



Treatment performance of palm oil mill effluent by utilizing Chitosan and ferric chloride coupled with activated carbon and ultrasound bath

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Received 12 December 2018; Accepted 26 August 2019

ABSTRACT

Although the palm oil industry contributes significantly to the Malaysian economy, it is creating environmental problems also, due to the palm oil mill effluent (POME). More than 85% of Malaysia's palm oil mills have adopted the ponding system to reduce the chemical oxygen demand (COD) and the biochemical oxygen demand (BOD) of POME to an acceptable limit because of its low equipment cost and ease of operation. However, given that the system requires a long hydraulic retention time, vast land, and that it releases methane gases, many mills are unable to achieve the discharge limit. This study addresses the issue by applying Chitosan and ferric chloride to decrease the COD and the BOD pollutants in POME before their discharge into the watercourse. A series of experiments were carried out to determine the characteristics performances and the optimum working conditions of each natural and synthetic coagulants paired with an ultrasound bath and activated carbon (AC). Results show that the best combination for POME treatment was with ultrasound cavitation, ferric chloride, and AC. The hybrid treatment was able to remove the BOD, the COD, the color and the total suspended solid up to 89.74%, 88.05%, 99.9%, and 99.5%, respectively. Therefore, the outcome of the study complies with the requirement of the Department of Environment Malaysia, which could assist palm oil mills to achieve environmental sustainability.

Keywords: Palm oil mill effluent; Ultrasound cavitation; Chitosan; Ferric chloride; Activated carbon

1. Introduction

The palm oil industry is the leading agricultural industry with a production of more than 13 million tons per year [1], and it contributes significantly to the Malaysian economy. However, this industry is creating environmental problems due to the discharge from palm oil processing mills known as palm oil mill effluent (POME). The oil palm fruit processing required a huge amount of water, thus, producing a large amount of wastewater. An amount up to 7,500 kg of water is required to produce 1,000 kg of crude palm oil, and most (>50%) of the water will turn to wastewater [2]. It was

reported that from the 19.66 million tons of crude palm oil produced, close to 44 million m³ of POME were generated in 2014 [3]. If the raw POME is discharged into the environment without further treatment, the biochemical oxygen demand (BOD) discharged is the same as the waste generated by 75 million people, which is 2.5 times the current population of Malaysia [3]. Reportedly, POME is 100 times more polluting than domestic sewage [4]. Moreover, the Ponding system is the most popular method to treat the effluent discharged by palm oil mills due to its low operating cost. Most Malaysian palm oil mills (>85%) adopt this method to reduce the BOD and the chemical oxygen demand (COD) of POME into an acceptable limit [5]. In the ponding system, POME is

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undergoing biological treatments, including anaerobic digestion process, followed by aerobic ponding with a hydraulic retention time (HRT) of 40 d or more. However, the ponding system presents adversely a long HRT; huge land is needed, and greenhouse gases (methane) are released. Reportedly, many palm oil mills are unable to achieve the discharge limit as per the ponding system [6]. Table 1 shows the typical characteristic of raw and treated POME obtained from the discharge point of a local palm oil mill in Sibul, Malaysia, and the Department of Environment (DOE) discharge limit. It could be observed that the BOD at treated POME is higher than the discharge limit outlined by DOE [2].

This study addresses the issue by applying Chitosan, ferric chloride combined with ultrasound cavitation and activated carbon (AC) as a new treatment method to decrease the pollutants responsible for the COD, the BOD, the color and the total suspended solids (TSS) in POME before their discharge into the watercourse, the outcome of which could contribute towards environmental sustainability of all palm oil mills.

1.1. Research objective

The main objective of this study is to determine the optimum dosage and the best combination among Chitosan and ferric chloride to pair with ultrasound cavitation and AC to degrade the POME by reducing the BOD, the COD, the TSS, and the color.

2. Materials and method

2.1. POME characterization

The raw POME samples are collected from a local palm oil refinery located in Sibul, Malaysia. Both the raw and the treated POME were characterized by measuring the BOD, the COD, the TSS, the pH, and the color.

