

CHAPTER II

LITERATURE REVIEWS

2.1 Palm Oil Mills Wastewater Treatment

In general, the milling process in palm oil industry must deal with myriad wastewater streams, which might require advanced treatment technology developed specifically for that stream. Wastewater generated from such activities usually is treated to remove oil and grease before disposal.

The extreme heat, agitation and pumping in the milling process further assist in the formation of undesirable oil droplets. These oil droplets are extremely stable as even when separated they would not coalesce to form a homogenous layer of oil.

General Oil Classification

- a. Free oil: oil droplets of 150 microns in diameter or larger.
- b. Dispersed oil: oil droplets are between 20 microns and 150 microns in diameter.
- c. Mechanically emulsified oil: oil droplets are less than 20 microns in diameter.
- d. Chemically emulsified oil: oil droplets are less than 20 microns in diameter that are chemically bonded to other molecules.
- e. Stable emulsion/dissolved oil: oil that is in solution with the continuous phase (in this case, the wastewater).

Free and dispersed oils

Gravity separation of free and dispersed oils can be accomplished by taking advantage of the density difference between water and most oils. Equation 2.1 Stokes' law describes the speed of gravity-based separation of oil and water for a specific oil droplet diameter:

$$v_r = K \frac{(g) (d^2) (r_w - r_o)}{\mu} \quad (2.1)$$

Where: v_r = oil droplet rise velocity

K = constant based on particle drag

- g = gravitational constant
 d = oil droplet diameter
 r_w = density of wastewater (continuous phase)
 r_o = density of oil (discontinuous phase)
 μ = wastewater viscosity

The relationship above shows that the rise velocity rises primarily in response to increased oil droplet diameter or size, and secondarily in response to an increased difference in water-to-oil density (buoyancy) and decreasing wastewater viscosity. A less obvious variable affecting the rise rate is the system temperature, which affects liquid densities and viscosities. In general, a warmer stream temperature leads to higher rise velocities. In addition, some oils may have nearly neutral buoyancy or may be heavier than water over wide temperature ranges. Although Stokes' law provides a good basic description of the physical variables influencing oil droplet separation from water, other factors also can interfere with the separation process. These factors include the degree of stream turbulence (Reynolds number), temperature and flow convection effects, short-circuiting and the presence of solids or emulsifying agents.

Emulsified and dissolved oils

When oil is emulsified in water, the oil essentially is broken down into microscopic oil particles. The particles behave like solid colloids such as clay. Colloids are so small that Stokes' law for such particles predicts extremely slow separation. In addition, forces that are too small to affect larger droplets cannot be ignored for colloids. For instance, molecular interaction at the particle surface breaks down chemical bonds, resulting in the formation of ionic molecules. Thus, colloids tend to have surface charges that repel each other, so they cannot coagulate. This description generally applies to all mechanical emulsions that are produced by pumping, mixing and other turbulence-inducing activities that break the droplets in smaller and smaller droplets.

2.2 Emulsion Classification

In the general, an emulsion is a dispersion of one liquid in another with which it is immiscible. The particle sizes of the dispersed phase lie between a few hundred nanometers and a few ten of micrometers. Emulsion technology had developed its own language and definitions. The two immiscible liquids that constitute an emulsion are referred to as "oil" and "water," as these is proverbial representatives of two such liquids. Within an emulsion, one liquid phase is in the form of droplets and is therefore distinguished from the other phase. A number of different terms, listed in Table 2.1 are used to express this distinction.

Table 2.1 Terminology of Phases

Phase 1	Phase 2
Droplet	Serum
Dispersed	Medium
Discontinuous	Continuous
Internal	External

Emulsions appear as two types: water droplets dispersed in oil, designated W/O, and oil droplets dispersed in water, designate O/W. Read W/O as water-in-oil, and O/W as oil-in-water.

2.3 Breaking Emulsions

Creaming

Due to the density differences between most edible oils and water, there is a tendency of the oil phase to concentrate at the top of the food emulsion. The rate of creaming can be lowered by reducing the droplet size, lowering the density difference between oil and the aqueous phase, and increasing the viscosity of the medium. In addition, the creaming rate is dependent on the volume fraction of the dispersed phase.

