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Effluent Quality of Anaerobic Palm Oil Mill Effluent (POME) Wastewater Using Organic Coagulant

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Abstract: ***Due to the increasing awareness about the toxicity of inorganic coagulants, several investigations have been done to replace/reduce inorganic coagulants with biodegradable and eco-friendly coagulants/flocculants. Applying Organo-floc coagulant would be a reasonable alternative for the typical inorganic coagulants. Shifting from biological and chemical to coagulation-flocculation treatment could lead to improved effluent treatment as well as gaining additional benefits through the recovery and recycling of water to the plant with minimum treatment. Compared with common chemical flocculants, bio-flocculants (Organo-floc) are safe and as biopolymers are biodegradable, hence the sludge can be efficiently degraded by microorganisms. Alum and organo-floc will be used as coagulants for POME treatment with the aid of flocculant. Dosage of coagulant and flocculant, pH of raw POME, speed and time of rapid mixing were varied accordingly for each run of the experiments was operated to treat wastewater for the simultaneous removal of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in order to learn more about the integrated system. Coagulation-flocculation organo-floc shows capability to treat anaerobic POME wastewater as great as alum does whereby organo-floc can remove almost 71% of solid from the wastewater by comparing to alum which only can remove at 65% of solid but for COD removal alum show 50% removal higher efficiencies of removal compared to organo-floc.***

Keywords: Palm oil mill effluent (POME), *organo-floc,* coagulant, flocculant.

1. Introduction

The Malaysian palm oil industry is growing rapidly and quickly becoming a significant agriculture-based industry in this country. The total production of crude palm oil in 2008 and 2009 were 17,734,441 and 16,044,874 tonnes respectively [1]. Malaysia nowadays is well known as one of major agriculture based-industry in South East Asia. The high production of crude palm oil reported by MPOB for year 2008 and 2009 that shows results in large amount of palm oil mill effluent (POME) which are 17,734,441 and 16,044,874 respectively [2], [3]. It is estimated that 5-7.5 tonnes of water are required for producing 1 tonne of crude palm oil and half of the water will end up as POME [4].

Generally, 1 tonne of crude palm oil production requires 5-7.5 tonnes of water; more than 50% of the water will end up as POME [4]. POME has been identified as one of the major sources of water pollution in Malaysia due to its high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) concentrations. Hence, the Malaysian government enacted Environmental Quality Acts (EQA) in 1978 and set parameter limits for the discharge of POME into the environment [5].
New planted area of oil palm that has been reported in 2011 already reached 5.00 million hectares, which are 0.15 million (3.0%) higher that what has been recorded in 2010 [6].Therefore in 2011, 18.91 million tons of crude palm oil (CPO) or 11.3% has been produced in that year [7] and 30 million tons of Palm Oil Mill Effluent (POME) generated by this number of CPO [8]. POME is a colloidal suspension formed from the mixture of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids [9]. Fresh POME is in brownish color. POME which is high in temperature (80-90°C) has a very high biological oxygen demand (BOD) as well [1].

The standards for POME discharges into the watercourses was proposed and legalized by Malaysian Government in 1977 [10]. Since then, POME from palm oil mills need to be treated before discharge it into the waterways. Therefore large amounts of POME from palm oil mills industry can give us high impacts to our environment if it is not treated properly prior to an acceptable level before it is discharge to the environments.

Table 1 shows the limits for parameters of effluent to be discharged into watercourses in Malaysia (Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations, 1977).

Table 1: Limits for parameters of POME to be discharged into a watercourse in Malaysia (Laws of Malaysia, 1994)

Parameter[a]	Limits according to periods of discharge					
	1/7/1978–30/6/1979	1/7/1979–30/6/1980	1/7/1980–30/6/1981	1/7/1981–30/6/1982	1/7/1982–31/12/1983	1/1/1984 and thereafter
BOD_3[b]	5000	2000	1000	500	250	100
COD	10000	4000	2000	1000	-	-
Total solids	4000	2500	2000	1500	-	-
Suspended solids	1200	800	600	400	400	400
Oil and grease	150	100	75	50	50	50
Ammoniacal nitrogen	25	15	15	10	150[c]	150[c]
Total nitrogen	200	100	75	50	300[c]	200[c]
pH	5.0-9.0	5.0-9.0	5.0-9.0	5.0-9.0	5.0-9.0	5.0-9.0
Temperature	45	45	45	45	45	45

With the introduction of effluent discharge standards imposed by the Department of Environment in Malaysia, the high COD and BOD loading of POME together with the colloidal nature of the suspended solids has to be treated before being released to the environment. This poses a great challenge to the palm oil industry in balancing the environmental protection, its economic viability, and sustainable development.

1.1 Coagulation and Flocculation

1.1.1 Theory and concept

Coagulation is a process where the colloidal particles in wastewater are destabilized so that aggregation of small particles into larger ones can occur as a result of particles collisions.

The term *chemical coagulation* includes all of the reaction and mechanisms that involves in the chemical destabilization of particles and followed by aggregation of particles in size range from 0.01 to 1 μm to form larger particles through flocculation [11].

The purpose of the coagulation process is to remove the colloidal particles that are present in the water and wastewater which have large surface area per unit volume and cannot be removed by conventional physical treatment method such as sedimentation. All colloidal particles are electrically charged (positive or negative) with respect to the surrounding medium. This create a repulsive force among the colloidal particles, prevent them from collide with each other and aggregates.

1.1.2 Application of coagulation and flocculation in POME treatment

Previous studies about the biological treatment of POME by anaerobic and aerobic digestion have shown that the constraints of these methods lie on the availability of sufficient land for the construction of ponds and the length of HRT taken to treat the POME.

Alternatively, coagulation and flocculation can be applied in the treatment of POME due to its short retention time and low capital costs. Coagulation and flocculation was used by [4] as the first stage chemical treatment in the pre-treatment of raw POME before the membrane filtration process show a reduction of COD by 35%.

Typically, the coagulants used include hydrolyzing metallic salts such as aluminiumsulphate (alum) and ferric sulphate, pre-hydrolyzed metal salts such as polyaluminium chloride (PACl) and polyiron chloride (PICl) and synthetic cationic polymers such as polyalkylene and polyamines. Hydrolyzing metal salts have poor capacity to eliminate organic particles but have a good capacity for adsorbing natural organic matter (NOM). On the other hand, synthetic cationic polymer coagulants eliminate organic particles effectively, but adsorb NOM poorly.

Natural coagulants have become increasingly important and being studied widely for their practicability to be used in wastewater treatment. Natural coagulant such as *organo-floc* and Moringa Oleifera which are extracted from plants or animals are environmentally friendly and can be a replaceable alternative to chemical coagulant. In addition, natural coagulants produce readily biodegradable and less volume of sludge that amounts only 20-30% that of alum treated counterpart [12].