2.2. Chitosan

The low molecular weight Chitosan samples (Deacetylated chitin, Poly-D-glucosamine) were obtained from Sigma-Aldrich (Malaysia) in the form of powder packaged in 500 g container. The 200 mL of POME with a pH of 4.5 is prepared for the Chitosan coagulation treatment. Different dosages

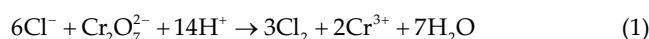
of Chitosan were added to the POME to coagulate the suspended solids. The COD, the color and the TSS of each sample before and after the experiment are measured and recorded.

2.3. Ferric chloride

The 200 mL of POME with various pH is prepared for ferric chloride coagulation treatment. Different dosages of ferric chloride are added to the POME to coagulate the suspended solids. The COD, the color and the TSS of each sample before and after the experiment are measured and recorded.

2.4. Chemical oxygen demand

The COD before and after the experiment was measured according to the APHA method for Examination of Water and Wastewater using HACH reagent (Loveland, Colorado, United States). The colorimetric determination of COD was carried out at 620 nm with a HACH spectrophotometer, DR 6000 (Loveland, Colorado, United States). Samples were heated for 2 h with sulfuric acid and strong oxidizing agent potassium dichromate. The reduction reaction is shown in Eq. (1).



The amount of Cr^{3+} produced is measured at wavelengths and reflected in mg/L of COD.

2.5. Biochemical oxygen demand

The BOD before and after the experiment was measured by Standard Method 5210 B [8]. Dissolved oxygen (DO) was measured by YSI 5000 dissolved oxygen meter. The method started with the filling of a specified sized airtight bottle with a diluted and seeded sample to overflowing and incubating it at the specified temperature for 5 d. DO is measured initially and after incubation, and the BOD reading is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement. The measurement of BOD is shown in Eq. (2).

$$\text{BOD} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{(D_1 - D_2) - (S)V_s}{P} \quad (2)$$

Table 1
Characteristic of raw and treated POME and DOE discharge limit [2]

Parameters	Raw POME	Treated POME	DOE discharge limit
Temperature (°C)	85	25–30	45
pH	4.2	8.4	5.0–9.0
Oil and grease (mg/L)	6,000	–	50
BOD (mg/L)	25,000	580	100
COD (mg/L)	51,000	4,500	–
TS (mg/L)	40,000	–	1,500
TSS (mg/L)	18,000	130	400
TVS (mg/L)	34,000	–	–
TN (mg/L)	750	127	200
Color (ADMI)	Above 500	Above 500	200

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; S = oxygen uptake of seed, DO/mL seed suspension added per bottle ($S = 0$ if Samples are not seeded); V_s = volume of seed in the respective test bottle, mL; P = decimal volumetric fraction of sample used; $1/P$ = dilution factor.

2.6. Total suspended solid

The TSS before and after the experiment was measured according to Standard Methods Section 2540 D [9], and total solids dried from 103°C to 105°C. The treated and the untreated POME samples were evaporated in a weighed dish and dried to a constant weight in an oven from 103°C to 105°C. The increase in weight over the empty dish represents the total solids. TSS calculation is shown in Eq. (3).

$$\text{TSS} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{\left(\text{Weight of dried residue + dish} - \text{weight of dish} \right) \text{mg} \times 1,000}{\text{sample volume, ml}} \quad (3)$$

2.7. pH

The pH reading was measured with pH meter (HACH SensION 4, Loveland, Colorado, United States) with a pH electrode (HACH 51910, Loveland, Colorado, United States). The pH meter was calibrated with pH 4.0, 7.0 and 10.0 buffers.

2.8. Color

The color was measured according to the HACH method (Loveland, Colorado, United States) (Method 8025). Colorimetric determination of color was carried out at 620 nm with a HACH spectrophotometer (Loveland, Colorado, United States), DR 6000. The color may be classified as apparent or true color. The apparent color is color from dissolved materials and suspended matter, while true color is determined by the removal of suspended materials with a filter or a centrifuge. The color units are based on the APHA recommendation, where 1 color unit is equal to 1 mg/L platinum as chloroplatinate ion.

