REMOVAL OF RESIDUE OIL FROM PALM OIL MILL EFFLUENT (POME) USING CHITOSAN

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by

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Specially dedicated to my lovely late mother Mrs. M. Damayanthi.
I love you Amma.

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NOMENCLATURE

1.	M_{w}	Molecular weight
2.	C_e (g/l)	Residue oil concentration at equilibrium
3.	C_o (g/l)	Initial concentration of residue oil
4.	K_1	Rate constant of pseudo first-order adsorption
5.	K_2	Rate constant of pseudo second-order adsorption
6.	K_F	Freundlich constant related to adsorption capacity
7.	K_L	Langmuir constant relate to energy of adsorption 1g of adsorbent per g of adsorbate
8.	a_L	Empirical constant for Langmuir
9.	n	Freundlich constant related to adsorption intensity
10.	q_e (g/g)	Amount of residue oil adsorbed at equilibrium
11.	q_t (min)	Amount of adsorption at time *t*
12.	R^2	Correlation coefficient
13.	q_o (g/g)	Maximum amount of adsorption corresponding to complete monolayer coverage
14.	R_L	Separation factor, dimensionless constant
15.	t (min)	Time taken for adsorption
16.	V (l)	Sample volume
17.	W (g)	Mass of adsorbent
18.	T (K. or °C)	Temperature
19.	E_a (kJ·mol^{-1})	Activation energy
20.	$\Delta G°$(kJ·mol^{-1})	Free energy change
21.	$\Delta H°$(kJ·mol^{-1})	Enthalpy change

22.	$\Delta S°$(kJ·mol^{-1}K^{-1})	Entropy change
23.	R (J/mol·K)	Gas constant = 8.314
24.	K_C	Equilibrium constant of ($\Delta G°$)
25.	K_T	Rate constants at different temperature

ABBREVIATIONS

1.	POME	Palm Oil Mill Effluent
2.	BOD	Biochemical Oxygen Demand
3.	COD	Chemical Oxygen Demand
4.	TKN	Total Kjeldahl Nitrogen
5.	DAF	Dissolved Air Flotation
6.	AFP	Agence France-Presse
7.	EFB	Empty Fruit Bunches
8.	PPF	Palm Pressed Fibres
9.	Alum	Aluminum Sulphate
10.	PAC	Poly Aluminum Chloride
11.	DOE	Malaysian Department of Environment
12.	CPO	Crude Palm Oil
13.	EQA	Environmental Quality Act
14.	CH_3	Methyl
15.	NH_2	Amine
16.	NHCO	Amide
17.	OH	Hydroxyl
18.	CH_2OH	Acetyl
19.	N_2	Nitrogen gas
20.	NH_3	Ammonium
21.	CONHR	Carbonyl
22.	KBr	Potassium Bromide

23.	KOH	Potassium Hydroxide
24.	BET	Brunauer-Emmett-Teller
25.	SEM	Scanning Electron Microscope
26.	FT-IR	Fourier Transform Infrared
27.	O/W	Oil in Water
29.	W/O	Water in Oil
30.	ER	Electrorheological
31.	vs.	Versus
32.	Fig.	Figure

PENYINGKIRAN MINYAK SISA DARIPADA KUMBAHAN KILANG KELAPA SAWIT MENGGUNAKAN KITOSAN

ABSTRAK

Penyelidikan ini difokuskan untuk menyelidik dan mengkaji penggunaan kitosan sebagai bahan penjerap serta pengental minyak sisa berlebihan dalam sebarang air sisa berminyak. Air kumbahan kilang kelapa sawit (POME) daripada kilang kelapa sawit tempatan digunakan sebagai sampel air sisa berminyak. Kitosan ialah satu biopolimer kationik yang boleh dibiodegradasikan dan dihasilkan daripada pengdeasetilan kitin sisa kulit udang secara meluas. Kitosan boleh mengental serta menjerap minyak sisa didalam POME. Kitosan juga secara spontan mengental pepejal terampai di dalam POME sambil menyingkir minyak sisa. Satu kajian perbandingan di antara kitosan, penjerap dan pengental komersial telah dilakukan. Satu kajian lengkap menggunakan serbuk dan kepingan kitosan, keseimbangan penjerapan, kinetik dan termodinamik juga dilakukan. Untuk menyingkirkan minyak sisa daripada POME satu siri eksperimen dilakukan menggunakan pelbagai keadaan dan parameter. Pemboleh ubah kawalan terdiri daripada berat dos, kepekatan awal, masa pemendapan, masa pencampuran, kelajuan pencampuran, pH dan suhu. Penyingkiran yang terbaik dicapai menggunakan 0.5g/l serbuk kitosan dengan 30min pemendapan, 30min pencampuran pada 100rpm, pH 4.0 - 5.0 dan suhu diantara 50-70°C. Peratus penyingkiran yang dicapai ialah 99%. Analisis FT-IR dan SEM kitosan serbuk dan kepingan sebelum dan selepas penjerapan ditunjukkan untuk membuktikan bahawa minyak sisa telah dijerap oleh kitosan daripada POME. Kitosan serbuk menunjukkan kapasiti yang lebih tinggi daripada kitosan kepingan untuk menyingkir minyak sisa. Keseimbangan penjerapan membuktikan bahawa kitosan mempunyai kapasiti yang tinggi terhadap penjerapan minyak sisa. Keseimbangan garis sesuhu penyingkiran minyak sisa pada kitosan padan dengan model persamaan Freundlich. Model kinetik “Pseudo Second-Order” sepadan dengan perlakuan dinamik kinetik penjerapan minyak sisa oleh kitosan. Ini mencadangkan bahawa kadar langkah mengehad proses ini kemungkinan disebabkan oleh penjerapan kimia. Kajian termodinamik menjelaskan bahawa penjerapan minyak sisa dikawal oleh resapan. Penjerapan minyak sisa dalam kolum berterusan dengan kitosan kepingan juga amat berkesan tapi dengan syarat ianya dipadatkan bersama dengan (1:2) nisbah padatan gelungan “pall” pada kadar aliran masuk pertengahan selaju 50ml/min. Penyelidikan kajian ini mengesahkan penggunaan kitosan iaitu sejenis biopolimer sebagai satu alternatif yang berupaya untuk penjerapan dan pengentalan minyak sisa daripada POME.

