



Palm Oil Mill Effluent Tertiary Treatment by Physicochemical Treatment Using Ferrous Sulphate

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A B S T R A C T

The palm oil milling industry in Malaysia will be imposed with more stringent treated waste water discharge requirement from currently at BOD of 100 ppm to BOD of 50 ppm and gradually to BOD of 20 ppm. Study was conducted to use Ferrous Sulphate as more economical coagulant to reduce the biological load for tertiary treatment in palm oil mill effluent treatment at laboratory and pilot scale facility to comply with the proposed new requirement. The feed water that was aerobically treated POME with BOD of below 100 ppm was treated with various dosage of ferrous sulphate, from 250 to 2250 ppm. It was found that at laboratory jar-test, the required ferrous sulphate dosage to meet BOD-50 ppm requirement was at 750 ppm while BOD-20 ppm requirement was achieved when the ferrous sulphate dosage was at 1,750 ppm and did not produce hazardous activated sludge. The laboratory findings was scaled-up to pilot scale facility with the capacity of 7 ton/hour to evaluate the physicochemical tertiary treatment based on continuous system. Ferrous sulphate dosage at 1,000 ppm and 1,750 ppm were able to comfortably comply with the discharge limit of BOD-50 ppm and BOD-20 ppm, respectively.

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INTRODUCTION

The palm oil industry in Malaysia is the main contributor from the agricultural sector to the national economy, which has contributed revenue of almost RM63.5 billion in 2014 from the export of palm products [1]. This is despite the oil palm plantations only covers 16 percent of the overall planted agricultural area in Malaysia, or equivalent to about 5.23 million hectares. The palm oil industry processed 95.4 million ton of oil palm fruits (Fresh Fruit Bunches (FFB)) in 429 palm oil mills throughout Malaysia that produced 19.65 million ton of CPO in year 2014.

Higher CPO production has increased the amount of waste generated from the palm oil extraction process, both solids and liquid waste. The wastes are in the form of empty fruit bunches, mesocarp fibre, palm shell,

decanter solid and liquid effluent (palm oil mill effluent (POME)) [2]. The highest waste streams is POME that makes up approximately about 0.5 - 0.8 ton of POME from every ton of FFB processed [3]. If the untreated effluent is discharged into water course, it is certain to cause considerable environmental problems due to its high pollution load in the form of biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total solids (TS) and suspended solids (SS). The palm oil mill industry in Malaysia has thus been identified as the one discharging the largest pollution load into the rivers throughout the country [4].

Almost all the palm oil mills in Malaysia are using biological anaerobic process following by aerobic process for the treatment of POME before discharge to the water way with majority of the mills are using ponding system that applied the biological processes. This means of treatment with effective control is able to meet the required discharge limit of BOD100 ppm before could be discharge to the water ways [5-6].

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Nevertheless, the Department of Environment of Malaysia has imposed more stringent requirement for treated effluent from palm oil mills especially for water catchment areas and specifically in East Malaysia whereby the BOD discharge limit have been set at either 20 ppm or 50 ppm. Tertiary treatment or polishing process are required to fulfil the more stringent requirement of the treated effluent discharge imposed by DoE of Malaysia [8-9]. Some of the commercially available tertiary treatments are membrane bioreactor (MBR), sequencing batch reactor system and aerobic suspended and submerged attached growth biological treatment processes.

The commercial tertiary treatment plant that commercially in operation mainly either using aerobic suspended and submerged attached growth biological treatment processes or membrane bioreactor [7-8]. Both processes require high capital expenditure and high operating expenditure either due to energy intensive or high maintenance cost for bio-media cleaning or membrane replacement. This will hinder individual palm oil mill owners in investing on tertiary treatment. Physicochemical process using alum based polymer though might be attractive in cost but will face difficulty in disposing the schedule waste sludge as Aluminium based sludge is categorised as schedule waste [9].

TABLE 1. Discharge limit for mill under BOD-100 ppm and typical characteristic of aerobically treated POME [9].

Parameters	Discharge limit for BOD-100	Typical characteristic
BOD	100 ppm	< 100 ppm
COD	-	< 500 ppm
Total Solid (TS)	-	4,000 – 6,000
Suspended Solid (SS)	Less than 400 ppm	500 – 2,000
Oil & Grease	50 ppm	10-30
Ammoniacal Nitrogen	150 ppm	30-70
Total Nitrogen	200 ppm	50 – 150
pH	5.0 – 9.0 (typically 8.0 – 9.0)	8.0 – 8.9
Temperature	Below 45 deg C	< 30

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difficulty in disposing the schedule waste sludge as Aluminium based sludge is categorised as schedule waste [9].