1.2 Aluminum Sulphate (Alum)

Aluminium sulphate is a chemical compound with the formula $Al_2(SO_4)_3$. It forms a number of different hydrates, of which the hexa-decahydrateAl_2 $(SO_4)_3$•$16H_2O$ and octa-dechydrate Al_2 $(SO_4)_3$•$18H_2O$ are the most common. Aluminium sulphate is rarely, if ever, encountered as the anhydrous salt. Aluminium sulphate is one of the most widely used coagulants in conventional water and wastewater treatments [13]. It is very effective in attracting inorganic suspended solids. In this study, Al_2 $(SO_4)_3$•$18H_2O$ is used as coagulant in the coagulation and flocculation process.

1.3 Natural Coagulants as Alternative Resources

Coagulation/flocculation promotes the aggregation of cellular matter found in POME and enables particles to reach sufficient size that they settle to the bottom of sedimentation tanks.

Facilitating the sedimentation process is common practices used treat various kinds of wastewater [14]. Whatever the coagulation technique chosen, it should not harm secondary use of the water whether downstream in a river or spread on agricultural lands. Inorganic salts (aluminium and ferric sulphates and chlorides), synthetic organic polymers (polyacrylamide derivatives and polyethylene amine) are common coagulants due to low cost and effectiveness at promoting sedimentation and as such has drawn significant research attention.

Inorganic coagulants such as those listed above tend to harm microorganisms in receiving waters and in agricultural soils. Alum, for example, is a proven coagulant but resulting sludge kills microorganisms and remaining wastewaters cannot be used for aquaculture. Sludge may not be used in the production of animal feeds or fertilizer. There may even be a link between these inorganic coagulants and Alzhemier's disease and carcinogenesis. They must be therefore kept from entering human food supply systems [14-15]. Organic coagulants that are environmentally friendly are the natural alternative to inorganic salts and polymers.

1.4 Organo-floc

Organo-floc is a low molecular weight cationic organic polymer which can act as a coagulant and also as a flocculant as well.This criteria may differ from other organic coagulant that can function both in the same time was supplied by WaterChem Pte Ltd. *Organo-floc* and acts in colloidal systems, neutralizing charges and creating electric bonds between particles, making them unstable. This produces floc and causes the sedimentation of suspended solids inside wastewater. *Organo-floc* effectively performs in a pH range from 4.5 to 8.0 and detailed characteristics are described in Table 2.

As an organic coagulant-flocculant, it is completely biodegradable and can totally digest during the various biological stages of the process. *Organo-floc* ensures the characteristics of coagulant and flocculants remain unchanged if stored in dry premises with ventilation and properly protected from sunlight. *Organo-floc* is packed in easy-to-handle 25kg/bags. Detailed characteristics of *Organo-floc* are described in Table 2.

Table 2: Specification of *Organo-floc*

Product Specification[a]	
Physical aspect	Powder
Moisture in package , %	4.5 – 6.5
pH (10% solution)	1.8 – 2.7

[a] Source : WaterChem Pte.Ltd

1.4.1 Advantages of Organo-floc

Organo-floc comes in organic powder form. It makes particles in a colloidal suspension unstable and enduces floc and subsequent sedimentation by neutralising ionic charges and making the particles unstable. Compared with other coagulants, *Organo-floc* can act as a coagulant and flocculant as well. One of the characteristics of *Organo-floc* is that it does not alter the pH of the anaerobic POME wastewater. This is because *Organo-floc* does not reduce the naturally occurring alkalinity. As such, *Organo-floc* performs well effective in a pH range from 4.5 to 8.0.

There are many advantages to using *Organo-floc* as a coagulant-flocculant. It can lead to a reduction in the consumption and handling of chemical products such as aluminium sulphate and it works efficiently in removing COD percentage in the wastewater studied. It also works well in the removal of oils and greases that exist in the anaerobic POME wastewater that was used in this research. The most important thing, however, is that *Organo-floc* is an organic sludge without any restriction for use in land farming systems and usage of the product is compatible with posterior biological treatment. Therefore, *Organo-floc* results in the environmental friendly generation of biodegradable sludge in wastewater treatment. *Organo-floc* coagulant-flocculant can increase the efficiency in physical/chemical treatment of various wastewater treatments and resulting effluent has a final pH of around 7.0 without need for correction with alkalizing agent.

There are several factors that influence the coagulation/flocculation process. The particular type of coagulant and flocculant, alkalinity or acidity of the wastewater, its temperature, and the speed and duration of mixing are all variables. Optimising them improves the efficiency and success of follow on biological treatment.

1.4.2 Organo-floc and Advantages of Organo-floc

Organo-floc is an organic powder form that can acts in colloidal systems neutralising charges and creating electric bonds between particles, making them unstable, producing flock and causing their sedimentation.

By comparing with other coagulant, *organo-floc* can act as coagulant and flocculant as well. The characteristics of *organo-floc* does not alter the pH of the anaerobic POME wastewater that being treated because it does not consume the environment's alkalinity and at the same time *organo-floc* perform well effective in a pH range from 4.5 to 8.0.

There are many advantage of using *organo-floc* as coagulant-flocculant which it can reduction in the consumption and handling of chemical products such as aluminium sulphate and it work efficiently in removing COD percentage in the wastewater studied as well as removal of oils and greases that exist in the anaerobic POME wastewater that was used in this research.

Most important thing is, *organo-floc* is an organic sludge without restriction of use in land farming system and usage of product compatible with the posterior biological treatment. So that,*organo-floc* is environmental friendly generation of biodegradable sludge in wastewater treatment.

Organo-floc coagulant-flocculant can increased efficiency in physical /chemical treatment of various wastewater treatment and resulted effluent with final pH of around 7.0 without need for correction with alkalizing agent.

1.5 Jar Test

Traditionally, the sequence of chemical addition for coagulation operations is to first add chemicals for pH correction, then add the metal coagulant, and then add the flocculant aid. Not all these chemicals are necessarily added, but the sequence logic is often as described.

However, there are instances when other sequences are more effective, including inverting the sequence of metal coagulant and polymer addition, and the sequence of coagulant addition and pH adjustment. The best sequence for a particular application can be determined by jar test experiments.

Jar testing is a pilot-scale test of the treatment chemicals used in a particular water and wastewater treatment plant. It simulates the coagulation/flocculation process in a water and wastewater treatment plant and helps to determine the right amount of treatment chemicals added, and, thus, improves the plant's performance.

Jar tests are a well-known and valuable tool to be used to estimate the effectiveness of coagulation. Jar tests are common laboratory procedure used to determine the optimum operating conditions for water or wastewater treatment.

Jar tests are conducted by using jar testing apparatus which contains six paddles to stir the contents in six beakers respectively. One beaker acts as a control while the operating conditions can be varied among the remaining five beakers. This method allows adjustments in pH, variations in coagulant dose, alternating mixing speeds, or testing of different coagulant or types, on a small scale in order to predict the functioning of a large scale treatment operation.