Flocculation

Flocculation is defined as a process by which two or more droplets aggregate without losing their individual identity. Bridging flocculation occurs in the presence of macromolecular emulsifying agents in

an emulsion. Emulsion droplets flocculate through interaction of the adsorbed macromolecules between droplets. Bridging flocculation is a very complex phenomena and greatly depends on the size, type, amount of the macromolecules used in the system. In addition, rate of flocculation can be affected by the pH and ionic strength of the aqueous environment. Interactions among protein, polysaccharide, and water soluble surfactants can also affect the stability of the emulsion.

Coalescence

Coalescence is the process when two or more droplets collide to each other and results in the formation of one larger droplet. Coalescence involves breaking the interfacial film and is irreversible. At extreme, a planar interface exists between the homogeneous lipid phase and the homogeneous aqueous phase. Various factors, such as solubility of the emulsifier, pH, salts, emulsifier concentration, phase-volume ratio, temperature, and properties of the film, affect coalescence stability of emulsion.

Further steps have to be taken if coalescence is to be promoted. These steps may be mechanical, thermal, or chemical.

Mechanical Demulsification

The rate of demulsification can be promoted by agitation, as in a blender. Many emulsions are sensitive to high shear, which throws the droplets into one another with consequent coalescence. Centrifugation is another mechanical method to accelerate creaming or breaking.

Thermal Demulsification

Most emulsions are less stable at higher temperatures, as the adsorption of the stabilizer decreases with temperature. In some cases the emulsifying agent is thermally decomposed. The PIT is the temperature at which the emulsion inverts, which is also the temperature at which it is least stable. Demulsification can then occur by heating or cooling the emulsion to the PIT.

Chemical Demulsification

An emulsion will often break if the emulsifying agent is chemically altered. Emulsions stabilized with alkali-metal soaps are broken on adding acid or metal ions. Emulsions stabilized with anionic agents can be broken by adding a cationic detergent. A more subtle chemical effect is to alter the HLB (Hydrophile-Lipophile Balance) number. This procedure depends on the two solutes being able to comicellize, which allows them to blend so intimately that the mixture behaves as a unit of intermediate HLB. Thus an O/W emulsion stabilize with an agent of high HLB may be vulnerable to the addition of an agent of low HLB.

2.4 Enhanced oil recovery

Within commercial emulsion breaking, a number of general rules help to form the basic philosophy of how emulsions behave:

- a. Emulsions are composed primarily of immiscible liquids. Separation should be the natural tendency of these liquids, providing a density differential between the liquids exists.
- b. The rate of gravitational settling or rising is dependent on the surface tension of the droplets that form the internal phase of the emulsion. Large droplets have less surface tension as a function of mass than small droplets; therefore, anything that can be done to increase droplet size, or coalescence, will increase the rate of separation.
- c. An emulsion is stable within a given environment. Altering the environment may affect the stability of an emulsion and thus allow separation of the phases.
- d. A stable emulsion exists only when emulsifying agents are present. Elimination, alteration, or neutralization of the emulsifying agents will allow immiscible liquids to separate.

From these four generalizations it becomes apparent that a number of options exist in emulsion breaking. Any single change in these areas may result in the resolution of an emulsion.

2.5 Important interfacial parameters

Interfacial tension

At the interface between the liquids there will be interactions between molecules of different type and the interfacial tension arises due to the attractive forces between the molecules in the different fluids. If interfacial tension between two phases becomes zero, then the two phases become miscible. This result is the ultimate aim of many type of enhanced oil recovery. In practice, it is difficult to make interfacial tension approach 0 for liquids of such different characteristics as oil and water.

Interfacial viscosity

Interfacial viscosity is related to the interactions of molecules located at interface with one another. Macromolecular surfactants are known to produce a high interfacial viscosity, as well as high MW molecules with functions that favor lateral interactions. Low interfacial viscosity is desirable in enhanced oil recovery operations, so that displaced oil globules may readily coalesce into an oil bank.