Few researchers have conducted trials using inorganic and organic polymers for the POME polishing process. Fenton oxidation has been applied to polish biologically treated POME that able to reduce the biological loads as well as the colour reduction, while hydrogen peroxide photolysis method has been in used that produced almost similar results [10]. Another researcher has studied metal coagulants such as Ferric Chloride, Aluminium Sulphate and Polyacrylamide for the tertiary treatment process, but only focused on colour reduction of the treated effluent [11,20]. Another group of researchers has conducted evaluation of the use of chemical polymers such as Alum, polyaluminium chloride (PACl), $FeCl_3$ or $FeSO_4$ and anionic polymers for the coagulation and flocculation process to reduce the biological loads of solid free-POME [12-13]. There was some reduction in biological loads such as BOD of up to 60% but was still higher than 1,000 ppm.

Alternative means of tertiary treatment based on physicochemical process is using ferrous sulphate that commonly in used coagulant in municipal waste treatment is proposed to be evaluated for POME treatment. In-depth study on physicochemical polishing treatment has not been commercially conducted to determine the effectiveness and economic viability on some of the chemical coagulants available in the market. Earlier study focused on treating supernatant recovered from POME after solid removal with the BOD range between 3,000 – 5,000 ppm but not for polishing or tertiary treatment purpose [13]. Ferrous sulphate has been selected due to its abundant availability at much competitive price in Malaysia as by-product from the manufacturing of titanium dioxide [14]. Besides, the sludge produce from the coagulation process using ferrous sulphate will not consider as harmful or categories as schedule waste that will be expensive for disposal when comparing with the use of aluminium based coagulant [9].

MATERIALS AND METHODS

Fresh aerobically treated POME (BOD less than 100 ppm) was collected from the last aerobic pond at Sime Darby mills in Carey Island, Selangor and Parit Buntar, Perak. Ferrous Sulphate Heptahydrate was obtained from Pacific Iron Sdn Bhd, Malaysia with Fe content of 20.5% minimum.

Jar-test (Velp Scientifica) experiment was conducted to determine the effective reduction of BOD using fresh aerobic treated POME for every batches of trial. Various dosage of ferrous sulphate heptahydrate at 0, 250, 500,

750, 1,000, 1,250, 1,500, 1,750, 2,000 and 2,250 ppm respectively that freshly prepared was added into 1L of aerobic treated POME collected from different day of production and location that will provide different effluent strength. It was stirred for 5 minutes before sedimentation took place for 30 minutes. The amount of supernatant and sludge sediment were measured in percentage. The supernatant samples were tested for full waste water analysis that includes BOD (YSI Dissolve Oxygen meter and Memmert incubator), COD (colorimetric method), Total Suspended Solid (TSS) and Suspended Solid(SS) (Mermmet oven), pH(Mettler Toledo pH meter), Oil & Grease (Soxchlet) and Total Nitrogen (Kjedhal method) using American Public Health Association Method for wastewater analysis. Analysis of trace metal was also conducted using ICP analyser (Perkin Elmer Model 5300DB).

The jar-test for each dosage of ferrous sulphate that was conducted in duplicate were repeated twice using fresh aerobically treated POME collected in different day. The same batch of aerobically treated POME was used for the jar-test conducted for different dosage of ferrous sulphate.

A 7 tonne/hour pilot plant was designed and installed to determine the effectiveness of the physicochemical tertiary treatment using ferrous sulphate in a continuous system. The pilot plant that was located at Sime Darby mill in Parit Buntar, Perak was consisted of ferrous sulphate dosing system, in-line mixer, 4 hours retention of static clarifier and sand filter that was designed in parallel with existing biological tertiary treatment system.

The pilot plant was operated for ten (10) hours daily and was operated for the period of one (1) month. Two hourly samples were collected from the overflow supernatant that was followed by the sand filtration and analysed for full waste water analysis.

RESULTS AND DISCUSSION

BOD and COD Reduction at laboratory scale trial

Figure 1 shows the BOD level against ferrous sulphate dosage that indicated significant reduction in the BOD level. Feed water with BOD level of below 100 ppm was able to be treated using ferrous sulphate to obtain BOD of lower than 50 ppm (ppm), while BOD of lower than 20 ppm could be achieved when the feed water BOD was below than 80 ppm. The required ferrous sulphate dosage to obtain BOD of below 50 ppm and 20 ppm were at 750 ppm and 1,750 ppm respectively. Figure 2 shows the COD reduction as against ferrous sulphate dosage, which also showing almost similar trend. However, the quantum of COD reduction was

lower when compared to BOD reduction via ferrous sulphate coagulation process.