By comparing the final water quality achieved in each beaker, the effect of the different treatment parameters can be determined.

1.6 Response Surface Methodology (RSM)

1.6.1 Theory of RSM

Optimization is a way of improving performance of the systems and increase in yield of the product without affecting the cost. Previously, optimization has been carried out by monitoring the influence of one-factor-at-a-time while only one parameter is changed; others are kept at constant level.

This type of optimization technique has major disadvantages which are it does not include interactive effect among the variables studied in the research and eventually it does not depict the complete effects of the parameters on the process studied. Moreover, this type of optimization technique increases the number of experiments compulsory to conduct the research that leads to an increase in the consumption of reagents and materials [16]. To solve this problem, optimization studies can be carried out using statistical technique which is known as Response Surface Methodology (RSM).

2. Materials and Methods

RSM is a design of statistical analysis and mathematical techniques that can use to develop improve and optimize processes in which a response of interest was influence by various variables and the main goal is to optimize these variables [17].

2.1 Advantages and Limitations of RSM

Many advantages of RSM while comparing to previous optimization processes (one-variables-at-a-time). Through RSM, large amount of information can be collected from small number of experiments that have been done. By using RSM also we can have an opportunity to know the interaction effects of the independent parameter studied on the response. Therefore, RSM is one of very useful design for optimization of chemical and biochemical processes to use [16].

2.2 POME Sample Collection

Sample of POME was collected from Felda Serting Hilir, Serting, Negeri Sembilan Darul Khusus (Figure 1) and was preserved at a temperature less than 40°C,but above the freezing point. It is because to prevent the wastewater from undergoing biodegradation due to microbial action [18]. Table 3 summarize detail description of each parameter.

Figure 3: Serting Hilir Palm Oil Mill

Table 3: Overview of the Serting Hilir Palm Oil Mill

Parameter	Description
Capacity	54t FFB/h
FFB processed	2007: 269,580 t FFB – Average 2005-7: 287,587 t FFB
POME treatment method	Anaerobic and aerobic ponds – 2 cooling ponds, 3 mixing ponds, 6 anaerobic tanks, 2 facultative pond and 12 algae ponds.
COD in POME (untreated)	50,000 to 65,000 mg/l (variable, depending on season)
COD in POME (discharged)	500 mg/l
POME quantities	2007: 192,372 m3 – Average 2005-7: 205,222 m3

2.2.1 Sample storage and preparation

All the anaerobic POME wastewater taken from the mill was stored in 20L container at 40°C (to ensure minimal changes of microbial communities) for microbial analysis and acclimatization [19]. Some of the container was stored at -20°C for Denaturing Gradient Gel Electrophoresis (DGGE). Freezing temperature was used to assist in disrupting and better lysis of cells that can improve measurements on microbial biomass and activity. The efficiency of coagulation and flocculation was assessed based on the removal of chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS).

2.3 Experimental Overview

In this study, anaerobic POME wastewater was taken from the mill and has been characterize. Then, the experiment start with pre-treatment using *organo-floc* (organic coagulant) and aluminium sulphate (chemical coagulant) as a comparison. These pre-treatment processes have been done using Jar Test to get a set of data *organo-floc* and aluminium sulphate respectively.

2.4 Aluminum Sulphate (Alum)

Analytical grade of aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) was obtained from Merck. For this study, aluminium sulphate was used as coagulant in the coagulation and flocculation process. To prepare the coagulant to be used in experiments, 173.684g of alum was dissolved in 1L distilled water. The solution was stirred using magnetic stirrer until the alum is completely dissolved in distilled water. The stock solution was stored in laboratory bottle for Jar test purpose.

2.5 Organo-floc

Organo-floc is a based low molecular weight cationic organic polymer which can act as coagulant, flocculant and as auxiliary flocculation agent was supplied by WaterChem Pte Ltd.*Organo-floc* acts in colloidal systems neutralizing charges and creating electric bonds between particles, making them unstable, producing floc and causing the sedimentation of suspended solid inside wastewater. *Organo-floc* effectively performs in a pH range from 4.5 to 8.0.

As an organic coagulant-flocculants, it is completely biodegradable and can totally digest during the various biological stages of the process. *Organo-floc* ensure the characteristics of coagulant and flocculant unchanged if property was stored in dry premises, ventilated room, protected from sunlight properly and as described in Table 2.

3. Analysis

3.1 Determination of Chemical Oxygen Demand (COD)

COD determination was done using standard method APHA 2005 [20]. For COD measuring; the sample measured was diluted into the desired concentration within the detectable range of COD. 2mL of diluted solution of sample was measured and pipetted into a high range COD (HACH) reagent kit vial that contain digestion solution for COD test, 0-1500 ppm. Then ensure vial cap was tightly closed before further heated in reactor block for 2 hours at 150°C.When digestion was completed, cooled down the sample before determined the COD reading by using spectrometer DR 2800 at appropriate wavelength of 620nm [20].

The COD is measured for both sample and blank and the oxygen demand from the blank was subtracted from the COD of the original sample to ensure a real measurement of the organic matter. COD value is represented by unit mg/L.

3.2 Determination of Biological Oxygen Demand (BOD)

The BOD test takes 5 days to complete and is performed using a dissolved oxygen test kit. The BOD level is determined by comparing the DO level of a water sample taken immediately with the DO level of a water sample that has been incubated in an incubator for 5 days.

The sample should diluted to lower concentration using specified dilution factor to get the desired concentration before tested.1mL of the diluted sample then was pipetted into a sealed BOD bottle.Then,1mL of each BOD reagent that prepared (Phosphate buffer solution, Magnesium Sulphate solution, Calcium Chloride solution and Ferric Chloride solution) was added in the BOD bottle. After completed, aerated distilled water was added into each BOD bottle until insertion of the stopper showed no bubbles in the bottle. The mixture in the BOD bottle then has to shake to make sure all the solution mix well.

The initial Dissolved Oxygen (DO) level was measured before the incubated the sample in incubator at 20°C for 5 days. After 5 days, DO in all diluted samples and blanks were checked [20]. Formula of calculation is as follow:

$$BOD_5(mg/L) = \frac{(D - D_2) - (S)Vs}{P} \quad (1)$$

Where,
D = DO of diluted sample immediately after preparation
D_2 = DO of diluted sample after 5 days incubation at 20°C
S = Oxygen uptake of seed
Vs = Volume of seed in the respective test bottle
P = Volumetric fraction of the sample used

3.3 Determination of Total Suspended Solids (TSS)

Measurement of Total Suspended Solid (TSS) also has determined according to Standard Method [20]. The 10 mL of well-mixed sample was filtered through standard glass-fiber filter paper. The filtration of sample is support by vacuum pump to filter the sample.