ABSTRACT

The focus of this research was to investigate and study the usage of chitosan as an adsorbent as well as a coagulant to adsorb and coagulate the excessive residue oil from an oily wastewater. Palm oil mill effluent (POME) from the local palm oil mill was identified as a sample of an oily wastewater. Chitosan is a biodegradable cationic biopolymer developed by the extensive deacetylation of chitin obtained from shrimp shell waste. Chitosan could coagulate as well as adsorb the residue oil in POME. Chitosan also spontaneously coagulates the suspended solid in POME while removing the residue oil. A comparative study between chitosan, commercial coagulants and adsorbents was done. A detailed batch study on chitosan powder and flake with respect to its adsorption equilibrium, isotherm, kinetics and thermodynamic study were also carried out. In order to remove the residue oil from POME, a series of experiments was carried out using different conditions and parameters. The control variables were weight dosage, initial concentration, sedimentation time, mixing time, mixing rate, pH and temperature. The best removal of residue oil was accomplished using 0.5g/l of powdered chitosan with sedimentation time of 30min, mixing time of 30min, mixing rate of 100rpm, pH 4.0 - 5.0 and at a temperature in the range of 50-70°C. The removal percentages obtained were very satisfactory i.e. 99%. FT-IR and SEM micrographs of chitosan powder and flake before and after adsorption were presented to prove that the residue oil had been adsorbed by chitosan. Chitosan powder showed a better capacity of residue oil removal compared to chitosan flake. The adsorption equilibrium suggested that chitosan had a high capacity for adsorbing residue oil. The Freundlich equation model fits well with the equilibrium isotherm of residue oil adsorption on chitosan. The Pseudo Second-Order kinetic model corresponds well with the dynamical behavior for the adsorption of residue oil on chitosan. This seemed to suggest that the rate-limiting step may be the chemical adsorption. Thermodynamic study has clarified that the residue oil adsorption was diffusion controlled. Adsorption of residue oil in a continuous column was successful with chitosan flake, provided that it was aided by a ratio of (1:2) pall ring packings in a medium with inlet flow rate of 50ml/min. The research study had attested chitosan, biopolymer as a potential alternative to coagulate and adsorb residue oil from POME.

CHAPTER 1

INTRODUCTION

1.1 Oily Wastewater

Over the recent years there has been an increasing concern for environmental risk of industrial activities associated with extraction, hydrocarbons, food processing, transportations and refining. These industries have increased the threat of oil pollution to the environment and subsequently concomitant discharged into the natural environment creates major ecological problem throughout the world.

The concentration of oil in effluents from different industrial sources can be as high as 40,000mg/l (Arcadio & Gregoria, 2003). Unlike free or floating oil spilled in the sea, lakes or rivers, most of industrial wastewaters contain oil-in-water emulsions among other basic contaminants. Emulsified oil in wastewater can lead to severe problems in different treatment stages. Oil in wastewaters has to be removed in order to: (1) prevent interfaces in water treatment units; (2) reduce fouling in process equipment; (3) avoid problems in biological treatment stages; and (4) comply with water discharge requirements.

The treatment of these wastes has been addressed by several techniques: (a) chemical destabilization by addition of organic and inorganic compounds; (b) adsorption; (c) electrical methods; (d) membrane processes and (e) dissolved air flotation (DAF) (Rios *et al.*, 1998).

1.2 Industrial Case Study in Malaysia

Vegetable oil processing plants are normally the big contributors of oily wastewater. Vegetable oil industries such as sunflower, olive and palm discharge large volumes of oily wastewaters. These wastewaters contain a very high volume of oil-in-water emulsions as their basic contaminant (Pushkarev *et al.*, 1983). These emulsified oil droplets are sheltered from spontaneous coalescence into larger flocs, thus making oil separation by simple gravity a difficult and time consuming process (Zouboulis & Avranas, 2000).

In this research study, palm oil mills wastewater has been used as an oily wastewater for the case study. Palm oil is one of the leading traded vegetable oil garnering nearly 50 percent of the world trade of about 36 million metric tons (Agricultural Data and Research, 2004). In accordance to this the Malaysian palm oil industry has upgraded its growth in the last decades to emerge as the leading agricultural industry particularly in oil palm. Oil palm (*Elaeis guineensis*) is vastly cultivated as a source of oil in Malaysia and concurrently has contributed significant to the economic growth of the country. According to Malaysian External Trade Statistics (2003) the export, revenue earner of palm oil valued at a total value of RM20.8 billion, soared by 38.2 per cent from RM15.1 billion in the preceding year. With the continuing development of the palm oil, it is forecasted that Malaysia's palm oil production in year 2003 will reach up to 13 million tons (AFP, Newsletter, 2004).