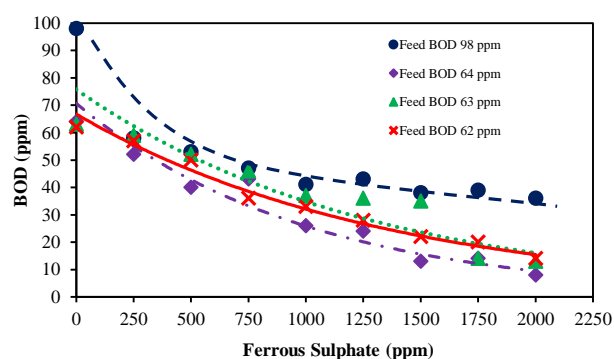


Figure 1. BOD level against ferrous sulphate dosage

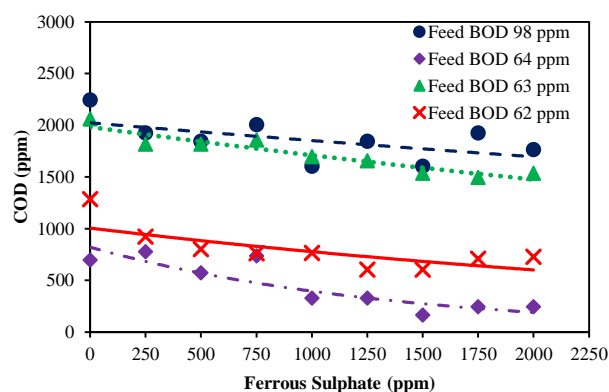


Figure 2. COD level against ferrous sulphate dosage

The required ferrous sulphate dosage is considerably high, at more than 1,000 ppm although in earlier study conducted shown the optimum dosage of ferrous sulphate for POME treatment was between 200-300 ppm [13]. The higher dosage was due to higher pH range during the aerobic treatment, whereby the pH was above 8.0 as against the optimum operating pH for metal based polymer coagulation process at pH 4 to 5 [15]. This reduction was due to the higher concentration of OH⁻ ion that will compete with organic molecules for adsorption sites. In addition, settling of metal hydroxides is unavoidable at high pH. The high pH caused the charge of the coagulating species become less positive and as a result, less attracted to anionic organic compounds [13, 16-17]. Besides, the solubility of the metal coagulant-precipitate solids was found to be strongly dependent on pH and precipitation was formed under acidic conditions [18]. Nevertheless, instead of adjusting the pH to reduce and optimise the ferrous sulphate dosage that will need the addition of acid, it will still economical to conduct the treatment at the existing pH range. Treated aerobic POME has very

strong buffering effect, therefore will need high quantity of acid or alkali in adjusting its pH.

pH and Metal Content

Ferrous sulphate is acidic in nature which will increase the soil acidity if the treated water and sludge is apply for irrigation [18-19]. Nevertheless, the pH of aerobic feed water is in alkaline range that will have buffering effect to the lowering of pH when applying the ferrous sulphate dosage for the physiochemical treatment. The pH of the treated water is still higher than 7 even at high dosage as shown in Figure 3, thus will not have impact to the soil and water quality.

Figure 4 shows that the dissolve Fe content in the treated effluent was in the increasing trend, in conjunction with the increased of ferrous sulphate dosage. The Fe content in supernatant for treatment of BOD below 50 ppm was at almost 100 ppm, while the Fe content in supernatant for treatment of BOD below 20 ppm was at almost 200 ppm. The Material Safety Data Sheet (MSDS) for ferrous sulphate indicated that product safety limit for Fe concentration for aquaculture shall be lower than 1,000 ppm, therefore the propose use of ferrous sulphate for tertiary treatment will not significantly disturbing the environment.

Table 3 shows the metal content analysis in the supernatant of the treated water which indicated that used of ferrous sulphate did not increase other metals categorised as scheduled waste, especially for aluminum. The analysis shows that Al has naturally present in the aerobic POME. The Fe content in sludge from the sedimentation process was at 640 ppm. The sludge would not be disposed into the water way as usually the sludge recovered from the sedimentation process will be left dried in drying bed and dispose for

land application. This will safeguard on possible long term adverse effect of high acidity of ferrous to the soil.