Interfacial wettability

The wettability of a liquid is defined as the contact angle between droplets of the liquid in thermal equilibrium on a horizontal surface. Depending on the type of surface and liquid the droplet may take a variety of shapes as illustrated in Figure 2.1. The contact angle θ is given by the angle between the interface of the droplet and the horizontal surface. The liquid is termed wetting when $90^\circ < \theta < 180^\circ$ degrees and non-wetting when $0^\circ < \theta < 90^\circ$. $\theta = 0^\circ$, 180° degree corresponds to perfect wetting and the drop spreads forming a film on the surface.



Figure 2.1 A liquid droplet in equilibrium with a horizontal surface surrounded by a gas.

2.6 Commercial emulsion breaking

Electrodialysis

Electrodialysis (ED) depends on two factors: first, the fact that if two electrodes are placed in an aqueous solution and a direct current passed through it, the ions in solution will migrate to the electrode of opposite charge; secondly, the fact that membrane will selectively pass only positive or negative ions. These cells can be stacked in parallel and operated continuously at substantial throughputs. Care must be taken to keep suspended solids or oils from plugging or fouling the membranes.

Reverse Osmosis

In ordinary osmosis water diffuses through a semipermeable membrane from a dilute to a more concentrated solution. The overall effect is to dilute the concentrated solution. The driving force is the concentration gradient, and the magnitude of the driving force is measured as the osmotic pressure. It has been found that osmosis can be prevented by imposing a pressure gradient on the system. Furthermore, if the pressure gradient is larger than the osmotic pressure, water will actually be removed from the concentrated solution.

Ultrafiltration

Ultrafiltration (UF) membranes actually have very small pores. These membranes will pass water and some smaller dissolved materials of low molecular weight but will hold back large particles. Again, the main flow passes over the membrane at right angles to it, and the smaller species are removed. Because of the small pore size and the pattern, the membranes do not clog easily. In this process the emulsion is concentrated, and at the same time low-molecular-weight materials are removed. The recovered water is not as pure as in reverse osmosis, but it is free of oils and suspended matter and can often be reused.

Filtration Coalescence

Coalescers are used to accelerate the merging of many droplets to form a lesser number of droplets, but with a greater diameter. This increases the buoyant forces in the Stokes Law equation. Settling of the larger droplets downstream of the coalescer element then requires considerably less residence time.

If membrane increase the size of the pores, ultrafiltration go to microfiltration and, finally, to actual filtration and fibrous-bed coalescers. Here any material that is too big to pass the "hole" in the membrane is held on the matrix and must eventually be removed in some way. There are several ways that filtration can aid in demulsification. If the emulsion is stabilized by solids, it may be possible to filter out the solids and thus destabilize the emulsion. In practice this is done by passing the emulsion through a filter that is just fine enough to hold back most of the solids, but that is a coarse enough to allow a reasonably fast flow. This rate of flow will tend to wash off some of the oily material that might otherwise be mechanically held on the filter cake, and come to the very coarse "filters" or coalescers. The action here is to force the droplets of oil into contact with each other or with an oil-wet surface and thus cause coalescence. The mode of action of coalescers has been the subject of many studies.

Coalescers can be of two general types depending on the type of packing. There are fibrous-bed types and porous-bed types packing. Both types have been found to be effective in certain cases.

2.7 Additional methods and areas in demulsification

Spielman and Goren (1972) studied the coalescence of dilute oil-in-aqueous suspensions at high ionic strength by flow through glass fibrous mats having uniform fiber diameters. Incoming mean drop diameter of 1 to 7 μm , fiber diameter of 3.5, 6.0, and 12.0 μm , suspension superficial velocity of 0.01 to 1.0 cm/sec, mat thickness of 0.1 and 0.3 cm, oil viscosity of 44 and 462 cP, and preferential wettability were independently varied while measuring the degree of coalescence by Coulter counting and

corresponding pressure drops. Measured single phase pressure drops are about 30% smaller than predicted by theory. Pressure drops during coalescence were found to be independent of both incoming drop size and oil viscosity, as theory predicts. The relative permeability of the aqueous-wetted mats is about 0.12, corresponding to a uniform coalesced oil saturation of 0.30 in the mats. Semiempirical correlations of a dimensionless filter coefficient against a dimensionless adhesion group are presented to describe the extent of coalescence.