2.9. Ultrasound cavitation

The ultrasound cavitation happens when a passage of high-frequency sound wave (16–100 kHz) transmits through the wastewater. Hydrodynamic cavitation happens when a liquid is passing through a constriction that causes its fluid pressure to drop to the vapor pressure. The 200 mL POME is left for cavitation at different durations, which are at 30, 60, 90, 120, 150, 180 min. The test temperature is set at room temperature (23.5°C) and the pH is set to 11. The COD of each sample before and after the experiment is measured and recorded. This study uses an ultrasonic bath with an energy rating of 1 kW.

2.10. AC adsorption treatment

The experiment was conducted by using a different amount of dosage, which ranges from 160 mg to 4,000 mg.

Granular AC is crushed and sieved to obtain the AC, with a size of fewer than 75 μm . The small particle size of adsorbent provides a larger specific surface area for adsorption [7]. Jar tester was used to stir the sample. The stirring speed was maintained at 200 rpm and the stirring duration was 60 min. The experiment was conducted at room temperature (23.5°C). The sample is filtered to separate the AC and POME, where the filtered POME was used to measure its COD and it is color intensity.

3. Results and discussion

3.1. Effect of Chitosan dosage on POME treatment

Fig. 1 presents the effect of Chitosan dosage towards the removed percentage of the COD, the color and the TSS. Table 2 shows the statistical analysis between the Chitosan dosage and the POME treatment quality.

The optimum condition for coagulation treatment with Chitosan as a coagulant is 20 mg for 200 mL of POME (100 ppm) at pH 4.5. The removal percentage for the COD, the color and the TSS is 15.39%, 85.79 and 97%, respectively. Results showed that a further increase in dosage does not increase the color and the TSS removal significantly. Also, a further increase in dosage causes the COD to increase. The negative result of the COD removal was observed with the addition of Chitosan, which is a natural biopolymer coagulant (an impurity) that causes the COD to increase when the dosage exceeds its saturation point. In essence, the low

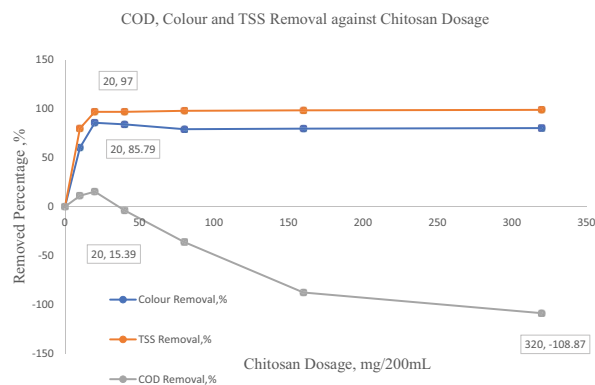


Fig. 1. COD, color and TSS removal percentage vs. Chitosan dosage.

Table 2

Statistical relationship between Chitosan dosage and POME treatment quality

Dependent variables	Correlation (r)	Significance (p -value)
Color removal	0.387	0.392
Total suspended solid (TSS) removal	0.944	0.001 ^a
COD Removal	0.422	0.346

^aOne tailed test at 95% confidence level.

COD removal was due to the natural properties of POME. The study from Musonge [10] stated that Chitosan is not effective to remove dissolved solids. Typical raw POME has a total solid of 40,000 mg/L, whilst 34,000 mg/L of it is dissolved solid [2]. Furthermore, TSS removal is very effective at low Chitosan dosage, and its result concurs with the research conducted by Ahmad et al. [11]. However, Chitosan is effective in removing suspended solids that contributes to the COD but not dissolved solids.

