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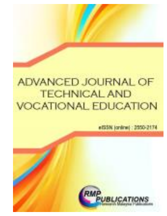

Chemical Oxygen Demand Reduction in Palm Oil Mill Effluent Treatment with Chitosan and Ferric Chloride

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Abstract: Palm oil industry is the leading agricultural industry that contributes significantly to Malaysian economy. In the meantime, this industry is also creating environmental problem due to the discharge from palm oil refineries known as palm oil mill effluent (POME). In Malaysia, there are more than 85% of palm oil mills adopted ponding system to reduce the chemical oxygen demand (COD) of POME into an acceptable limit due to its low equipment cost and easy to operate. However, ponding system requires long hydraulic retention time (HRT), huge land, release methane gases and most importantly, many mills are unable to achieve the discharge limit. In this regard, this study addressed this issue by using chitosan as natural coagulant and ferric chloride (Ferric chloride) as synthetic coagulant to decrease the COD pollutant in POME before discharge into the watercourse. To achieve the objectives of this study, a series of experiments will be carried out to determine the characteristics performances and optimum working conditions of each natural and synthetic coagulants. The most optimum working condition for POME treatment with chitosan was found to be 100ppm with pH of 4.5. As for ferric chloride was 450ppm with pH 5.0. The optimum conditions allowed the coagulants to remove COD, colour and total suspended solid up to 38.54%, 97% and 91.5% respectively which is within discharge limit set by Department of Environment. The outcome of this study would contribute to all palm oil mill that currently using ponding system to achieve environmental sustainability.

Key words: *Chemical oxygen demand, Palm oil mill effluent, Water treatment, Coagulant*

INTRODUCTION

Palm oil industry is the leading agricultural industry with production of more than 13million ton per year [1]. This industry contributes significantly to Malaysian economy and at the same this industry is creating environmental problem due to the discharge from palm oil processing mill known as palm oil mill effluent (POME). The process of extracting crude palm oil from the fresh fruit bunch (FFB) consume a lot of water and therefore produce large volume of waste water. It was reported that about 5-7.5 tons of water is required to produce one ton of crude palm oil and more than 50% of these water would become POME [2]. In year 2014, it was estimated 19.66 million tons of crude palm oil produced with approximately 44 million cubic meter of POME generated [3]. If the raw POME is discharged into environment without any further treatment, the biochemical oxygen demand (BOD) discharged is the same as the waste generated by 75 million people which is the 2.5 times of the current Malaysia's population [3]. It was also reported that POME is 100 times more polluting than domestic sewage [4]. This POME will undergo biodegradation and used up dissolved oxygen in the water which will kill the fish in the river. Excessive nitrogen discharge can pose several pollution and health issues. Nitrogen in the form of ammonia will create oxygen demand on a receiving stream. Ammonia itself is high in pH and also toxic to fish. The nitrogen discharged will enhance the growth of algae (eutrophication). Furthermore, the presence of nitrates in drinking water can cause methemoglobinemia or blue baby syndrome. The high concentration of suspended solid will settle to the bottom of the river and undergoing biodegradation

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which cause sludge oxygen demand (SOD) and deplete the dissolved oxygen [5].

The most popular method to treat the POME in Malaysia is ponding system as its low equipment cost and easy to operate. In Malaysia, there are more than 85% of palm oil mills adopt this method to reduce the BOD and COD of POME into an acceptable limit [6]. In ponding system, the POME is undergoing biological treatments which include anaerobic digestion process followed by aerobic ponding with hydraulic retention time of 40 days or above. However, ponding system also cause some drawbacks which long hydraulic retention are time (HRT), huge land needed and the release of greenhouse gases (methane). There are also many palm oil mills which are unable to achieve the discharge limit by using ponding system [7]. Table 1 shows the typical characteristic of raw and treated POME obtained from the discharge point of local palm oil mill in Malaysia and also DOE discharge limit. The BOD is higher than the discharge limit set by Department of Environment (DOE) [2].