The filtered sample then transferred into a crucible dish and dried in oven for at least 1 hour at 105°C. Process of measuring TS (heating, cooling, desiccation, and weighing) were repeated until a constant weight was obtained which is the changes of weight were less than 4% of previous weight. The TSS can be calculated by using the following formula:

$$Total\ Suspended\ Solid\ (mg\ /\ L) = \frac{(A-B)x1000}{Sample\ volume,\ mL} \quad (2)$$

Where,
A = weight of dried residue + glass-fibre filter paper (mg)
B = weight of glass-fibre filter paper (mg)

3.4 Experimental Procedures (Jar Test)

Coagulation and flocculation of POME was carried out using the jar test apparatus (VelpScientifica JLT 6). A series of six beakers were filled with 500 mL of POME respectively for each test run.

The initial pH of each sample was measured using pH meter (Eutech Instruments pH Tutor) and adjusted to the desired initial pH (pH 2, pH 7 and pH 9) by adding 5M of H_2SO_4 (R&M Chemicals) or 5M of NaOH (R&M Chemicals) drop by drop into the samples. Coagulation and flocculation tests were performed using dosage of coagulant (1 mg/L, 20 mg/L and 1000 mg/L) and dosage of flocculant (1 mg/L, 20 mg/L and 40 mg/L).

After the desired dosage of coagulant was added, the POME samples were agitated at desired rapid mixing speed (250 rpm and 300 rpm) and rapid mixing time (30 s and 180 s). The slow mix (50 rpm and 20 min) operation was then applied; flocculent was added according to the desired dosage. This is followed by final settling of 2 hours. At the end of sedimentation process, supernatants are pipetted out for COD, TS and TSS analysis. All experiments were duplicated.

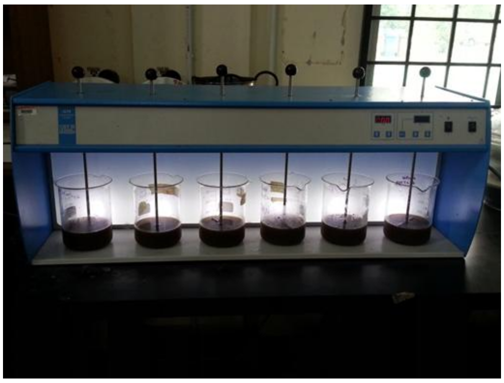

Figure 2: Jar Test Unit

Table 4: Characteristics of Anaerobically Palm Oil Mill Effluent (POME)

Parameters	Concentration [a]
pH	7.5 ± 0.2
BOD_5	1405
COD	3850
Total Suspended Solids (TSS)	452
Temperature	28 ± 1

[a] except pH and temperature all other parameters are in mg/L, temperature in °C

4. Results and Discussions

4.1 Characteristics of POME Anaerobic Wastewater

Anaerobically digested POME was obtained from Serting Hilir Mill, at Serting, Negeri Sembilan, Malaysia. Because effluent treatment practiced at Serting Hilir Mill consists of closed-type anaerobic digesters followed by use of aerobic ponds for further treatment, the POME collected for analysis had been digested in a closed-type anaerobic digester system.Within the experimental study, samples of POME were taken out and chemically analysed. Effluent characteristics from closed-type anaerobic digester before entering aerobic pond were further studied and summarized in Table 4.

POME wastewater in this study contained 3850 mg/L of COD after treatment with open ponding system. The effluent also contains high quantities of organic content represented by the value BOD5 which was 1405 mg/L exceeded regulatory standard of discharge limit of 100 mg/L which indirectly indicated that POME need to undergo pre-treatment process before directly discharge into the water bodies. Despite the fact that the concentration of TSS in this study was lower (452 mg/L) as compared to those reported by Taha and Ibrahim [21] which about 1070 mg/L, the value was still failed to meet the requirement for final discharge to river water; ~400 mg/L of TSS. Therefore, an appropriate treatment for final discharge of POME for the removal of COD and TSS need tobe developed in order to achieve the river water quality. The characteristics of the anaerobically digested POME were analyzed and summarized in Table 5.

Table 5: Characteristics of anaerobically digested POME obtained in this study and other literature

Parameters[a]	This Study	Y J Chan (2010)	Ho and Tan (1989)	Phang and Ong (1988)	Vijayaraghavan et.al (2007)
	Average Concentration	Average Concentration	Average Concentration	Average Concentration	Average Concentration
pH	7.1	7.4	7.1	7.24	7.8
BOD[b]	1520	1355	655	1938	-
COD	3040	13650	5430	20314	1372
TSS	334	12750	3100	14686	512
TN	-	320	-	-	134

[a] All parameters in mg/L except pH

[b] Sample incubated for 3days at 30°C

4.2 Characteristics of Organo-floc

Natural products such as natural organic flocculants which are based on polysaccharides or natural polymers has become widely popular due to it's environmentally behaviour. Bio-flocculants and biodegradable polymers are observed to be safer, easily available and emit no secondary pollution in comparison to conventional chemical flocculants [22]. Detail chaaceristic of *organo-floc* is as show in Table 6.

4.3 Scanning electron microscopy (SEM) micrographs

Figure 3a shows the SEM image of the *Organo-floc* particles as near-spherical nodules. In comparison to the images of *Organo-floc* after treatment (Figure 3b), the flocs produced from *Organo-floc* treatment were seen in a honeycomb-like structure with colloidal particles caught in the spaces [23].

The honeycomb-like structure stemmed from the presence of POME fibrous pollutant substances that had been set by the *Organo-floc* .From these SEM microphotographs, *Organo-floc*'s potential in anaerobic POME wastewater treatment is high, in comparison to inorganic coagulant treatments such as alum.

Table 6: Characteristic of *Organo-floc*

Type of Analysis	Concentration[a]
N	6.86
P_2O_5	0.05
K_2O	0.70
MgO	0.18
Ca	0.09
B	0.009
Cu	-0.8
Zn	196.1
Fe	35.0
Mn	11.5
pH	1.7

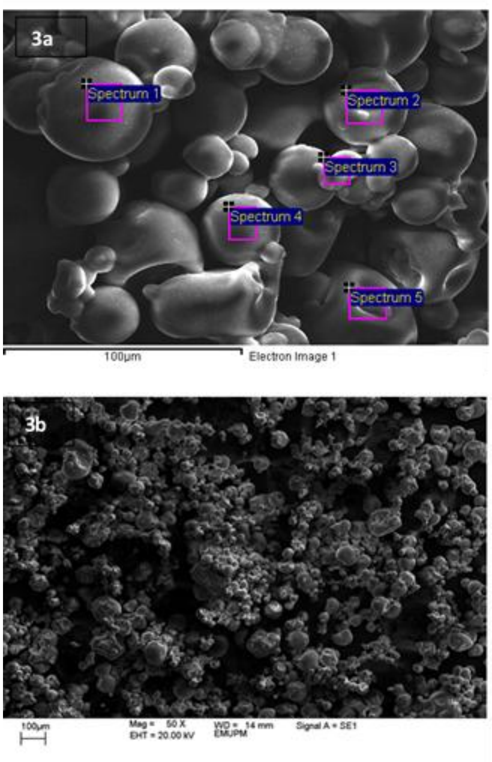

Figure 3: (a): SEM images of *Organo-floc* in powder form; (b) SEM images of *Organo-floc* and flocs formed through coagulation - flocculation process