Burford et al. (1976) studied the effects of intermittent permeate flow and crossflow on membrane coalescence of oil-in-water emulsions. The effect of oil droplet residence time within the membrane porous matrix was investigated and a novel process is proposed based on intermittent permeate flow: flow or no flow, at 0.01 Hz. Polytetrafluoroethylene membranes with 0.45 and 1.20 μm nominal average pore size were used to coalesce emulsions with an average 1.5 μm droplet diameter. Experiments were carried out in a crossflow filtration cell and crossflow velocities were varied from 0.07 to 0.28 m/sec. Fluxes were found to increase with crossflow although oil rejection was zero, implying no concentration polarization. Results also demonstrated an improvement in coalescence performance during intermittent operation at low crossflow velocities. Under some conditions intermittent permeate flow operation produced higher permeate fluxes than without intermittent operation and is a potential novel process for membrane coalescence.

Spielman and Su (1977) studied the coalescence of dilute oil-in-water suspensions at steady state by flow through beds of glass beads having uniform diameters of 0.26, 0.36 and 0.50 mm. The diameters of the oil droplets in the incoming suspensions were 1 to 5 μm with oil viscosities are 50 and 500 cP, total suspended volume fractions are 2×10^{-4} and 8×10^{-4} , and superficial velocities are 0.3 and 0.6 cm/sec. The data are interpreted using equations that assume three distinct regimes of coalescing phase: oil microdrops suspended in capillary-conducted water; capillary-conducted oil forming well connected

channels; held-up oil as discrete coalescing globules that act as an intermediary between the oil microdrops and the capillary-conducted oil. Filter coefficients characterizing microdrop capture are reported and correlated assuming capture is governed by van der Waals forces. The rate of coalescence of the intermediary held-up oil is found to be approximately first order in the fraction saturation of the intermediary held-up oil with a rate coefficient of about $1 \times 10^{-4} \text{sec}^{-1}$.

Soo and Radke (1984) studied the flow mechanism of dilute, stable emulsions in fine grained porous media. Oil-in-water emulsions of mean drop sizes ranging from 1 to 10 μm are studied in sandpacks of 0.57 and 1.15 μm^2 permeability at a superficial velocity of 0.07 mm/s. Low viscosity oil drops cause permeability reductions of up to 80%, with 4 to 5 μm size drops being the most effective. By examining drop sizes and pores sizes, as well as transient effluent emulsion concentration and transient pressure data, and found that Permeability reductions during emulsion flow are caused by droplet capture mechanisms similar to those found for solid particle deep-bed filtration.

Walsh et al. (1996) studied the effect of solid and liquid aerosol particle loading on fibrous filter material performance. In this work samples of prefilter material of 12% packing density have been loaded with solid particles of 0.6, 1.4, and 2.2 μm stearic acid aerosol particles, at a face velocity of 0.10ms^{-1} . Major differences between the behaviour of fibrous filters under solid and liquid load can be related back to the fundamental difference between the ability to flow of liquids and solids. Solid particle creates permanent intrusive structures that are difficult to disturb. Because liquid particles can coalesce, and ultimately flow, the nature of the loading behaviour is much more variable, with internal relocation, drainage, re-entrainment, all possible outcomes of the loading process. Figure 2.2 illustrates the internal structure of a filter is altered by solid and liquid particles.