Table 1: Characteristic of Raw and Treated POME and DOE Discharge Limit

Parameters	Raw POME	Treated POME	DOE Discharge Limit
Temperature (°C)	85	25-30	45
pH	4.2	8.4	5.0-9.0
Oil & Grease (mg/L)	6000	-	50
BOD (mg/L)	25000	580	100
COD (mg/L)	51000	4500	-
TS (mg/L)	40000	-	1500
TSS (mg/L)	18000	130	400
TVS (mg/L)	34000	-	-
TN (mg/L)	750	127	200
Color (ADMI)	Above 500	Above 500	200

This study addressed this issue by using chitosan and ferric chloride as natural and synthetic coagulant to decrease the pollutant in POME before discharge into the watercourse. The outcome of this study would contribute to all palm oil mill that currently using ponding system to achieve environmental sustainability.

Research Objective

The main objective of this study is to determine the optimum dosage of chitosan and ferric chloride to degrade the palm oil mill effluent (POME) by reducing COD, colour and total suspended solid (TSS).

LITERATURE REVIEW

Conventional Method in POME Treatment

The natural chemical properties of the POME make it easily treated by biological approach. Currently there are three biological processes employed in the palm oil industry which are anaerobic, facultative anaerobic, and aerobic treatments. The anaerobic treatment is the major part which in removing pollutant (COD)[8]. In anaerobic treatment process, it involved four main stages which are hydrolytic, acidogenic, acetogenesis and methanogenic.

i. Hydrolysis: The process begins with bacteria hydrolysis of insoluble organic polymers (carbohydrate) and complex organic compound (protein and lipid) to make them available for other bacteria. Hydrolytic microorganisms will secrete extracellular enzymes for hydrolysis. This process will convert organics into simpler molecule such as amino acids, glycerol, triglycerides, sugar and fatty acids.
ii. Acidogenesis: In this process, the hydrolyzed or soluble products from the first stage are further broken down by acidogen into simpler organic compound such as volatile fatty acid (VFA), ammonia, carbon dioxide, hydrogen and hydrogen sulfide.
iii. Acetogenesis: The simple molecule from the previous stage are further digested by acetogens to produce carbon dioxide, hydrogen and acetic acid.
iv. Methanogenesis: The acetic acid, hydrogen and volatile fatty acid (VFA) are converted to methane, carbon dioxide and water by methanogens.

Ponding System

The ponding system is a combination of a series anaerobic, facultative, and algae (aerobic) ponds. Ponding system especially anaerobic and facultative ponds require less energy as it does not need mechanical mixing, operation control or monitoring. The major drawback of ponding system is a large area of land is needed to accommodate a series of ponds to achieve the discharge limit [8]. In constructing the ponds, the depth is the main consideration for different ponds. The length and the width is differ based on the availability of the land. The optimum depth for the anaerobic pond is 5-

7m, facultative anaerobic pond is 1-1.5m and aerobic pond is 0.5-1m. The effective hydraulic retention time (HRT) of anaerobic, facultative anaerobic and aerobic ponds are 45, 20 and 14 days, respectively [8].
The problems arise from the ponding system is the formation of scum. Scum is formed when the bubbles rise to the surface together with the fine suspended solids. This is caused by the by the oil and grease presence in the POME. Another drawback of the ponding system is the solid sludge accumulates at the bottom of the ponds. This will affect the effectiveness of the pond as it decrease the volumetric capacity and hydraulics retention time (HRT) [8]. Therefore, de-sludging is required when the sludge is more than one third of the pond.

Coagulants
Chitosan is a kind of biopolymer coagulants which is non-toxic, biodegradable, renewable and environmental friendly [9]. Chitosan is a type of marine polymer which has been widely used in practical fields such as waste water management, pharmacology, bio-chemistry and biomedical. Chitosan is a cellulose-like polyelectrolyte biopolymer which derived from de-acetylation of chitin. Chitin can be easily found in marine nature, it is occurring in the insects, yeast, fungi and exoskeletons of crustaceans [10]. Chitosan contains high amount of amino functions that provide novel binding properties for heavy metals in waste water [11]. Chitosan can coagulate effectively at pH less than 4.5 as strong acidic condition exaggerates POME to form unstable flocs [12].