The most popular and widely-used technique in surface analytical is scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). The high focus of scanning primary electron beam produces high resolution images, with excellent depth of field, of the surface topography. In the preliminary test, the elemental analysis of *Organo-floc* was a combination of 57.71 – 61.03% of carbon element, 20.74 – 24.88 % of oxygen, 16.35 – 100 % of chlorine and 0.86% of kalium as illustrated in Figure 4. As *Organo-floc* is high in chlorine, treatment of anaerobic POME wastewater can be implemented due to its chlorine behaviour of disinfecting action. Chlorine oxidizes itself by having a strong tendency to acquire an extra electron to complete a shell of eight, since an outer shell of eight electrons offers great stability.

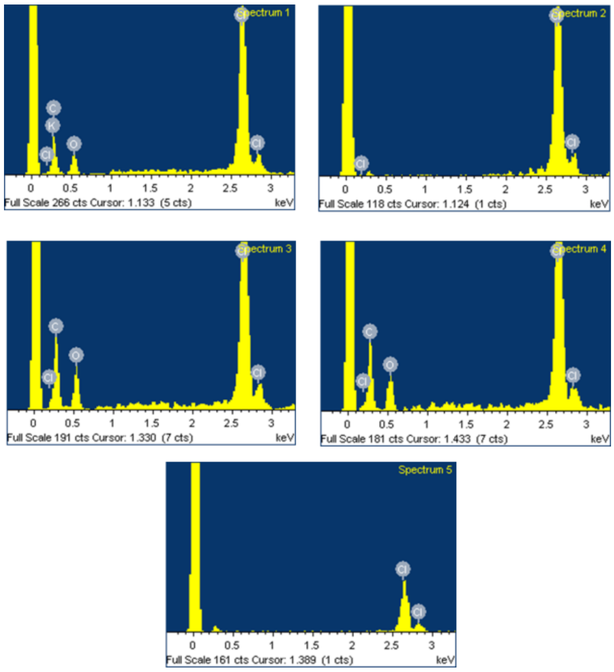

Figure 4: SEM EDX analysis images of *Organo-floc* particles

Pre-treatment of coagulation and flocculation is important choose significant coagulant-flocculant in wastewater treatment. Coagulation and flocculation is one of the methods used to treat industrial wastewater. Flocculation is a process to remove suspended particles by aggregating small particles into larger-size flocs [24].

Recently, various flocculant catagories have been developed including inorganic flocculants, organic flocculants and composite flocculants and its play an important role in industrial process to separate solid-liquid waste during primary purification [25]. In this study, two (2) type of coagulant-flocculant have been used; aluminium sulphate (alum), and *organo-floc* (organic flocculant). This research focussed on performance and capability of *organo-floc* as oganic flocculant to treat anaerobic POME wastewater by comparing to current practice in nowadays Palm Oil Mill Industry in treating their wastewater.

At the mill, alum is used at water inlet process.*Organo-floc* has been studied in this research to treat POME wastewater at early stage after clarifier tank which is the characteristic of POME wastewater is anaerobic condition. Figure 5 shows that *organo-floc* have a capability to treat anaerobic POME wastewater as well as alum does. At certain point, result shows that *organo-floc* can work even better than alum in solid removal.

From the beginning of the experiment until day-8, percentage removal of solid by *organo-floc* is lower than alum. After day-8, organic-floc shows better results as compared to alum. It may be due to organic coagulant taking longer time than chemical coagulant to react with the wastewater. Figure 6 indicates that alum has worked better than *organo-floc* as an organic coagulant in reducing COD. The relatively short catalytic may attributed to the inactivation of the *organo-floc*, hence, reduces it efficiency.

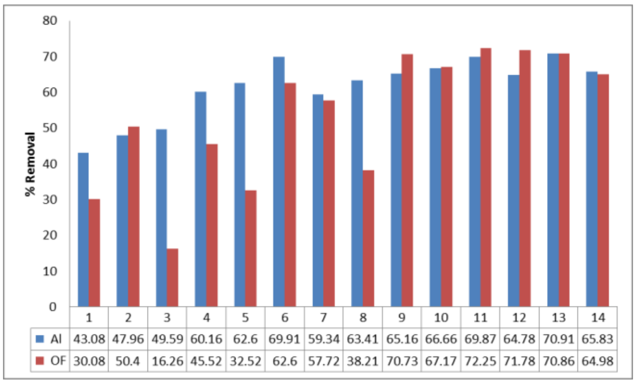

Figure 5: Solid removal of *Organo-floc* and Alum

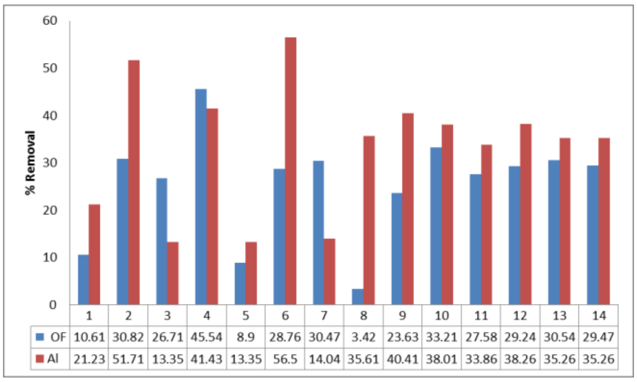

Figure 6: COD removal of *Organo-floc* and Alum. Optimization of COD and Solid Removal of POME by Different Type of Coagulant-Flocculant Using RSM

4.5 Optimization of COD and Solid Removal of POME by Different Type of Coagulant-Flocculant Using RSM

Response surface methodology (RSM) is powerful tool to determine the influences of individual factors and also their interactive manipulates. RSM is a statistical technique for designing experiments, building models, evaluating the effects of various factors and searching optimum conditions for desirable responses.

With RSM, the interactions of possible influencing parameters on treatment efficiency can be evaluated with a minimum number of planned experiments without the need for studying all possible combinations of the parameters. In this study 2-Level Factorial Design and RSM were used to design the experiments, build models and determine the optimum conditions to treat anaerobically digested POME using coagulation-flocculation process.

The statistical design was based on these factors: coagulant dosage, mixing time, mixing speed and type of coagulants. Solid and COD removal efficiencies will be taken as responses.