3.2. Effect of ferric chloride dosage on POME treatment

To determine the effect of COD and color removal against pH, the POME was added with sulphuric acid (H₂SO₄) and sodium hydroxide (NaOH) to produce the sample with different pH. The 200 mL of POME is prepared with a pH of 3, 5, 6, 7, 8, and 11. 50 mg of FeCl₃ (250 ppm) is added into the POME to coagulate the pollutants. The COD, color, and TSS of each sample before and after the experiment are measured and recorded.

On the separate experiments to determine the optimum dosage of ferric chloride for COD, color and TSS removal, the 200 mL of POME with a pH of 5 is prepared for FeCl₃ coagulation treatment. Different dosages of FeCl₃ (30, 60, 90, 120, 150, and 180 mg) are added to the POME to coagulate the pollutant. The COD, color, and TSS of each sample before and after the experiment are measured and recorded.

Figs. 2 and 3 present the relationship of POME pH and ferric chloride dosage towards color removal and COD removal percentage. Table 3 shows the statistical analysis among the aforementioned parameters.

Fig. 2 shows that the optimum working pH for ferric chloride was 5.0. Fig. 3 indicates that the TSS and color removal display similar trends as with Chitosan, whereby the removals increase when the dosage of ferric chloride is increased to 90 mg; at which, the removal percentage of the COD and color are 38.54% and 88.64%, respectively. Moreover, the further increase of the ferric chloride dosage does not increase the removal percentage of the COD and the color significantly. The COD and color removal rate drop slightly and fluctuates when a further 90 mg of the ferric chloride is added. The TSS removal rate increases proportionally with the ferric chloride dosage and reaches 91.5% at 90 mg. Further increase of ferric chloride dosage from 90 mg does not increase the TSS removed percentage significantly. Table 3 validates that ferric

chloride is effective in removing the TSS as the correlation is 0.891 with 0.007 of the *p*-value.

3.3. Effect of ultra sound cavitation time on POME treatment

The 200 mL of POME is left for cavitation for different durations which are 30, 60, 90, 120, 150, and 180 min. The temperature is set at room temperature which is 23.5°C and the pH is set as 11. The COD of each sample before and after the experiment is measured and recorded. Fig. 4 shows the effect of ultrasound cavitation time on the removal percentage of the COD, and the color.

Fig. 4 shows that the COD and the color removal percentage increases when the cavitation time increases until it

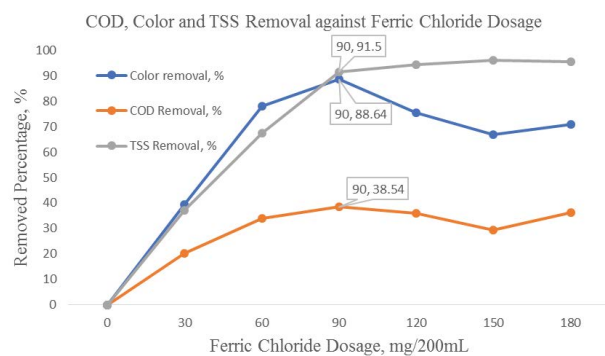


Fig. 3. COD, color, TSS removal percentage vs. ferric chloride dosage.

Table 3 Statistical relationship of ferric chloride and POME treatment quality

Dependent variables	Correlation (r)	Significance (p-value)
Color removal	0.671	0.099
Total suspended solid (TSS) removal	0.891	0.007 ^a
COD removal	0.726	0.065

^aOne tailed test at 95% confidence level.

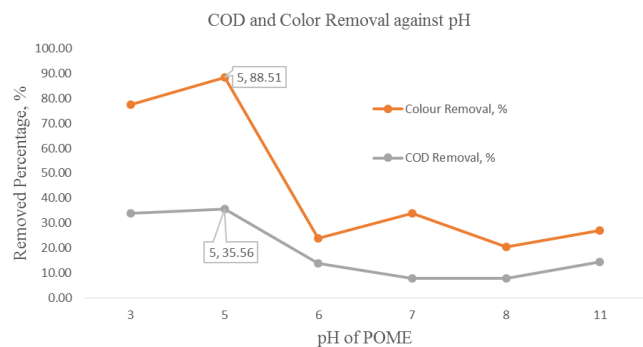


Fig. 2. COD and color removal percentage vs. POME pH.

