

PALM OIL REFINERY WASTES TREATMENT

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Abstract—Effluent from the refining of crude palm oil was subjected to physical-chemical and biological treatment. An inclined corrugated parallel plates oil separator spaced at 25 mm was used with hydraulic loading rates of 0.2, 0.5 and 1 m³ m⁻²-h. 91% oil and grease removal could be achieved at 0.2 m³ m⁻²-h. Coagulation and flocculation carried out on batch samples after oil and grease separation revealed that with 100 mg l⁻¹ alum addition BOD was reduced from 3500 to 450 mg l⁻¹ and COD from 8600 to 750 mg l⁻¹ after 30 min settling. Higher doses of alum and doses of polyelectrolyte, activated carbon and sodium hypochloride did not yield significant additional reductions in BOD and COD. Batch dissolved air flotation (DAF) removed 90% of the suspended solids with 2.7% solids in the thickened sludge at an A/S ratio of 0.014. This method yielded the similar effluent quality as the inclined corrugated plates oil and grease separator. Field data from a DAF plant compare closely with data achieved in this study. Activated sludge treatment on the effluent from the oil separator yielded a BOD of 46 mg l⁻¹ with a loading rate of 0.3 g BOD (g MLVSS)⁻¹-day. Total dissolved solids (TDS) remained high and removal through coagulation and chemical oxidation brought the COD level down to around 180 mg l⁻¹. Biokinetic coefficients Y , k_d , K and K_s were found to be 0.85 g VSS (g BOD)⁻¹, 0.016 day⁻¹, 0.12 g BOD (g VSS)⁻¹-day and 510 mg l⁻¹ BOD respectively.

INTRODUCTION

Edible oil products in Singapore and Malaysia are derived mainly from refining crude palm oil which is a mixture of glyceride esters containing mainly C₁₆-C₁₈ fatty acids, free glycerine, proteins, and gums (Table 1). The refining process involves the segregation of its constituents by physical and chemical means to produce olein, stearin and acid oils (Fig. 1). Most of the refineries are operating near urban centres or within the drainage area of streams providing potable water supply. The effluent standards for Watercourse in Singapore and Malaysia specify that BOD, COD, total suspended solids, and total oil and grease should not exceed 50, 100, 50 and 10 mg l⁻¹ respectively.

An average refinery generates around 400 m³ day⁻¹ of wastewaters. Major constituents include alkaline neutralization wash water, soap stock splitting effluent, spent liquor from chemicals and solvent extraction, detergent fractionation blowdown, circuit bleed of cooling water, carrier liquids of unwanted oil frac-

tions and spillages, floor wash and equipment cleaning water. The final effluent contains high concentrations of free and dissolved oil and fatty acids, sodium soaps, glycerine, crude oil solids, heavy metals from earth bleaching, ionized caustic soda and sulphuric acids, and detergent such as sodium lauryl sulphate.

Characteristics of the effluent vary widely from day to day and from plant to plant (Table 2). Treatment to meet the effluent standards is complicated. This paper summarizes treatment studies using physical-chemical and biological processes for the wastewater.

MATERIALS AND METHODS

Samples were collected fresh from the refinery for laboratory scale physical-chemical treatment studies. pH and temperature of the combined wastes were around 5.0 and 60°C respectively. Processes investigated include inclined corrugated parallel plates separation, chemical coagulation and flocculation, and dissolved air flotation. Field data from a 500 tons day⁻¹ mill treating around 20 m³ h⁻¹ refinery effluent using oil and grease separation, coagulation

Table 1. Characteristics of palm oil and fractionated products

Fatty acid	Palm oil	Range (%)	
		Palm olein	Palm stearin
Saturated			
Lauric	0.1-0.4	0.1-0.6	0.1-0.4
Myristic	0.9-1.4	0.9-1.4	1.1-1.8
Palmitic	41.9-46.7	37.9-41.8	46.6-73.8
Stearic	4.3-5.1	4.0-4.8	
Arachidic	0.3-0.7	0.3-0.8	