The mechanisms involve in the coagulation can be divided into two main categories which are charge neutralization or electrostatic interaction and sweep coagulation/co-precipitation [13]. The chitosan coagulation process is charge neutralization while ferric chloride (Ferric chloride) is sweep coagulation as shown in Figure 1 [14]. The flocs formed by charge neutralization are smaller than the flocs formed through sweep coagulation [15]. The smaller sized flocs could bring fouling risk to the membrane if membrane technologies are used.

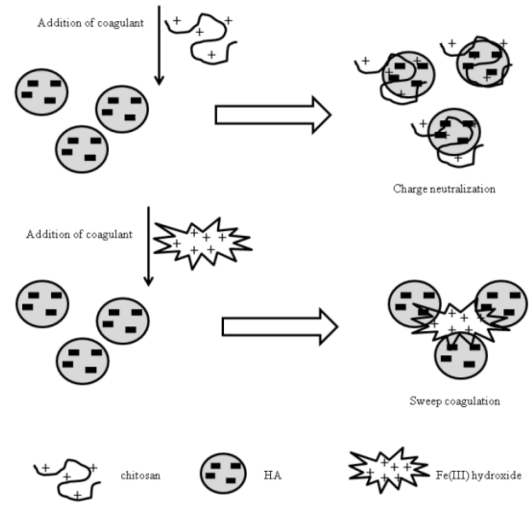

Fig 1 Chitosan charge neutralization and ferric chloride sweep coagulation

RESEARCH METHODOLOGY

To achieve the objective of this study, the methodology plan is divided into 2 phases shown below and in Figure 2.

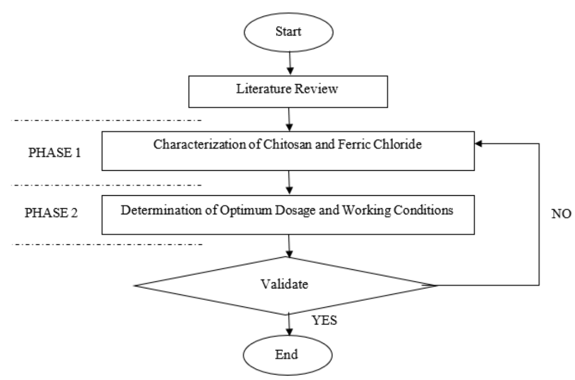

Fig 2 Research methodology

Phase 1: Natural and Synthetic Coagulants Characterization
In this phase of work, POME samples are collected from local palm oil refineries. Scientific publication in this area are reviewed. A series of experiments are carried out to determine the characteristics and performances of each natural and synthetic coagulants.

Phase 2: Determination of the Optimum Dosage and Working Conditions of the Coagulants
In this phase, a series of experimentations will be carried out in laboratories to determine the optimum dosage and working conditions of the natural and synthetic coagulants in POME treatment. The natural or synthetic coagulants or the combinations will be determined.

RESULT AND DISCUSSION

Effect of Chitosan Dosage on POME Treatment

The 200mL of POME with pH of 4.5 is prepared for chitosan coagulation treatment. Different dosages of chitosan (10mg, 20mg, 40mg, 80mg, 160mg, 320mg) were added to the POME to coagulate the pollutant. The COD, colour and TSS of each sample before and after experiment is measured and recorded. The result is shown in Figure 3. The output for statistical analysis is shown in Table 2.

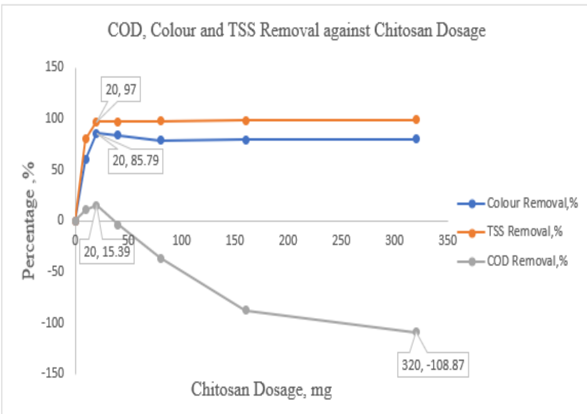

Fig 3 Chitosan dosage in POME treatment

Table 2: Statistical Relationship of Chitosan Dosage and POME Treatment Qualities

