as possible. The ANOVA test was used to confirm the developed response statistical models that demonstrated significant terms for interacting process variables. Each model had an $R^2$ value that was closer to 1.0 and a $Prob > F$ value that was less than 0.01. The optimum thermally activated SR-AOP process condition of $67.4^\circ C$, $9.8 S_2O_8^{2-}$/COD ratio and 120 min reaction time predicted 85.65% and 85.74% removal of COD and color. The total cost estimated per liter of BIOTPOME was RM0.94. The final quality of BIOTPOME satisfied the discharge limit under the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977 with a COD level of 598 mg/L and a color level of 560 Pt/Co. Based on these results, a thermally activated SR-AOP process at a certain level may be employed as an efficient and effective post-treatment technique before discharge to suit the needs.

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