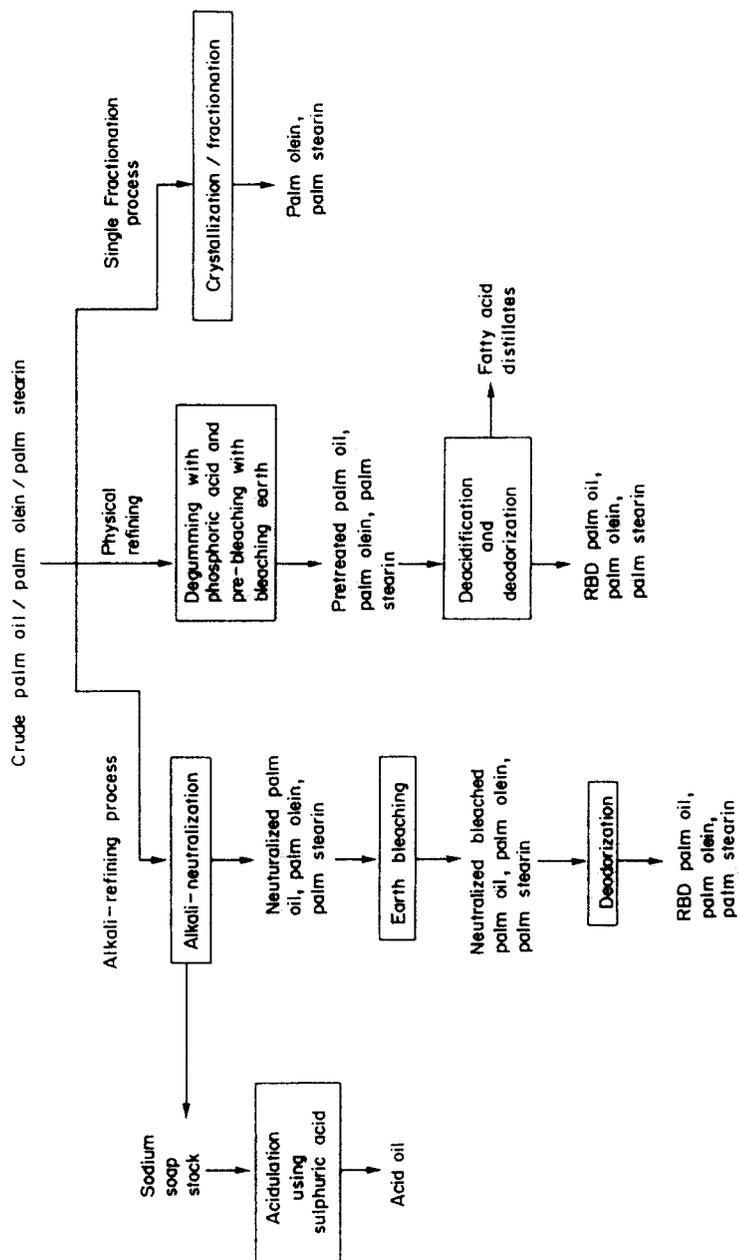


Fig. 1. Schematic diagram of palm oil refining processes.

Table 2. Characteristics of palm oil refinery wastes

Parameters	Combined wastewater	
	Range	Mean
Temperature, °C	58-65	60
pH	2-6	4.5
BOD, mg l ⁻¹	3500-16,000	5000
COD, mg l ⁻¹	6500-32,000	15,000
TDS, mg l ⁻¹	8700-15,800	9200
TSS, mg l ⁻¹	3000-12,000	5000
TP, mg l ⁻¹	20-80	60
TKN, mg l ⁻¹	30-300	180
Oil and grease, mg l ⁻¹	1250-23,800	4230

and flocculation with a polyelectrolyte, and dissolved air flotation were included for comparison with laboratory data.