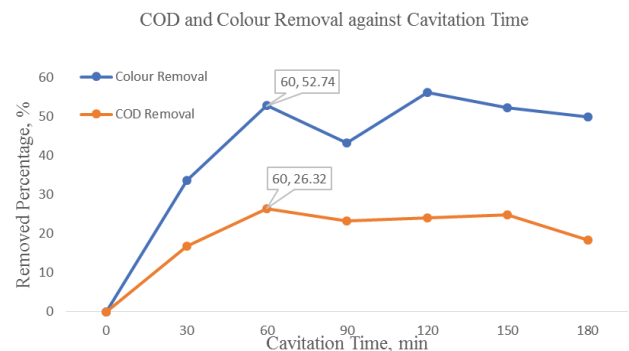


Fig. 4. COD and color removal percentage vs. cavitation time.

reached its highest percentage, which is 26.32% and 52.74% at 60 min. However, a further increase in cavitation time does not increase the COD and the color removal significantly; the COD and the color removal rate fluctuates when the cavitation time is beyond 60 min. The deduction from the results is that the best condition for ultrasound cavitation treatment is 60 min of cavitation time and pH of 11. The COD degradation is significant at alkali condition, in which pH is greater than 11, due to more hydroxyl radical (OH^*) being present in alkali. Advanced oxidation processes are the processes that degrade the organic pollutant by the powerful and reactive hydroxyl radical (OH^*). Hydroxyl radical (OH^*) generated would have an oxidation potential of 2.8 eV [12], therefore, the more the hydroxyl radical, the greater the degradation of organic pollutants.

3.4. Effect of AC dosage on POME treatment

The experiment was conducted by using a different amount of dosage. The dosage is ranging from 160 to 4,000 mg. Granular AC is crushed and sieved to get the AC size of less than $75 \mu\text{m}$. The smaller particle size of adsorbent provided a larger specific surface area for adsorption to occur [7]. Jar tester is used to stir the sample. The stirring speed is maintained at 200 rpm and the stirring time is 60 min. The experiment is conducted at a room temperature of 23.5°C . The sample is filtered to separate the AC from POME. The filtered POME is collected to measure its COD, color intensity. The 200 mL of POME is prepared for AC adsorption treatment. Different dosages of AC (160, 320, 480, 640, 800, 16,000, 2,400, 3,200, and 4,000 mg) are added to the POME to adsorb the pollutant. The COD and color of each sample before and after the experiment are measured and recorded. Fig. 5 shows the effect of AC dosage on the removal percentage of the COD and the color.

From Fig. 5, both the COD and the color removal percentages show a similar trend as they increase with the dosage of AC. Both the COD and the color removal increase and reach a saturated point at 800 mg of AC; at which point, the COD and color removal percentage are 64.25% and 99.16%, respectively. Further increase in AC dosage does not increase either the COD or the color removal percentage significantly.

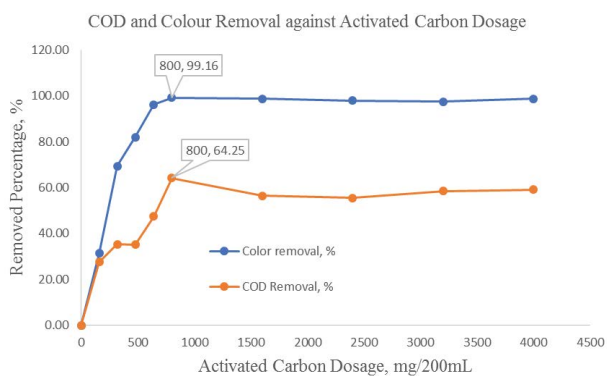


Fig. 5. COD and color removal percentage vs. AC dosage.