4.6 Two-Level Factorial Design

In this study, 2-Level Factorial Design and CentralComposite Design (CCD) were used to design the experiments, build models and determine the optimum conditions to treat anaerobically digested POME using coagulation-flocculation process. A screening process is important to identify the most significant factor affecting the flocculants POME wastewater treatment. A factorial design was used to study the effect of coagulant dosage, mixing time and mixing speed on solid and COD removal efficiencies of anaerobic POME wastewater. The experimental range for each of the factors were as follows; coagulant dosage (1-5 g/L), mixing time (15-30 min) and mixing speed (50-100 rpm).

Table 7 show the experimental design for all factors were according to 2-Level Factorial of the Design Expert Software and the responses (COD removal and solid removal) using *Organo-floc*. There was a wide variation of COD removal from 3.42-45.54% and solid removal efficiency ranging from 16.26-72.25% in the all run of experiment combinations for *Organo-floc*. This explains the importance of optimization process to increase the treatment process.

Table 7: 2-Level Factorial Design of Variables with COD Removal (%) and Solid Removal (%) as Response

Run	Factor 1 A:Dosage	Factor 2 B:Mixing Time	Factor 3 C:Speed	Factor 4 D:Type of Coagulant	Response 1 COD Removal	Response 2 :Solid Removal
1	1	15	50	organo-floc	10.61	30.08
2	5	15	50	organo-floc	30.82	50.40
3	1	30	50	organo-floc	26.71	16.26
4	5	30	50	organo-floc	45.54	45.52
5	1	15	100	organo-floc	08.90	32.52
6	5	15	100	organo-floc	28.76	62.60
7	1	30	100	organo-floc	30.47	57.72
8	5	30	100	organo-floc	03.42	38.21
9	1	15	50	alum	21.23	43.08
10	5	15	50	alum	51.71	47.96
11	1	30	50	alum	13.35	49.59
12	5	30	50	alum	41.43	60.16
13	1	15	100	alum	13.35	62.60
14	5	15	100	alum	56.50	69.91
15	1	30	100	alum	14.04	59.34
16	5	30	100	alum	35.61	63.41
17	3	22.5	75	organo-floc	23.63	70.73
18	3	22.5	75	alum	40.41	65.16
19	3	22.5	75	organo-floc	33.21	67.17
20	3	22.5	75	alum	38.01	66.66
21	3	22.5	75	organo-floc	27.58	72.25
22	3	22.5	75	alum	33.86	69.87
23	3	22.5	75	organo-floc	29.24	71.78
24	3	22.5	75	alum	38.26	64.78
25	3	22.5	75	organo-floc	30.54	70.86
26	3	22.5	75	alum	35.26	70.91
27	3	22.5	75	organo-floc	29.47	64.98
28	3	22.5	75	alum	35.26	65.83

In this research, there is two (2) coagulants that have been study with pre-treatment at early stage of research using Jar Test and with help of 2 Level Response Surface Methodology (RSM), then will choose which one (1) is more significant and will give good result. On the basis of study, dosage of coagulant, mixing time, speed of stirrer also type of coagulant were significant factors and have been selected as the variable factors for optimization.

This experiment was designed and done by two-level factorial designs as a preliminary screening test to choose most significant coagulant either aluminium sulphate or *organo-floc*. All the data that have gained throughout the experiment were analyzed using analysis of variance (ANOVA).

The analysis of the regression coefficient of COD and solid removal by *Organo-floc* are shown in Tables 8 and 9.

Variables with a 95% or higher chance of nonrandom correlation were considered significant parameters (i.e., $p<.05$). All variables such as the dosage of coagulant, mixingspeed and mixing time gave positive impact on COD removal by *Organo-floc* whereas it took only the dosage of coagulant and mixing speed with confidence level more than 95% to remove the solids. In the results, COD and solid removal by alum and *Organo-floc* gave the value of R2 more than 0.94, which means that the model could be explained more than 94% of the total variation in the model. All model were found significant with $p < 0.05$.Based on the ANOVA results, it can be concluded that the dosage of the coagulant and the mixing speed were the significant variables in producing positive impact to the COD and solid removal of POME using *Organo-floc* coagulant, indicated by p value < 0.05.

Table 8: ANOVA 2-Level Effect of Variables and Statistical Analysis of 2-Level Factorial for COD Removal (%)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	4050.185	15	270.0123	36.5147	< 0.0001	significant
A	1504.218	1	1504.218	203.4206	< 0.0001	
B	7.98256	1	7.98256	1.079509	0.3211	
C	158.3977	1	158.3977	21.42067	0.0007	
D	427.1582	1	427.1582	57.76607	< 0.0001	
AB	326.3467	1	326.3467	44.13299	< 0.0001	
AC	100.3428	1	100.3428	13.5697	0.0036	
AD	522.5608	1	522.5608	70.6677	< 0.0001	
BC	83.92317	1	83.92317	11.34922	0.0063	Series " OF" Point 7 Value: 30.47
BD	267.4121	1	267.4121	36.16306	< 0.0001	
CD	71.84304	1	71.84304	9.715582	0.0098	
ABC	261.8412	1	261.8412	35.40968	< 0.0001	
ABD	36.95141	1	36.95141	4.997067	0.0471	
ACD	171.5921	1	171.5921	23.20499	0.0005	
BCD	66.15483	1	66.15483	8.946345	0.0123	
ABCD	43.4606	1	43.4606	5.877327	0.0337	
Curvature	235.9204	1	235.9204	31.90433	0.0001	significant
Residual	81.34082	11	7.39462			
Lack of Fit	0.037526	1	0.037526	0.004616	0.9472	not significant
Pure Error	81.3033	10	8.13033			
Cor Total	4367.446	27				

Mixing times that resulted in confidence levels less than 95% were deemed not statistically significant and removed from the next optimization process. Although the dosage and mixing speed were considered significant, the optimal parameters for specific factors should be remains unknown. The optimize condition could be determined by the following optimization process in central composite design.

Table 9: ANOVA 2-Level Effect of Variables and Statistical Analysis of 2-Level Factorial for Solid Removal (%)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2665.81	15	177.72	3.17	0.0297	significant
A	472.97	1	472.97	8.44	0.0143	
B	5.00	1	5.00	0.089	0.7708	
C	666.31	1	666.31	11.89	0.0054	
D	418.22	1	418.22	7.46	0.0195	
AB	91.26	1	91.26	1.63	0.2282	
AC	116.04	1	116.04	2.07	0.1780	
AD	69.44	1	69.44	1.24	0.2893	
BC	5.00	1	5.00	0.089	0.7708	
BD	44.09	1	44.99	0.80	0.3894	
CD	2.02	1	2.02	0.036	0.8527	
ABC	284.59	1	284.59	5.08	0.0456	
ABD	116.04	1	116.04	2.07	0.1780	
ACD	76.38	1	76.38	1.36	0.2677	
BCD	143.80	1	143.80	2.57	0.1375	
ABCD	153.72	1	153.72	2.74	0.1259	
Curvature	2496.16	1	2496.16	44.55	<0.0001	significant
Residual	616.39	11	56.04			
Lack of Fit	541.36	1	541.36	72.15	<0.0001	not significant
Pure Error	75.03	10	7.50			
Cor Total	5778.36	27				

The relationship between the dosage (g/), mixing time (min) and mixing speed (rpm) can be further elucidated using response surface of two-level factorial, each at two level, which was lower (-1) and upper level (+1) range of variables. CCD was used to separate and evaluate variables that affect COD and solid removal. The effect of variables on COD and solid removal of POME wastewater are shown in Figures 7 - 8.