For biological studies on the composite effluent from physical-chemical treatment, the activated sludge runs were carried out in 50-l. reactors made of perspex sheet and fashioned after a similar continuous feed unit developed by Ludzack (1960). A diffused air system was used to maintain the dissolved oxygen concentration in the mixed liquor at around 1 mg l⁻¹. The system was started by seeding with activated sludge acclimated cultures from a domestic sewage treatment plant. The progress of the treatment system was monitored at regular intervals for BOD, COD, mixed liquor volatile suspended solids (MLVSS), pH, nitrogen, and phosphate. Specific values of the solids retention time θ_c were estimated by $X/(\Delta X/\Delta t)$, where X is volatile solids in the reactor and $\Delta X/\Delta t$ represents the total volatile solids wasted per day. MLVSS was maintained at relatively constant level 2500 mg l⁻¹ by cell recycling and wasting from the reactor. To ensure that steady-state conditions prevailed, each unit was operated for at least three solids retention times before operational parameters were measured and used in the system analysis.

All physical and chemical analyses were carried out following APHA (1975).

RESULTS AND DISCUSSION

Three separate runs at 0.2, 0.5 and 1 m³ m⁻²-h hydraulic loading rates were carried out for the 25 mm spacing inclined corrugated parallel plate oil separator. The results of these runs are given in Table 3.

Around 91% of the oil and grease were removed at a loading rate of 0.2 m³ m⁻²-h. Even at 1.0 m³ m⁻²-h loading 81% removal of the oil and grease were achieved. BOD, COD and suspended solids separations at these loading rates were, however, low.

Batch samples after oil and grease separation were treated by chemical coagulation and flocculation using polyelectrolyte and alum. Results of effluent

quality analysis after 30 min settling are given in Table 4.

With doses of 100 mg l⁻¹ alum, the BOD level was reduced from 3500 to 450 mg l⁻¹ and COD from 8600 to 750 mg l⁻¹. There were significant reduction in BOD and COD when alum dose was increased to 200 mg l⁻¹. Above 200 mg l⁻¹ increased alum dose had little effect on COD removal. The addition of polyelectrolyte, activated carbon, and sodium hypochlorite showed little improvement in BOD and COD removal. Results also show considerable variations in treated water quality. The flocs after chemical coagulation and flocculation did not settle well. For effective flocs removal combined sedimentation and flotation units may have to be installed.

Batch dissolved air flotation runs were carried out using an apparatus described by Eckenfelder (1966). The water and air were mixed under pressure for at least 2 min for dissolution of air into water. Around 20 min was allowed for solids separation and concentration at atmospheric pressure. Results of the test runs are given in Figs 2 and 3. 90% removal of the suspended solids with 2.7% solids in the thickened sludge can be expected using the dissolved air flotation systems for suspended solids removal at an air-solids (A/S) ratio of 0.014. The expected effluent COD concentration would be around 800 mg l⁻¹, and oil and grease 20 mg l⁻¹. Dissolved air flotation system operated at 0.014 A/S ratio (equivalent gauge pressure = 4 atm) thus achieved the same quality effluent as that of a system using corrugated parallel plate separation at 0.2 m³ m⁻²-h loading rate coupled with plain sedimentation when the same amount of coagulating chemicals were applied. Field data from a full scale dissolved air flotation plant treating around 20 m³ h⁻¹ of the wastes compare closely with data attained in the laboratory (Table 5).

This plant has been in operation for more than 3 months at a gauge pressure of 6 Bar and chemical dosing rates of 1700 alum and 2.5 mg l⁻¹ polyelectrolyte. Physical-chemical treatment is thus unable to produce an effluent quality meeting the effluent standards.