The removal rates fluctuate with a further increase of dosage after 800 mg of AC. Therefore, the results indicate that the best adsorption occurs at 800 mg of AC for 200 mL of POME (4,000 ppm). As aforementioned, at 800 mg, the color removal percentage is 99.16% and thus produces very clear treated POME. The increasing trend of removal percentage for the COD and the color was due to the increase of the specific surface area of the available AC [7]. The specific surface area could be increased by increasing the dosage of AC, therefore, the larger the specific surface area, the higher the rate of adsorption.

3.5. Hybrid treatment with combination of ultrasound cavitation, Chitosan and ferric chloride

This study combines ultrasound cavitation, Chitosan and ferric chloride (FeCl_3) in different ways to determine the best combination and order of treatment. Every treatment method is conducted by following the result of the optimum condition obtained from the previous experiment. The result is shown in Fig. 6.

From the graph, the COD removal for the combination of ultrasound (US) cavitation, followed by ferric chloride coagulation treatment, is the highest, at 56.26%. Also, the color removal for this combination is the highest among other combinations, at 92.41%. Furthermore, among all these combinations where Chitosan is present, the COD removal percentage is less substantially, ranging from 35.1% to 40.12%, which can be seen at the combination of US- FeCl_3 (ultrasound and ferric chloride) that shows the COD removal at 56.26%. However, when Chitosan is added after it, the COD removal percentage drops to 38.61%, due to Chitosan being a natural coagulant that is biodegradable [13]. Chitosan is not very effective in coagulating the organic pollutant (COD), which dissolved in the POME [10]. Therefore, Chitosan will become the pollutant, contributing to COD and causing the COD removal percentage to decrease.

3.6. Hybrid treatment of ultrasound cavitation, ferric chloride and AC

Fig. 7 shows the effect of hybrid treatment with ultrasound cavitation, ferric chloride, and AC. It was found that the hybrid treatment of the US, FeCl_3 , and AC has triggered the COD, the BOD, the color and the TSS removal percentage to increase up to 88.05%, 89.74%, 99.9% and 99.5, respectively. The AC added significantly improved the COD removal in POME from 56.26% to 88.05%.

The hybrid treatment of US- FeCl_3 -AC tends to decrease the COD, the BOD, the TSS, the color and the pH until it is below the discharge limit set by DOE. The COD removal efficiency (88.05%) decreases the COD from 962 to 115 mg/L. Also, the BOD removal (89.74%) reduces the BOD from 468 to 48 mg/L, which is lower than the discharge limit (West Malaysia: 100 mg/L, East Malaysia: 50 mg/L). The TSS removal (99.5%) reduces from 200 to 1 mg/L. Moreover, the data obtained are compared with the DOE discharge limit, as shown in Table 4. The color and the TSS removals are very high, showing efficiency of nearly 100%. Therefore, the color and the TSS in POME are easier to remove, compared to the BOD and the COD.