The RSM was employed for the optimal experimental design of the coagulation–flocculation process. From 2-Level effect of variables; parameter COD and solid removal are most significant response in this study, referring to value of probability of $F < 0.05$ which is shown in Table 8. Designing central composite design has design based on the parameter chose and calculates the value of parameter using following equation.

Final Equation in Terms of Coded Factors:

COD removal = 27.03 + 9.70 A - 0.71 B - 3.15C + 3.91D - 4.52 AB - 2.50AC + 5.71AD - 2.29BC - 4.09BD + 2.12CD - 4.05 ABC + 1.52ABD + 3.27ACD + +2.03BCD + 1.65ABCD *(Eq 1)*

Final Equation in Terms of Actual Factors:

Flocculant organofloc:

COD removal = + 7.58816 - 5.90753 (Dosage) - 0.028539 (mixing time) - 0.36986 (speed) + 0.73630(Dosage)(mixing time) + 0.22603 (Dosage)(speed) + 0.022489 (mixing time) (speed) - 0.015183(Dosage) (mixing time) (speed)

Flocculant alum:

COD removal = + 45.32280 + 0.25685 (Dosage) - 1.37557 (mixing time) - 0.48801 (speed) + 0.27968 (Dosage) (mixing time) + 0.15925 (Dosage) (speed) + 0.017808 (mixing time) (speed) - 6.39269E-003 (Dosage) (mixing time) (speed)

Final Equation in Terms of Coded Factors:

Solid removal = + 49.34 + 5.44A - 0.56B + 6.45C + 3.86D - 2.39AB - 2.69AC - 2.08AD - 0.56BC + 1.68BD + 0.36CD - 4.22ABC + 2.69ABD + 2.18ACD - 3.00BCD + 3.10ABCD *(Eq 2)*

Final Equation in Terms of Actual Factors:

Flocculant organofloc:

Solid removal = + 98.52342 - 14.22764 (Dosage) - 4.64770 (mixing time) - 1.07317 (speed) + 1.12466 (Dosage)(mixing time) + 0.34146 (Dosage) (speed) + 0.071545(mixing time)(speed) - 0.019512 (Dosage) (mixing time) (speed)

Flocculant alum:

Solid removal = + 6.55788 - 3.04878 (Dosage) + 0.84011(mixing time) + 0.52846 (speed) + 0.24390 (Dosage) (mixing time) + 0.056911(Dosage) (speed) - 0.010027 (mixing time) (speed) - 2.98103E-003 (Dosage) (mixing time) (speed)

The responses surfaces of the quadratic model for COD removal are shown in Figure 7. The surface graph indicates that the optimal conditions were exactly located inside the design boundary.

The curves with noticeable bend imply that there are significant interactions between the COD removal efficiency and the process variables, dosage of coagulant and speed of stirrer. It is clearly noted that the optimal conditions for the COD removal efficiency were located in the region where dosage of coagulant range from 5.0 to 7.0 mg/L and speed of stirrer from 50.0 to 75.00 rpm.

Organo-floc is most effective between dosages of coagulant range from 5.0 to 7.0 mg/L. Hence, dosage of coagulant range from 5.05 mg/L as shown in Table 4.4 was reasonably an optimal and effective range for maximum COD removal of 34.16%.

The responses surfaces of the quadratic model for solid removal are shown in Figure 8. The surface graph indicates that the optimal conditions were exactly located inside the design boundary.

The curves with noticeable bend imply that there are significant interactions between the COD removal efficiency and the process variables. The changes in solid removal efficiency with variables such as dosage of coagulant and speed of stirrer were studied.

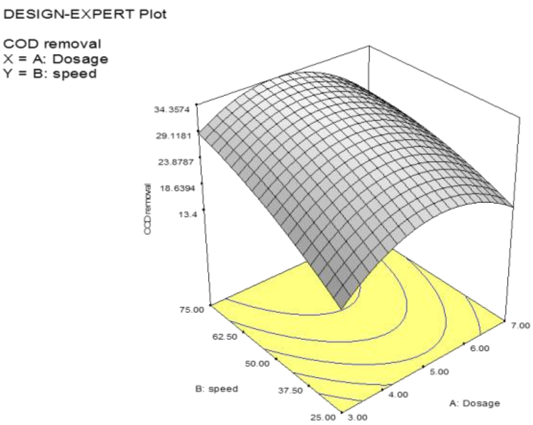

Figure 7: Dosage versus Speed of COD Removal for RSM

It can be seen that the optimal conditions for the solid removal efficiency were located in the region where dosage of coagulant range from 5.0 to 7.0 mg/L and speed of stirrer from 50.0 to 75.00 rpm. *Organo-floc* is most effective between dosages of coagulant range from 5.0 to 7.0 mg/L. Hence, dosage of coagulant range from 5.05 mg/L as shown in Table 7 is reasonably an optimal and effective range for maximum solid removal of 65.67 %.

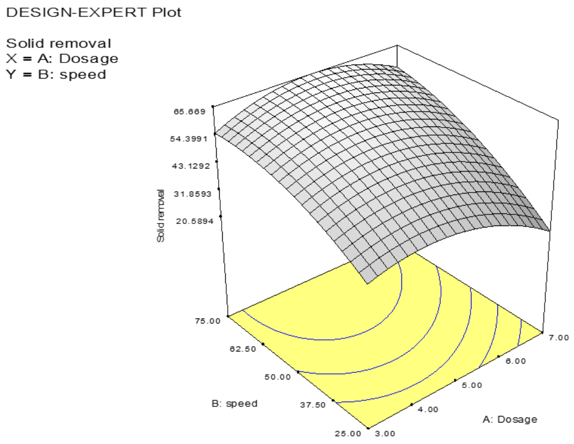

Figure 8: Dosage vs Speed of Solid Removal for RSM

The optimal conditions generated from the quadratic form of RSM models are shown in Table 9. Both predicted data are close to experimental data, in which it corresponded to the dosage of 5 g/L coagulant, speed between 75 to 90 rpm, in which it removes approximately 30% of COD and ~60% of solid.

Validity was confirmed by duplicating the statistical experiment. The condition of coagulant dosage (g/L) and mixing speed (rpm) equaled the predicted optimized condition by RSM. Under the optimal condition, the maximum COD removal and solid removal were found to be close to the predicted values, using their respective regression models. It can be concluded that RSM was appropriate for optimizing the operational conditions of the coagulation-flocculation process of POME wastewater by *Organo-floc*.