Activated sludge treatment was carried out using effluent from the oil separator running at 0.2 m³ m⁻²-h. The BOD:N:P ratio after oil separation was around 100:3.6:1.1. Whenever necessary, urea was added as nutrient supplement for continuous bacteria growth in the reactors. Experimental units were set up respectively using loading rates of

Table 3. Corrugated plate treatment data

	Influent	Effluent conc. (mg l ⁻¹)		
		0.2 m ³ m ⁻² -h	0.5 m ³ m ⁻² -h	1 m ³ m ⁻² -h
BOD, mg l ⁻¹	5200	3500	3760	3980
COD, mg l ⁻¹	14,800	8600	9200	9800
Oil and grease, mg l ⁻¹	4230	350	886	1640
Total suspended solids, mg l ⁻¹	4950	3200	3600	3850

Table 4. Batch physical-chemical treatment data

Chemical doses	100	200	300	500	1000	1000	1000	1000
Alum, mg l ⁻¹	8 ± 0.5	8 ± 0.3	7.9 ± 0.3	6.8 ± 1	6.7 ± 0.8	6.5 ± 0.6	6.5 ± 0.3	6.7 ± 0.4
Polyelectrolyte, mg l ⁻¹	6200 ± 420	6500 ± 480	5800 ± 410	6000 ± 390	5800 ± 360	6100 ± 360	5900 ± 400	5800 ± 210
Activated carbon, mg l ⁻¹	530 ± 120	480 ± 180	490 ± 165	290 ± 96	260 ± 84	210 ± 78	206 ± 81	230 ± 92
N/a OCl ₂ , mg l ⁻¹	450 ± 130	280 ± 98	280 ± 105	230 ± 78	230 ± 66	180 ± 84	186 ± 72	200 ± 106
pH	750 ± 280	570 ± 210	520 ± 196	540 ± 183	460 ± 136	360 ± 138	340 ± 98	420 ± 74.3
TDS, mg l ⁻¹								
TSS, mg l ⁻¹								
BOD, mg l ⁻¹								
COD, mg l ⁻¹								

1.23, 0.58 and 0.3 g BOD per g MLVSS per day. The MLVSS concentrations of all units were maintained at around 2500 mg l⁻¹ through cell recycling and wasting. The steady state parameters are given in Table 6.

At a loading rate of 0.3 (g BOD) (g MLVSS)⁻¹ day, the BOD level was reduced to around 50 mg l⁻¹ which met with the effluent standards. COD remained at relatively high levels. The system, however, was able to maintain a MLVSS level of around 2500 mg l⁻¹ with good settling of the biological flocs. Total dissolved solids remained very high and thus could not be substantially removed by the activated sludge process. Similarly, colour content was high with a value of around 800 Hazen units. High TDS and colour would be a problem for discharge into the receiving waters. Further treatment through coagulation with 200 mg l⁻¹ alum and 50 mg l⁻¹ of activated carbon reduced the COD level to 220 mg l⁻¹ and colour to 680 Hazen units. Chemical oxidation with sodium hypochlorite up to 50 mg l⁻¹ brought the COD level down to around 180 mg l⁻¹. This was above the allowable values of 100 mg l⁻¹ COD.

A rational evaluation of the biokinetics of the activated sludge study based upon Monod's (1949) work was carried out with:

$$\frac{X}{S_0 - S} = \frac{K_s}{k} \frac{1}{S} + \frac{1}{k}$$

and

$$\frac{1}{\theta_c} = \frac{Y(S_0 - S)}{\theta X} - k_d$$

where

- X = Microbial mass concentration (measured in MLVSS)
- θ = Hydraulic retention time
- θ_c = Solids retention time
- S₀ = Influent growth limiting substrate concentration (measured in BOD)
- S = Effluent growth limiting substrate concentration
- K_s = Half-velocity constant
- k = Maximum rate of substrate utilization per unit mass of microorganisms
- k_d = Endogenous decay coefficient
- Y = Maximum yield coefficient
- θ_c^m, the minimum cell retention time is defined as:

$$\frac{1}{\theta_c^m} = \frac{kYS_0}{K_s + S_0} - k_d$$

The biokinetics constants Y, k_d, k and K_s were determined to be 0.85 (g VSS) (g BOD)⁻¹, 0.016 day⁻¹, 0.12 (g BOD) (g VSS)⁻¹ day and 510 mg l⁻¹ BOD respectively. These values were not significantly different from biokinetics evaluated for raw palm oil sludge (Chin, 1978). The minimum cell residue time θ_c^m was determined to be around 13 days.