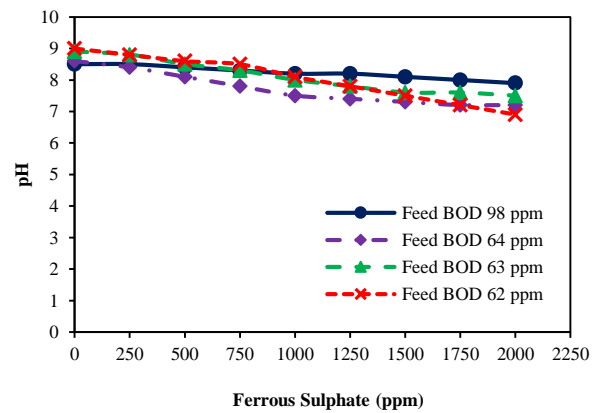


Figure 3. pH against ferrous sulphate dosage

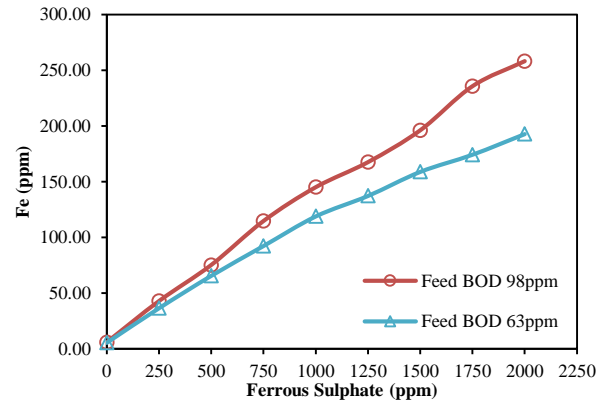


Figure 4. Fe content against ferrous sulphate dosage

TABLE 2. Metal content in supernatant against chemical dosage

Concentration (ppm)	Metal Content in Supernatant (ppm)								
	Fe	Al	Mg	Ca	K	P	Sn	Ti	Mo
0	5.66	2.01	259.20	116.20	1802.00	162.70	3.06	1.40	2.29
250	42.61	1.02	260.70	114.10	1790.00	152.30	2.72	0.69	1.30
500	75.02	1.08	256.80	113.80	1834.00	147.60	3.08	0.58	1.23
750	114.50	0.55	266.30	112.00	1819.00	140.80	2.97	0.54	1.15
1000	144.90	0.73	258.00	112.90	1828.00	142.40	3.14	0.52	1.08
1250	167.40	2.36	261.70	117.70	1830.00	124.00	2.84	0.42	1.18
1500	196.00	0.77	259.40	109.50	1826.00	118.50	2.94	0.50	1.04
1750	235.60	1.82	261.70	109.50	1797.00	120.80	3.14	0.54	1.06
2000	258.10	1.88	262.50	107.60	1858.00	105.70	3.17	0.53	1.00

TABLE 3. Metal content analysis in sludge with ferrous sulphate dosage of 1000ppm

Concentration (ppm)	Metal Content in Sludge(ppm)								
	Fe	Al	Mg	Ca	K	P	Sn	Ti	Mo
1000	640.20	1.69	429.70	113.00	2190.00	25.47	ND*	1.53	0.50

Where ND* = Not Detected

Treated Supernatant

Treated supernatant obtained after 30 minutes sedimentation process was high, at more than 80% in height at different ferrous sulphate dosage, as shown in Figure 5. There was reduction in supernatant level when the ferrous sulphate dosage was higher. It could be due to the higher ferrous sulphate dosage produced higher quantity of flocs that will take longer time to settle.

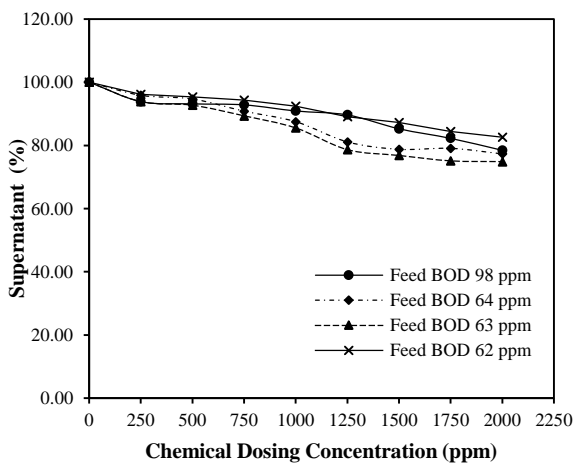


Figure 5. % Supernatant Vs chemical dosage

Pilot Scale Results

The effectiveness of the physicochemical tertiary treatment was evaluated at a 7 ton/hour pilot scale plant that was installed at an existing mill with feed BOD of almost 100 ppm (average at 98 ppm). Figure 6 shows the effectiveness of ferrous sulphate in reducing the BOD, with dosing of 1,000 ppm able to comfortably meeting the BOD-50 ppm discharge requirement, with BOD reduction efficiency of higher than 50 %. The BOD reduction to below BOD-20 ppm limit could only be achieved when the feed BOD was lower than 60 ppm.