Table 9: Optimum Operating Condition Predicted by RSM

Variables and Responses	Predicted RSM
Dosage	5.05
Speed	75.00
COD removal	34.16
Solid removal	65.67

5. Conclusion

In this study a treatment of anaerobic POME wastewater prior with pre-treatment and optimization of coagulation-flocculation using RSM. Performance of *organo-floc* compared to aluminum sulphate was studied during coagulation and flocculation process. From the coagulation-flocculation *organo-floc* shows capability to treat anaerobic POME wastewater as great as alum does whereby *organo-floc* can remove almost 71% of solid from the wastewater by comparing to alum which only can remove at 65% of solid but for COD removal alum show 50% removal higher efficiencies of removal compared to *organo-floc*.

Performance of *organo-floc* compared to aluminum sulphate was studied during coagulation and flocculation process. From the coagulation-flocculation *organo-floc* shows capability to treat anaerobic POME wastewater as great as alum does whereby *organo-floc* can remove almost 71% of solid from the wastewater by comparing to alum which only can remove at 65% of solid but for COD removal alum show 50% removal higher efficiencies of removal compared to *organo-floc*.

The Response Surface Methodology (RSM) has designed 2-level factorial of variables with percentage of COD removal and percentage of solid removal as a response in this design of study and four (4) factor of operating conditions that affecting these two (2) response are (i) dosage of coagulant; (ii) Mixing time ; (iii) Speed of stirrer; and (iv) type of coagulant.The performance of the SBR was dependent of COD and Solid removal efficiencies.

From Central Composite Design (CCD) which is has been design to see optimal conditions of *organo-floc* as a coagulant shows that the set of data gained from the experiment in slightly same.That shows the accuracy of the data of experiment have been done in this research.The optimum operating condition that has been predicted by RSM in this study were at dosage of 5.05 mg/L *organo-floc* with speed of 75rpm will resulted in 34.16% of COD removal and 65.67% of solid removal.

References

[1] Wu, T. Y., Mohammad, A. W., Jahim, J. M., and Anuar, N., “Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes.” Journal of Environmental Management, 91(7), pp. 1467-1490, 2010.
[2] MPOB, “Monthly production of crude palm oil’’, 2008. [online]. Available: http://econ.mpob.gov.my/economy/annual/stat2008/ei_production08.htm. [Accessed: Jan. 12, 2010].
[3] MPOB, “*Summary of industry performance: 2009*’’, 2009. [online]. Available: http://econ.mpob.gov.my/economy/EID_web.htm [Accessed Jan. 12, 2010).
[4] Ahmad, A. L., Ismail, S., Ibrahim, N., and Bhatia, S., “Removal of Suspended Solids and Residual Oil from Palm Oil Mill Effluent,” Journal of Chemical Technology and Biotechnology, 78(9), pp. 971-978, 2003.
[5] Chan, Y. J., Chong, M. F., and Law, C. L., “Biological treatment of anaerobically digested palm oil mill effluent (POME) using a Lab-Scale Sequencing Batch Reactor (SBR),” Journal of Environmental Management, 91(8), pp.1738-1746, 2010.
[6] Mohammed, R. R., and Chong, M. F. “Treatment and decolorization of biologically treated Palm Oil Mill Effluent (POME) using banana peel as novel biosorbent,” Journal of Environmental Management, 132, pp. 237-249, 2014.
[7] Malaysian Palm Oil Council (MPOC), 2013. [online]. Available: http://www.mpoc.org.my/Default.aspx [Accessed Jan. 10, 2013].
[8] Tengku, E.M., Sultan, A.I., Hakimi, M.I., “Vermifiltration of palm oil mill effluent (POME)’’ In UMT 11th International Annual Symposium on Sustainability Science and Management, Terengganu, Malaysia, pp. 1292-1297, 2012.
[9] Malaysian Palm Oil Board (MPOB). 2009. http:// econ.mpob.gov.my/economy/EID_web.htm.
[10] Wood, B. J., “A Review on Current Methods of Dealing with Palm Oil Mill Effluent,” Planter, 53, pp. 477-495, 1977.
[11] Metcalf, E., Wastewater Engineering, Treatment and Reuse, McGraw-Hill, New York, 2003.
[12] Narasiah, K., Vogel, A., and Kramadhati, N., “Coagulation of turbid waters using Moringa oleifera seeds from two distinct sources,” Water Supply 2(5-6), pp. 83-88, 2002.
[13] F.Renault,B.Sancey,P.-M.Badot and G.Crini., “Chitosan for Coagulation/Flocculation Processes,” 45 (5), pp 1337 - 1348, 2009
[14] Ahmad, A.L., Mat Yasin, N.H., Derek, C.J.C., Lim J.K., “Optimization of microalgae coagulation process using chitosan,” Chemical Engineering Journal, 173 (3), pp. 879 - 882, 2011.
[15] Tetsuji Okuda,Aloysius U Baes,Wataru Nishijima and Mitsumasa Okuda., “Isolation and characterization of coagulant extracted from *moringa oleifera* seed by salt solution,” Water Research, 35 (2), pp. 405 – 410,2001
[16] Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., and Escaleira, L. A., “Response surface methodology (RSM) as a tool for optimization in analytical chemistry,” Talanta, 76 (5), pp. 965-977, 2008.
[17] Baş, D., and Boyacı, İ. H., “Modeling and optimization II: Comparison of estimation capabilities of response surface methodology with artificial neural networks in a biochemical reaction,” Journal of Food Engineering, 78(3), pp. 846-854, 2007.
[18] APHA, Standard Methods for the Examination of Water and Wastewater 16ed. APHA American Public Health Association, 1985.
[19] Susanne, K., Claudio, M. and Heribert, I., “Microbial community fingerprints of composts stored under different conditions,” Annals of Microbiology 4, pp. 299-305, 2005.
[20] APHA. (2005). Standard Methods for the Examination of Water and Wastewater 16ed. APHA American Public Health Association.
[21] Taha, M. R., and Ibrahim, A. H. (2014). Characterization of nano zero-valent iron (nZVI) and its application in sono-Fenton process to remove COD in palm oil mill effluent. Journal of Environmental Chemical Engineering. 2(1): 1-8.
[22] Bolto, B., and Gregory, J., “Organic polyelectrolytes in water treatment,” Water Research, 41(11), pp. 2301-2324, 2007.
[23] N. Verma et al., 2012.
[24] Khadidi, J., Al-Shorgani, M. H., Ali, N. K., Abdul Hamid E., and Kalil, M. S., “A New Flocculant-Coagulant with Potential Use for Industrial Wastewater Treatment,” In International Proceedings of Chemical, Biological and Environmental Engineering 51, 2013.
[25] Otterpohl, R., Grottker, M., and Lange, J., “Sustainable water and waste management in urban areas,” Water Science and Technology, 35(9), pp. 121-133, 1997.