While it is recognized for its contribution towards economic growth, the rapid development has also contributed to environmental pollution correspondingly to the large quantity of waste products produced from the oil extraction process. These waste products consist of fibrous material such as empty fruit bunches (EFB), palm pressed fibres (PPF) and palm kernel shell, less fibrous material such as palm kernel cake and liquid discharge palm oil mill effluent (POME) (Cheah, 2003).

In line with the Malaysian Environmental Quality Act 1974 and Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations (1977), all these palm oil by-products requires a sound and efficient management system in order to utilize, treat and dispose with the aim of reducing the environmental conservation and deteriorating air and river water quality. Table 1.1 displays the parameter limits for effluent discharge.
The effluent discharge by palm oil mills must comply with the Malaysian Environmental Quality Act 1974 and Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 dated 01.01.1984 and thereafter set by the Department of Environment, Malaysia.

POME is a colloidal suspension containing 95-96% water, 0.6-0.7% oil and grease and 4-5% total solids. It is thick, brown liquid with a discharge temperature of between 80°C and 90°C and fairly acidic with a pH value in the range 4.0 - 5.0. Typically POME contains a mean value of 6000 mg/l of oil and grease (Industrial Processes & The Environment, 1999).

Table 1.1: Prevailing effluent discharge standards for crude palm oil mills (Industrial Processes & The Environment, 1999)

PARAMETER		**PARAMETER LIMITS**	**REMARKS**
pH	-	5 – 9	
Temperature	°C	45	
Oil and Grease	mg/L	50	
BOD; 3-day, 30°C	mg/L	100	
(COD)	mg/L	-	No discharge standard after 1984
Suspended Solid	mg/L	-	No discharge standard after 1984
Ammonical Nitrogen	mg/L	150	Value of filtered sample
Total Nitrogen	mg/L	200	Value of filtered sample

The oil droplets occur in two phases. It is suspended in the solids of POME and also floating in the supernatant of POME. Approximately 2000 mg/l residue oil is present in an emulsified form in the supernatant of POME (Ibrahim, 2001). Furthermore, POME possesses a very high concentration of surface active compound (Chow & Ho, 2002). These natural surfactants stabilize the oil droplets and thereby make it impossible to recover or remove residue oil from the sludge.

Residue oil is one of the key ingredients of POME which influences the high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) values. COD and BOD parameters were identified as the major problem in POME by Ma (2000a). The maximum allowable limit set by the Malaysian Department of Environment (DOE) for residue oil is 50mg/l. Hence, the challenge of converting POME into an environmental friendly waste requires sound and efficient treatment and effective disposal. Therefore, in order to achieve the above target, a reliable and effective treatment process has to be opted. Basically this can be achieved by destabilizing oil droplets and destroying emulsions via the addition of coagulants or adsorbents. The use of inorganic polyelectrolytes such as aluminum sulphate (alum), aluminum hydroxide, ferric chloride, hydrate lime and poly aluminum chloride (PAC) has been proved an effective pretreatment in the wastewater (Eilbeck & Mattoc, 1987). They are the most widely used coagulants, because they are cheap, effective and easy to handle. The addition of alum or aluminum hydroxide coagulants has been shown to be effective as a pretreatment to an ultrafiltration unit to separate oil and grease (Cawley, 1980). Most important of all, aluminum can be overdosed to ensure coagulation efficiency. However major problem arises when the sludge obtained from such treatment is difficult to dispose as it contains aluminum and tends to accumulate in the environment. Furthermore, it was found that over-use of aluminum salt coagulants elevates the aluminum concentration and turbidity in the treated waste. The worst scenario occurs when the treated waste contains aluminum as residue.

Currently public awareness on Aluminum’s influence on Alzheimer’s disease is high (Pontius, 2000; Stauber *et al.*, 1999). The usage of natural adsorbents was considered much safer to adsorb and remove the residue oil. Successful removal and treatment of oil from concentrated wastewater using adsorbents such as attapulgite, clay and peat have been studied by Qiu *et al.* (1995); Demirci *et al.* (1998); and Benito *et al.* (2002) respectively. Though the results were promising, one important set back is that the suggested adsorbents in the system were applied collectively with the inorganic coagulants. The adsorbents were used in mixture with the inorganic salts to improve the treatment processes and technologies, and also used as coagulant aids. Dalmacija *et* *al.* (1996) has also reported the possibility of applying bio-sorption system with granulated activated carbon for the tertiary treatment of oil-field brine. Nevertheless, the system requires a preliminary treatment using physicochemical and microbiological. Thus, it has become necessary to develop more efficient and environmental-friendly coagulants or adsorbents for removal of residue oil from POME. Probably an integrated coagulant which is natural, biodegradable and adsorptive is preferred to overcome this problem.