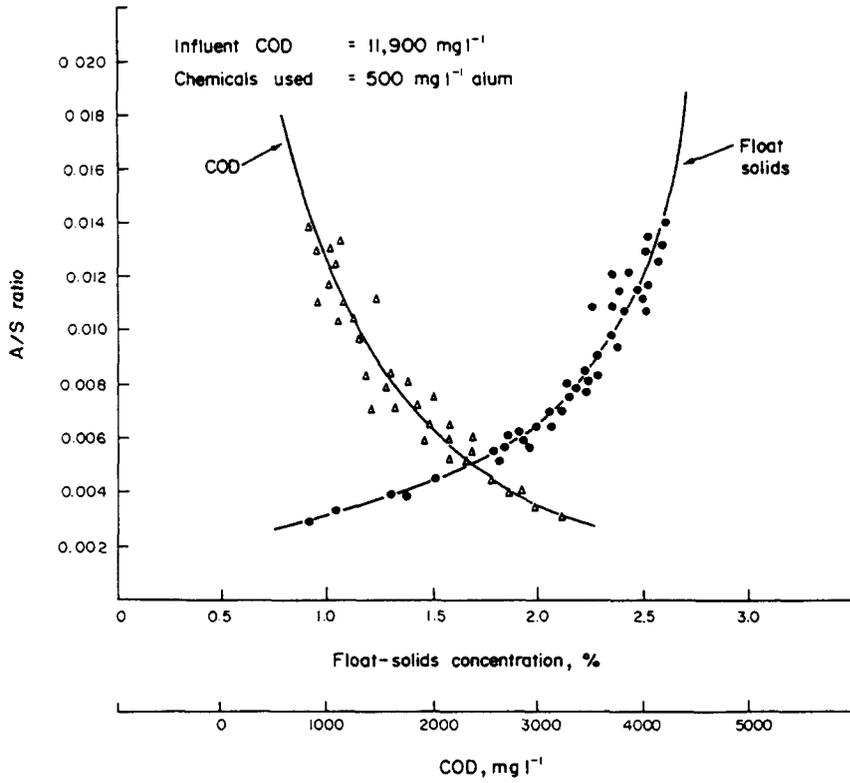


Fig. 2. Relationship between A/S ratio, float solids and COD.