Ferrous sulphate can potentially be used for the physicochemical tertiary treatment for POME treatment if based on the findings done at laboratory and pilot scale study. With the anticipation of more stringent requirement in future to be imposed on palm oil mill discharge to BOD 50 ppm in Peninsular and already imposed of BOD 20 ppm for East Malaysia, the millers have no choice but to install tertiary treatment facility.

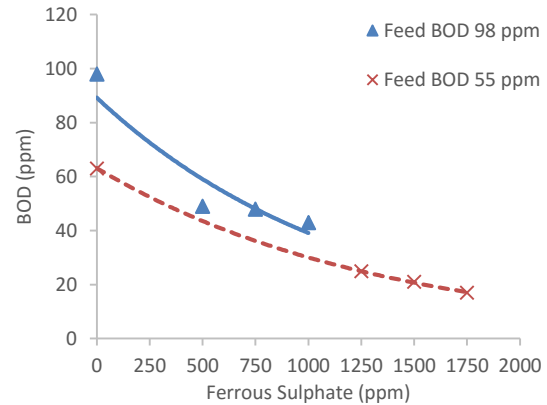


Figure 6. BOD reduction when treated with Ferrous Sulphate at pilot scale facility

The biological tertiary treatment plant cost more than RM2.0 million for a 60 ton FFB/hour palm oil mill, with the operating cost of more than RM1.00 per ton of FFB processed.

The high cost of investment and high operating cost has avoided the palm oil miller from investing into the biological based tertiary treatment to tackle on the treated effluent discharge issue. Besides, the present biological based tertiary treatment will require periodic cleaning to clean-up the bio-media that will always choke-up after more than a year in operation that is very laborious in nature, time consuming and costly [7,8, 10]. Physicochemical tertiary plant will consist of chemical preparation and dosing facility, clarifier or sedimentation tank and sand filter unit is expected to cost much lower than the biological tertiary treatment plant.

CONCLUSIONS

Ferrous sulphate though considered as weak metal coagulant but able to significantly reduced the biological effluent load in the form of BOD during the tertiary treatment of palm oil mill effluent (POME). The required dosage of ferrous sulphate to produce treated water with BOD of below 50 ppm was at 750 ppm while for BOD of below 20 ppm required dosage of 1,750 ppm from the feed BOD of below 80 ppm. With the competitive price of the ferrous sulphate will make it viable to use the coagulant for physicochemical tertiary treatment to treat POME, and will simplify the tertiary

treatment which is currently costly to build and operate and laborious in nature.

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Persian Abstract

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چکیده

به صنعت تولید روغن پالم در مالزی، تیمار بیشتر فاضلاب تخلیه شده برای رسیدن از BOD از صد به پنجاه قسمت در میلیون و تدریجاً به بیست قسمت در میلیون تحمیل خواهد شد. مطالعه به سمت استفاده از آهن سولفات به عنوان یک عامل اقتصادی به منظور کاهش بار بیولوژیکی برای سومین تیمار در تصفیه^۳ فاضلاب روغن پالم در مقیاس آزمایشگاهی و پایلوت مطابق با نیازهای جدید ارائه شده، هدایت شده است. آبی که POME با BOD زیر صد قسمت در میلیون را تصفیه کرده بود، با دوزهای مختلف آهن سولفات، از دویست و پنجاه تا دو هزار و دویست و پنجاه قسمت در میلیون، تصفیه شد. با استفاده از لوله های آزمایشگاهی مشخص شد که دوز آهن سولفات مورد نیاز برای رسیدن به BOD، پنجاه قسمت در میلیون، هزار و دویست و پنجاه قسمت در میلیون بود در حالی که برای رسیدن به بیست، هزار و هفتصد و پنجاه قسمت در میلیون آهن سولفات مورد نیاز بود و لجن فعال مضر تولید نکرد. یافته های آزمایشگاهی به مقیاس پایلوت با ظرفیت هفت تن بر ساعت افزایش مقیاس داده شد تا میزان تصفیه فیزیکی و شیمیایی بر اساس سیستم پیوسته ارزیابی شود. دوز هزار تا هزار و هفتصد و پنجاه قسمت در میلیون آهن سولفات قادر است به ترتیب BOD را به حد تخلیه پنجاه و بیست قسمت در میلیون برساند.