Chitosan, obtained by deacetylation of chitin (a biopolymer widely distributed in nature and occurring in crustaceans), is described as a biodegradable cationic polyelectrolyte (Muzzarelli, 1977) and with this it is expected that chitosan could adsorb as well as coagulate the suspended residue oil of POME. The interplay of amine functional groups in chitosan has a high potential for adsorbing residue oil. The cationic nature is believed to coagulate the negatively charged oily suspended solids of POME. Chitosan is a high charge density material with a positive charge; it interacts strongly with negative groups to obtain electrical neutrality (Pinotti *et al.*, 1997). These factors lead to the conclusion that the addition of sufficient chitosan to an oily wastewater could increase the rate of droplet destabilization and agglomeration, and allow the oily droplets to be adsorbed either electrostatically and/or through van de Waals attractive forces. In spite of this potential, no work has been done or published on the effects of residue oil removal by chitosan on POME. In fact, this process could be adopted as a natural follow-up to residue oil removal in oily wastewaters.

Studies on the use of chitosan in conjunction with inorganic coagulants such as alum and ferric chloride have been reported by Bough (1975a); Bough (1975b); Bough *et al.*

(1975) and Kawamura (1991). Applications of chitosan in flocculation of montmorillonite, bentonite and kaolinite suspensions have been reported earlier by Peniston & Johnson (1970), Huang & Chen (1996), Pan *et al.* (1999) and Divakaran & Pillai (2001).

1.3 Objectives

In the present research, the effectiveness of chitosan as a coagulant as well as an adsorbent, in removing the residue oil from POME was examined and analyzed.

The objectives of this research were focused to:

- study the capability of chitosan compared to other types of adsorbents and coagulants such as peat, claytone, bentonite, activated carbon, PAC and alum to remove residue oil;
- study in detail the ability and effect of chitosan powder and flake with various parameters and optimize the best condition for residue oil removal from POME in a batch system;
- study the equilibrium, isotherm, kinetic and thermodynamic of the chitosan and residue oil adsorption process; and
- design and build a lab scale packed bed adsorption column to analyze the potential of continuous adsorption system to adsorb residue oil.

1.4 Scope of work

Basically, this study can be divided into four phases which are;

- A comparative batch studies between chitosan, chitin, peat, bentonite, claytone, activated carbon, alum and PAC;
- A comprehensive batch study on two types of chitosan i.e. powder and flake;
- Equilibrium, isotherm, kinetic and thermodynamic studies for residue oil adsorption by chitosan; and
- Preliminary continuous column study.

CHAPTER 2

LITERATURE REVIEW

2.1 The Origin of Palm Oil Mill Effluent

Palm oil mill effluent is a waste produced from the palm oil processing plants. This oily waste is produced in large volumes and contributes major problem to the palm oil processing mill's waste stream. Thus it has to be treated efficiently to avoid environmental hazard.

2.1.1 *Palm Oil Processing Industry*

The extraction process for crude palm oil (CPO) starts from the local palm oil mills throughout Malaysia. The mills processes FFB received from the oil palm plantations into CPO and other by-products. A schematic process flow of palm oil milling for the extraction of crude palm oil and sources of waste generation is shown in Fig. 2.1. Palm oil mills typically generate large quantities of extremely oily organic contented liquid (Industrial Processes and The Environment, 1999).