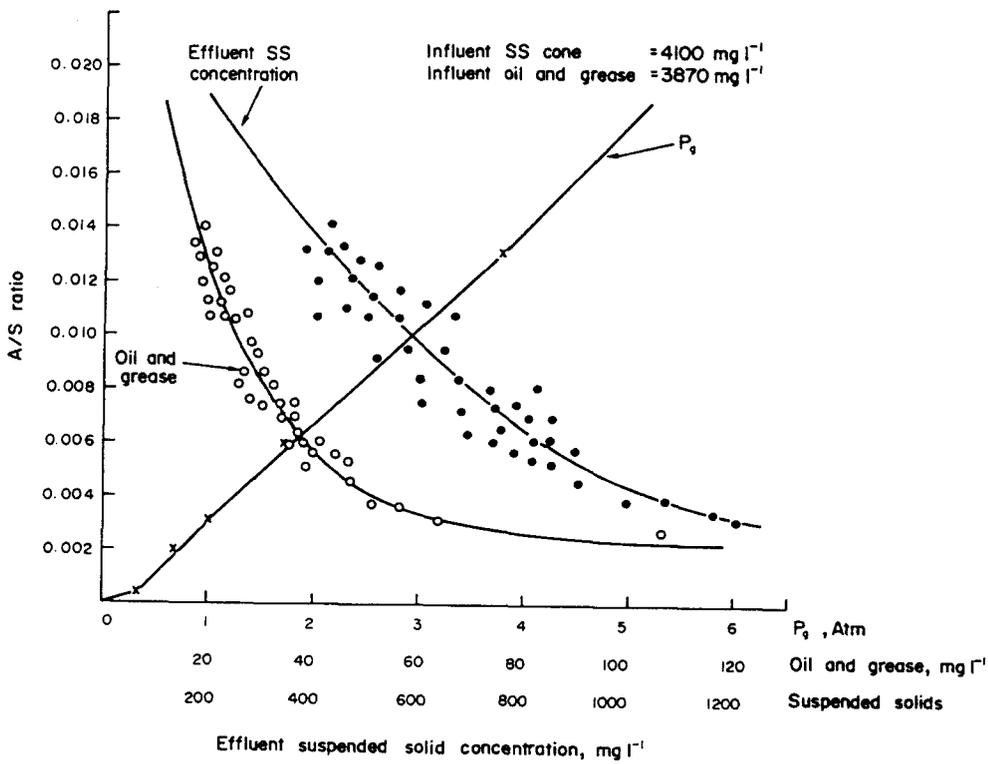


Fig. 3. Relationship between A/S ratio, SS concentration and oil and grease.

Table 5. Effluent quality from full scale plant (Sorenson & Dencker, 1980)

	Range		Ave. removal (%)
	Influent	Effluent	
BOD, mg l ⁻¹	6000-15,000	780-2020	89.6
COD, mg l ⁻¹	6670-35,200	890-6560	89.1
Oil and grease, mg l ⁻¹	2010-9210	6.5-23.5	99.7
Suspended solids, mg l ⁻¹	2350-9810	45-350	97.4
pH	2.1-3.0	6	—

Table 6. Steady state operating parameters

	1	2.5	5
θ , days			
Loading rates			
g BOD (g MLVSS) ⁻¹	1.23	0.58	0.30
g COD (g MLVSS) ⁻¹	3.03	1.42	0.73
Settled effluent			
BOD, mg l ⁻¹	580	280	46
COD, mg l ⁻¹	1200	740	380
SS, mg l ⁻¹	230	110	68
MLVSS, mg l ⁻¹	2840	2430	2360
pH	7.8	7.8	7.8
Colour, Hazen units	870	740	790
TDS, mg l ⁻¹	5800	5400	5600
SVI	150	80	80
θ_c , day	15	28	45
F/M BOD basis	1.36	0.58	0.30
Oil and grease, mg l ⁻¹	12	11.2	10.6
Waste sludge, g day ⁻¹	9.47	4.34	2.62

CONCLUSION

Palm oil refineries generate a wastewater which is high in organics and solids. An inclined plate oil separator removed more than 90% of the oil and grease and 30% of the BOD. With doses of 1000 mg l⁻¹ alum and 2.0 mg l⁻¹ polyelectrolyte, and 50 mg l⁻¹ activated carbon, BOD and COD were brought down to 200 and 420 mg l⁻¹ respectively. Dissolved air flotation removed more than 90% of the oil and grease and produced an effluent quality similar to a system using corrugated parallel plate separation followed by sedimentation after chemical coagulation and flocculation. Full scale plant operation data agree well with laboratory dissolved air flotation runs. Activated sludge treatment on the physical-chemical treated effluent at 0.3 g BOD (g MLVSS)⁻¹-day reduced the BOD concentration level to 46 mg l⁻¹ and COD to 380 mg l⁻¹. Colour and total dissolved solids remained high at around 790 Hazen units and 5600 mg l⁻¹ respectively. Further treatment of the

activated sludge effluent with alum, carbon adsorption and sodium hypochlorite oxidation, brought the COD level down to only 180 mg l⁻¹.

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