Dependent Variables	Correlation (r)	Significance (p-value)
Colour Removal	0.387	0.392
Total Suspended Solid (TSS) Removal	0.944	0.001**
COD Removal	0.422	0.346

**One tailed test at 95% confidence level

The optimum condition for coagulation treatment using chitosan as coagulant is 20mg for 200mL of POME (100ppm) at pH 4.5. The COD removal, colour removal and TSS removal is 15.39%, 85.79 and 97%. The further increase in dosage does not significantly increase the colour and TSS removal. At the same time, further increase in dosage will cause the COD to increase. The negative result of COD removal was observed when further addition of chitosan. This is due to the fact that chitosan is a kind of natural biopolymer coagulants in which itself is the impurities which cause COD to increase when the dosage exceeds the saturation point. The COD removal is not high enough is caused by the natural properties of POME. A study from Musonge stated that the chitosan is not effective in removing dissolved solid [16]. Raw POME has the total solid of 40000 mg/L while 34000 mg/L of them is dissolved solid [2]. On top of that, TSS removal is also very effective at low dosage. This TSS removal result have the same trend with the research that had been conducted by Ahmad [10]. Chitosan can effectively remove colour and TSS, but not COD as it can only remove COD which is contributed by total suspended solid (TSS), but not total dissolved solid (TDS).

Effect of Ferric Chloride Dosage on POME Treatment

The 200mL of POME with pH of 5 is prepared for Ferric chloride coagulation treatment. Different dosages of Ferric chloride (30mg, 60mg, 90mg, 120mg, 150mg, 180mg) are added to the POME to coagulate the pollutant. The COD, colour and TSS of each sample before and after experiment is measured and recorded. The findings are presented in Figure 4. The output for statistical analysis is shown in Table 3.

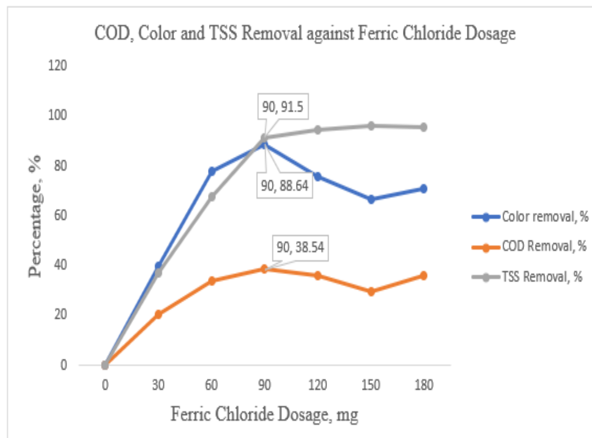

Fig 4 Ferric chloride dosage in POME treatment

Table 3: Statistical Relationship of Ferric Chloride and POME Treatment Qualities

Dependent Variables	Correlation (r)	Significance (p-value)
Colour Removal	0.671	0.099
Total Suspended Solid (TSS) Removal	0.891	0.007**
COD Removal	0.726	0.065

**One tailed test at 95% confidence level

The COD and colour removal showed similar trend in which the removals are increasing when the dosage of Ferric chloride is increased until it reached 90mg. The removal at 90mg are 38.54% and 88.64% respectively. The further increase of the Ferric chloride dosage does not significantly increases those removal. COD, and colour removal rate drop slightly and fluctuate when the

Ferric chloride is added after 90mg. For TSS removal, the removal is also increasing when the dosage of Ferric chloride increases until it reaches 90mg with removal of 91.5%. Any further increase in Ferric chloride dosage after 90mg does not significantly increase then TSS removal. Ferric chloride is significant in TSS removal as shown in Table 3 to validate the experimental results obtained.

CONCLUSION

This study concludes that both coagulants significantly contributed in TSS removal process. However, chitosan performed better in lower dosage but not effective in POME treatment in which itself will become one of the contributors to increase COD. The optimum condition for chitosan is 20mg/200mL (100ppm). As for ferric chloride, the optimum dosage is 90mg/200mL (450ppm). For future study, the individual coagulant could be combined with other polishing methods such as ultrasound cavitation to achieve better performance in POME treatment.

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