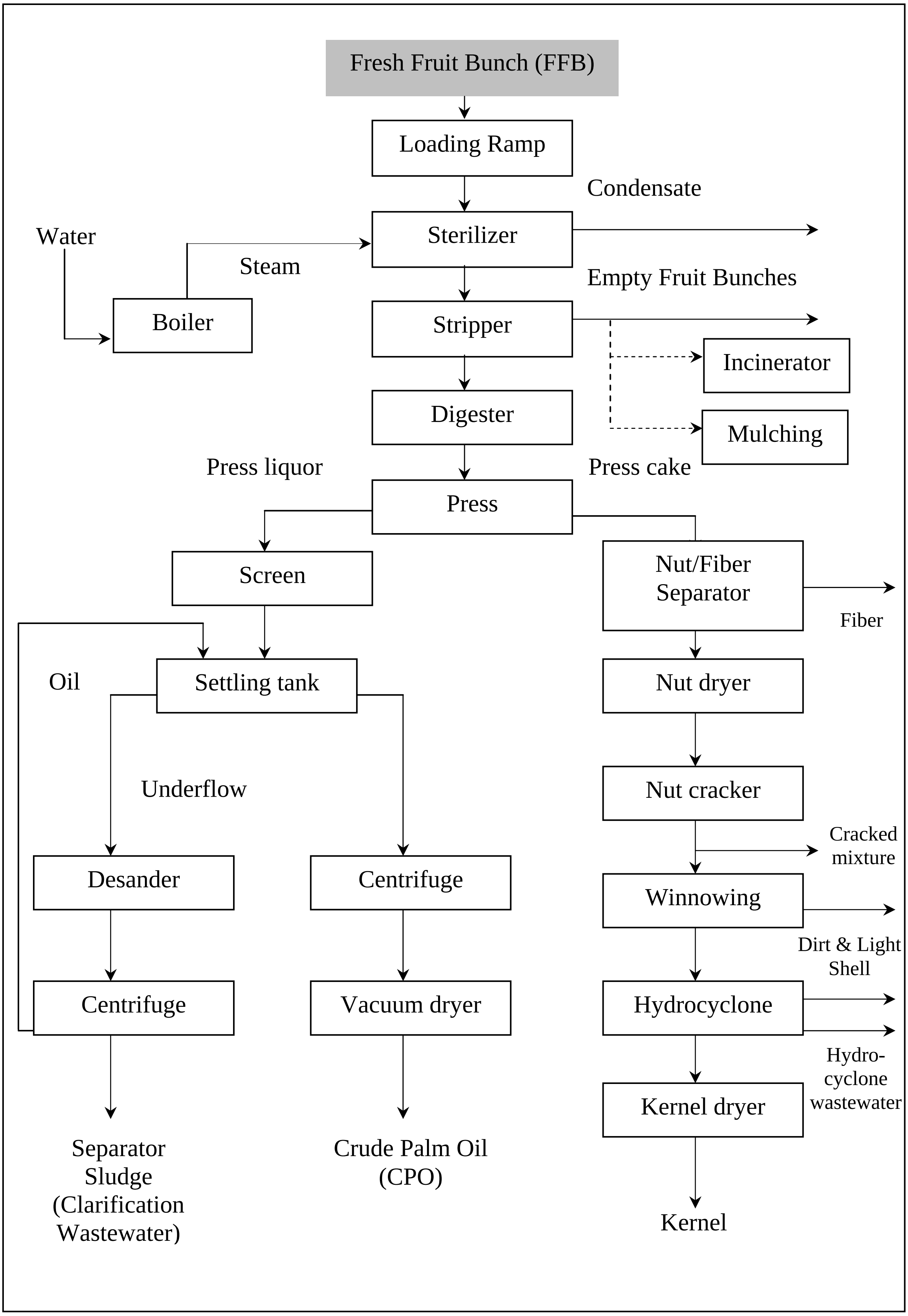


Fig. 2.1: Process flow of a typical palm oil milling (Industrial Processes and The Environment, 1999)

The environmental issues of the CPO industry are primarily related to numerous factors such as:

- Water pollution due to indiscriminate discharge of untreated or partially treated palm oil mill effluents into public watercourses;
- Improper interim storage of solid waste materials including boiler and incinerator ash, decanter solids, spent bleaching earth and sludge separator residue;
- Improper land-application techniques or practices for solid and/or liquid wastes;
- Air pollution due to the use of solid fuel fired boilers for empty bunches;
- Odor emission from poorly managed effluent treatment systems, especially, if they are located in close proximity to neighboring residential areas; and
- Noise from the milling processes

Palm oil mills are traditionally located near rivers from which water is abstracted for their milling operations. A number of palm oil mills conveniently discharged their treated effluents into the river in an untreated or partially treated condition as this was the cheapest method of POME disposal since POME was a non-toxic oily waste. Certain beneficial effects may have been initially derived due to available nutrients and enhanced growth of micro-plankton which is an essential food for aquatic life. However excessive quantities of untreated POME deplete a waterbody of its oxygen and suffocate the aquatic life. Thus, the impact of raw POME discharge to a relatively small river can be devastating to its eco-system and beneficial uses. The advent of strict environment regulations has made the palm oil proprietor to realize the eco-concern and learnt to treat the waste into an environmental friendly waste.

2.1.2 *Palm Oil Mill Effluent (POME)*

Large quantities of water are used during the crude oil extraction process. Up to about 1.5 cubic meters of water are characteristically used to process one tonne of FFB. From this quantity, about 50% of the water results in the POME, the other 50% being lost as steam, mainly through sterilizer exhaust, piping leakages, as well as wash waters (Oil Palm & The Environment A Malaysian Perspective, 1999).

POME comprises a combination of the wastewaters which are principally generated and discharged from the following major processing operations as seen early in Fig. 2.1.

- Sterilization of FFB - sterilizer condensate is about 36% of total POME;
- Clarification of the extracted CPO - clarification wastewater is about 60% of total POME; and
- Hydrocyclone separation of cracked mixture of kernel and shell-hydrocyclone wastewater is about 4% of total POME.

There are other minor sources of relatively clean wastewater that may be included in the combined mill effluent POME which is sent to the wastewater stream. These include turbine cooling water and steam condensates, boiler blow-downs, overflows from the vacuum dryers and some floor washings. The volume of the combined POME discharged depends to a large extent on the milling operations.

2.1.3 *Characteristics of POME*

Distinctive quality characteristics of the individual wastewater streams from the three principal sources of generation are presented in Table 2.1. POME, when fresh is a thick brownish in color colloidal slurry of water, oil and fine cellulosic fruit residues. POME is charged at a temperature of between 80°C and 90°C and it is slightly acidic with a pH between 4 to 5. The characteristics of a usual raw combined POME are presented in Table 2.2. Table 2.2 attests that POME has a very high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), which is 100 times more than the domestic sewage. POME is a non-toxic waste, as no chemical is added during the oil extraction process.

Table 2.1: Characteristics of individual wastewater streams (Industrial Processes and The Environment, 1999)

Parameters	Sterilizer Condensate	Oil Clarification Wastewater	Hydrocyclone Wastewater
pH	5.0	4.5	-
Oil & Grease	4,000	7,000	300
BOD; 3-day, 30°C	23,000	29,000	5,000
COD	47,000	64,000	15,000
Suspended Solid	5,000	23,000	7,000
Dissolved Solids	34,000	22,000	100
Ammonical Nitrogen	20	40	-
Total Nitrogen	500	1,200	100

*All units are in mg/l except for pH

However it contains appreciable amounts of N, P, K, Mg and Ca which are the vital nutrient elements for plant growth (Industrial Processes & The Environment, 1999).