COD and Colour Removal against Different Treatment Combination

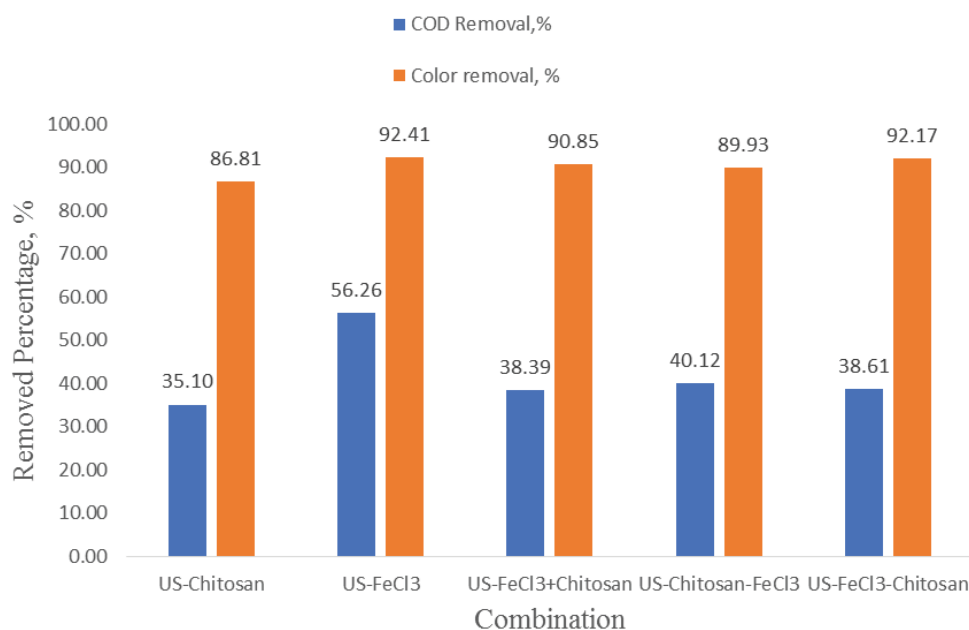


Fig. 6. COD and color removal percentage with different treatment combination.

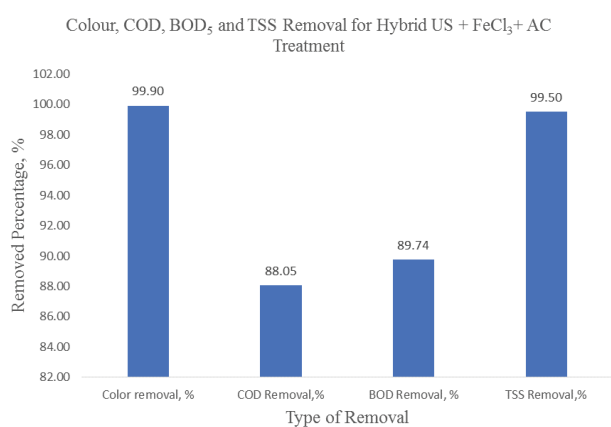


Fig. 7. Hybrid treatment performance.

Table 4
Comparison of POME sample, DOE discharge limit and treated POME

Parameters	POME sample	DOE discharge limit	US + ferric chloride + AC treatment
Temperature (°C)	33	45	23.5 ^a
pH	8.3	5.0–9.0	5 ^a
BOD ₅ (mg/L)	468	100	48 ^a
COD (mg/L)	962	–	115 ^a
TSS (mg/L)	200 ^a	400	1 ^a
Color (ADMI)	2,055	200	2 ^a

^aWithin DOE acceptable discharge limit.

4. Conclusions

This study presents the treatment performance of POME by utilizing Chitosan and ferric chloride coupled with AC and ultrasound bath. The following conclusions can be drawn from the results:

- The best treatment combination for POME treatment was with ultrasound cavitation, ferric chloride, and AC.
- The hybrid treatment was able to remove the BOD, the COD, the color and the TSS up to 89.74%, 88.05%, 99.9%, and 99.5%, respectively.
- The outcome (BOD, COD, TSS, color) complied with the discharge limit regulated by DOE Malaysia.
- Both coagulants contributed significantly to the TSS removal process. However, Chitosan performed better in lower dosage but not effective in POME treatment, in which it would become one of the contributors in increasing the COD. The optimum condition for Chitosan is 20 mg/200 mL (100 ppm).
- The optimum dosage of ferric chloride is 90 mg/200 mL (450 ppm).

For future studies, it is recommended that Chitosan be used to treat the wastewater whereby its pollutant is contributed mostly by suspended solids. POME with more dissolved solid than suspended solid is not suitable to be treated with Chitosan. However, Chitosan is biodegradable and can effectively remove color and suspended solid at very low dosage, therefore, making it a promising material in the water treatment industry that aims at the color and suspended solid removal. Lastly, although AC requires a high dosage to provide a very high removal efficiency, it may not be a problem to palm oil mill if the mill is

interested to use it as one of the treatment processes, particularly, because the palm oil mills can produce the AC by themselves.

Acknowledgement

The authors acknowledge the financial support from the University College of Technology Sarawak, Malaysia, and the support from the staff of the School of Engineering and AAA Zenith Services for reviewing the manuscript.

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