Table 2.2: Characteristics of combined palm oil mill effluent (POME) (Industrial Processes & The Environment, 1999)

Parameters	**Mean**	**Range**	**Metals & Other Constituents**	**Mean**
pH	4.2	3.4-5.2	Phosphorus	180
Oil & Grease	6,000	150-18,000	Potassium	2,270
BOD; 3-day, 30°C	25,000	10,000-44,000	Magnesium	615
COD	50,000	16, 000-100,000	Boron	7.6
Suspended Solid	40,500	11,500-79,000	Iron	47
Dissolved Solids	18,000	5,000-54,000	Manganese	2.0
Ammonical Nitrogen	35	4-80	Copper	0.9
Total Nitrogen	750	80-1,400	Zinc	2.3
			Calcium	440

*All units are in mg/l except for pH

2.1.4 *Pollution Load and Effect of Discharge*

The production of CPO in 2003 increased markedly by 12.1% or 1.4 million tons to 13.35 million tons from 11.91 million tons in 2002 (Malaysian Palm Oil Board, 2004) which is about 46,000 cubic meters per day. Based on this quantity of daily CPO production, the total quantity of effluent generated per day can be averaged up to 161,000 m^3 and the total BOD_3 load of raw effluent generated per day is about 4,025 tons. Finally the population-equivalent of raw effluent BOD_3 load (@ 0.05 kg BOD/Capita/Day) is equal to 64,000,000 persons.

The above pollution statistics indicate that if the entire palm oil industry discharges raw effluent, then the total pollution load of the industry would be equivalent to that of a POME when discharged untreated or partially treated into the river stream undergoes natural decomposition during which the dissolved oxygen of the river or stream is rapidly depleted (Oil Palm & The Environment A Malaysian Perspective, 1999).

The palm oil present in the effluent may float to the surface of the waterbody and form a wide-spread film which can efficiently cut-off and avert atmospheric oxygen from dissolving into its waters. Furthermore, when the organic load far exceeds its waste assimilation capacity, the available oxygen in the waterbody is rapidly consumed as a result of the natural biochemical processes that take place. The waterbody may become completely devoid of dissolved oxygen. This will lead to anaerobic conditions in which hydrogen sulphide and other malodorous gases are generated and released to the environment resulting in objectionable odors. Additional damaging effects include the decline and eventual destruction of aquatic life and deterioration in the riverine eco-system.

Moreover it is predicted that, the Malaysian oil palm industry in 2004 to remain bullish. The production of CPO is projected to increase by 2.3% to 13.66 million tons (Malaysian Palm Oil Board, 2004). Hence serious measures have to be taken in order to prevent the growing pollution caused by palm oil mill effluents.

2.2 Regulatory Control of Effluent Discharge

Oil palm cultivation and processing are regulated by a number of environmental legislations aimed at conserving and protecting the natural environment. These rules and regulations, together with the growing awareness for a clean and pollution-free environment play a significant role in minimizing the degradation of the soil, water and atmospheric environment. The DOE being the government agency acted responsibility in enacting the Environmental Quality Act in 1974 (EQA) and specific regulations for palm oil mill effluent in 1977.

EQA is an enabling act aimed to prevent, abate and control pollution for the protection of public health and the environment. The highlighting agenda of EQA was to set acceptable standards for the emission and discharge or deposits of pollutants into the environment rather than prevention, with an exception given to the necessities on environmental impact measurements. Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 were promulgated under the Section 51 Environment Quality Act 1974 for environmental control of palm oil mills discharge. Table 1.1 in Chapter One, represents the current effluent discharge standards ordinarily applicable to the crude palm oil mills. Therefore the palm oil millers have to encompass proper pollution control practices to fulfill the discharge limits set by the DOE (Environmental Quality Act and Regulations. Amended November, 2001).

2.3 Treatment Technologies of POME

The effluent treatment technologies for POME are invariably combinations of physical, chemical and biological processes. However over the last two decades, the refineries sought to reduce effluent and other forms of pollution by;

- Changing chemical refining to physical refining;
- Automation and strict process control to prevent spillage and product loss; and
- Installation of new equipment which is based on low energy and water consumption.

There are four types of treatments that have been employed in the local palm oil mill effluents to treat POME.

2.3.1 *Pre-Treatment*

This physical pre-treatment of POME basically includes stages such as screening, sedimentation and oil removal in oil traps prior to the secondary treatment in biological treatment systems. Residual oil and fat are recovered by oil trappers, titled-plate separators, dissolved air flotation units, centrifuges and electro-flotation systems (Donnelly, 1980). Coagulants and flocculants such as ferric chloride, aluminium sulphate, lime and polyelectrolytes were used to reduce the total fatty matter and other suspended solids prior to the separation by physical treatment (Industrial Processes & The Environment, 1999).

2.3.2 *Biological Treatment Technologies*

POME contains a very high organic matter which indirectly contributes to the excessive BOD. The organic substance of POME is generally biodegradable and treatments are based on anaerobic, aerobic and facultative processes (Chin & Wong, 1985; Cheah & Ma, 1985; Razi & Noor, 1999). The biological treatment relies greatly on a mixed population of active microorganisms which utilizes the organic substances polluting the water as nutrients and finally breakdown the organic matter into simple end-product gases such as methane, carbon dioxide and hydrogen sulphide, and water.

Biological treatment system needs proper maintenance and monitoring. Biological processes rely solely on the microorganisms to breakdown the pollutants. These microorganisms are very sensitive to the surge of pollutants in the environment. Thus great care has to be taken to ensure that conducive environment is maintained for the microorganisms to thrive and undoubtedly it is of the lowest priority as far as maintenance budget is concerned (Chan & Chooi, 1982; Chooi, 1984).

2.3.3 *Land Application System*

Land application of POME has become a standard practice in mills where they have plantations nearby. The anaerobically digested POME contains high concentrations of plant nutrients. The application of the effluent to the cropland, not only provides nutrient and water to the vegetation, but also a means of alternative disposal of the effluent. This has resulted in substantial saving in fertilizer bills and increased income due to higher crop yield. However such practices are only feasible to the plantation groups with enough land in the vicinity of their palm oil mills (Quah *et al.*, 1982).

2.3.4 *Zero Waste Evaporation Technology*

Evaporation is one of the most widely used unit operation in water regeneration in a wide range of processing applications. POME is made up of about 95 - 96% water thus by this evaporation technology the water could be recovered and the residual solid can be concentrated for advanced utilization (Ma, 2000a). The energy requirement is the major consideration in the evaporation technology. However the heat required is largely inherent in the fresh POME itself which is discharged at a temperature of above 80°C. The additional energy can be economically generated from the surplus electricity normally generated by palm oil mills or combustions of EFB (Ma *et al.*, 1995).

2.4 Residue Oil

Fatty acids are the main constituents of any types of oils. A fatty acid is characterized as a long-chain aliphatic hydrocarbon with a carboxylate group on one end. The naturally occurring fatty acids have common names such as oleic, linoleic, eleosteric, etc. There are two types of fatty acids, saturated and unsaturated. There are also branched-chain fatty acids with the most frequent branch being a methyl group, ($-CH_3$) and also some which are attached to other functional groups (Genium Publishing Corporation, 2004).

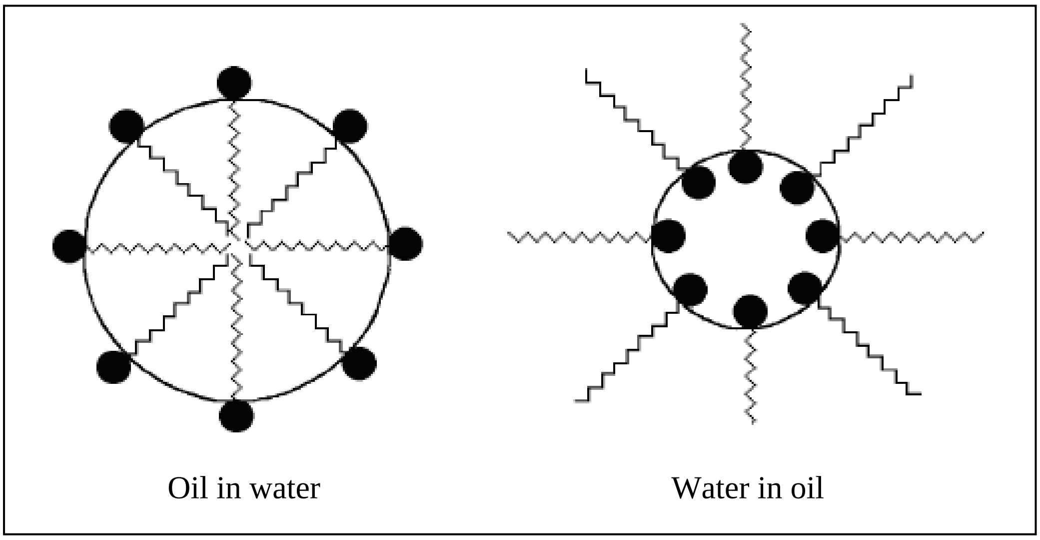
Fatty acid is a weak acid. In the acid form it is soluble in organic solvents, poorly soluble in the very non-polar organic solvents like hexane, but very soluble in more polar organic solvents like methylene chloride, ether, or alcohols. The fatty acid salts of the alkali metal cations and ammonia tend to be soluble in water, but salts with other cations such as calcium or magnesium can be quite insoluble. Fatty acids are structural component of the triglycerides. Another member of the family is phospholipids, where up to three fatty acids are esterified to a phosphate, $P(=O)(O\text{-fatty acid})_3$. Collectively the family is known as the lipids, which are a component of fat (Genium Publishing Corporation, 2004).

2.4.1 *Surfactants*

Surfactants will frequently be contributors to the oil and grease results, although they are not normally considered to be in the group of substances that fall under oil and grease definition. Surfactants are substances that have long organic molecules with a water soluble (hydrophilic) head and a water insoluble (hydrophobic) tail (McClements, 1999). This substance decreases the level of surface energy and can present significant environmental pollution problems such as;

- Interference with the gill-based respiration of fish and other aquatic life forms;
- Formation of unsightly scrums and foams downstream from effluent points; and
- Degradation into potential hazardous compounds.

Normally the mixtures of oil and water will form two separate layers. If there are sufficient amounts of oil in the sample, the oil will form a distinctive monomolecular layer on the surface of water. The oil will only exist as tiny droplets suspended in the water if there are insufficient amounts of oil in the sample. Under this circumstances the surfactants acts as a bridging agent to bridge the gap between the oil and water. The charged head of the surfactant will reside in the water layer, while the greasy tail will be dissolved in the oil. Consequently these surfactants allow formation of a stable emulsion of water in oil, or oil in water (Fig. 2.2) and making the separation of oil from water, or water from oil a complicated and problematic process. The surfactant stabilized droplets are termed as micelles.



Oil in water

Water in oil

Fig 2.2: Surfactant stabilized micelles

Solubility in water is an important characteristic of surfactants: insoluble or low-soluble (carboxylic acids, amines, alcohols of the aliphatic series, ethers), colloid-soluble (fatty soaps, fatty acid soaps, synthetic soaps), and soluble surfactants. Surfactants are also classified by their degree of dissociation in water as ionogenic and nonionogenic substances. Ionogenic compounds dissociate in water and are subdivided into anionic and cationic compounds. Nonionogenic compounds do not dissociate in an aqueous medium although they are characterized by significant solubility due to the presence of polar groups in the molecules. Based on the wetting capacity, surfactants have various properties for example lubricating, froth-forming, dispersing, solubilizing, detergent, etc (McClements, 1999).

2.4.2 *Emulsions*

Emulsions are heterogeneous systems in which the external phase (dispersion medium) is water, and the internal phase (dispersed phase) is oil (Dickinson, 1999). Therefore emulsion can be conveniently classified according to the distribution of oil and aqueous phases. In oily wastewater systems, when the interfacial tension of the oil and the sludge is thermodynamically low, the system is favorable enough for emulsification of oil in water. Hence, a system which consists of oil droplets in an aqueous phase is called as oil-in-water or O/W emulsion and a system with water droplets dispersed in oil phase is termed as water-in-oil or W/O emulsion (McClements, 1999). The usage of emulsifiers, extreme heat, agitation and pumping in the milling process further assist the formation of these undesirable oil droplets.

In a waste stream, the oil droplets tend to merge with their neighbors when they collide to each other, which could lead to complete phase separation. However when these droplets are transformed into emulsions caused by the milling processes, they are extremely stable and their specific density is very close to water (McClements, 1999). Stabilized emulsions are very difficult to be separated and even when separated they would not coalesce to form a homogenous layer of oil which can be easily removed by physical separation. The traditional methods for the separation of oil and emulsion in wastewater can be classified as chemical, mechanical and thermal (Hupka & Miller, 1999).

2.4.2(a) *Emulsified Oil Droplet*

O/W emulsions are kinetically stable but thermodynamically unstable (Laemmle, 1992). Thus, the state of lowest free energy is total phase separation. In a typical O/W emulsion, oil globules are sequestered by a polar emulsifier, which consist of an oil soluble end and a negatively charged oleophilic/hydrophilic end. A schematic of an emulsified oil droplet is presented in Fig. 2.3. The hydrophilic end of O/W is negatively charged, and imparts a negative surface charge to the oil droplet.

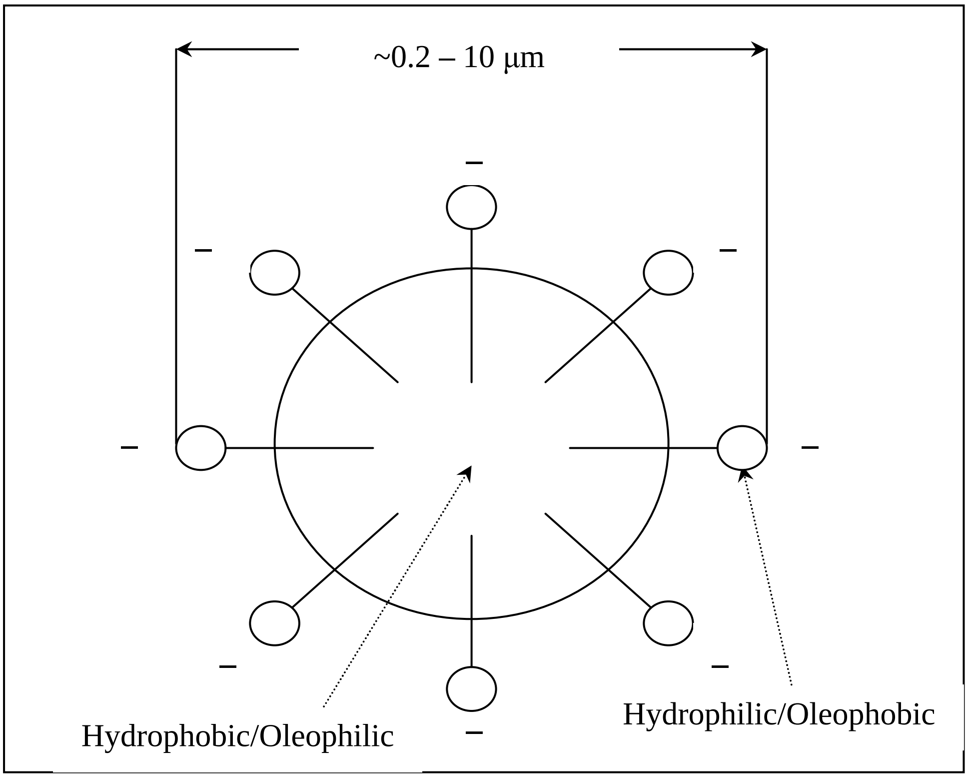


Fig. 2.3: Schematic of an emulsified oil droplet

This electrostatic repulsion between the negative charged droplets prevents the droplets from agglomerating. In time, the emulsifiers are degraded through a variety of chemical and biochemical reactions. Eventually, the repulsive force reduced to the extent that individual oil droplets can approach each other at short enough distance that Van der Waal's forces become operative. Larger oil droplets are formed, and the agglomeration process proceeds (Ronald *et al.*, 2000).