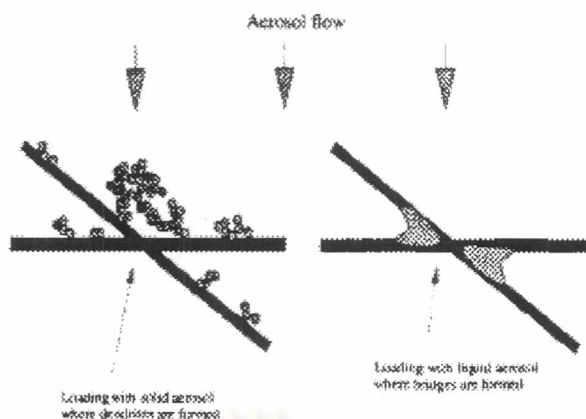


Figure 2.2 Illustration of dendrite formation under solid load, and bridge formation under liquid load

Actual porous-bed coalescers do not try to hold back either phase. They act to force the suspended droplets into close contact and thus encourage coalescence. The coalescers are conceded to work best if the material of the filter unit is wet by the disperse phase. Then the drops are forced into contact with each other or the wet filter and form a compact second phase which moves through the filter and releases large drops on the downstream side. These large drops settle readily, and the coalesced phase can be removed from the system.

Sharifi and Shaw (1996) studied the separation of secondary oil in water dispersions in packed-bed coalescers. Both fluid properties of Toluene, Sunflower oil, Engine oil, n-Decane, and Tap water were studied, viscosity of 0.00107, 0.0574, 0.0453, 0.00092, and 0.001 Pa.s, interracial tension of 0.0189, 0.0085, 0.0242, and 0.0473 N/m, density of 866.7, 911.7, 880, 760, and 997 kg/m³, and surface properties of Teflon, polypropylene, polyethylene, PVC, glass, stainless steel, and ceramic (Berl saddles were varied). In this study show that while drops from all size ranges varied from 90 to 100 μm coalesce on packing surfaces, secondary drops are also produced during drop detachment from all packing surfaces and the net coalescence rate for secondary drops is low. Our principal conclusions are that the maximum size of secondary drops produced on packing surfaces is independent of the nature of the packing material, and that this drop size can be expressed as

a simple function of the physical properties of the dispersion.

Radmila et al. (1997) studied the separation of oil-in-water emulsion by bed coalescence using polyurethane foam chips as the filter media in a steady-state regime, including gravity settling. A study was made of the effect of working conditions such as fluid velocity of 10, 13, 16, 19, 30, 35, 40, and 45 m h⁻¹, bed length of 3, 5, 7, 10, and 15cm, and influent oil content of 500mg L⁻¹, 800mg L⁻¹, 1100mg L⁻¹, 1400mg L⁻¹ and 2000mg L⁻¹ on the effluent oil concentration and separation efficiency. When the fluid velocity exceeds its critical value, the influence of concentration and bed length is changed. The increase in the influent concentration causes an increase in the effluent concentration, the more so the higher the fluid velocity. The obtained empirical equations may serve to choose the working parameters, ensuring a desired effluent concentration and separation efficiency.

Jingquan and Yongan (2004) studied the coalescence of the oil-in-water emulsions through fibrous and granular beds. Three different coalescing media are used in this study, which include polypropylene fibers and nylon fibers for the fibrous beds and polypropylene particles for the granular beds. The major purpose of this study is to examine the effects of some controlling parameters on the coalescence performance. Controlling parameters are Flow rate varied to include 206.21, 308.92, 468.59, and 542.68 ml/min, inlet oil concentration of 2000, 5000, and 10,000 ppm, bed length at the three outlets of 20, 40 and 70 cm, and Fiber size of two different fibrous materials, both of which are oleophilic. The polypropylene fiber with the characteristic size of 170 μm and the other is the nylon fibers with the characteristic size of 80 μm . In the parametric studies, first, it has been found that the overall coalescence efficiency is not a monotonous function of flow rate in the granular beds. The coalescence efficiency is higher at some intermediate superficial velocities. Secondly, the higher the inlet oil concentration is, the lower the overall coalescence efficiency is. Thirdly, the coalescence performance is insensitive to the length

of the granular bed tested in this study. It has also been found that the coalescence performance is better for a fibrous bed packed with smaller fibers.

Yan and Masliyah (1994) studied the demulsification of Oil-in-water emulsions stabilized by asphaltene-treated kaolinite clay particles by the addition of fresh oil. The effect of oil droplets diameter was varied from 56 μm to 194 μm , Contact angle was varied from 26° to 143° , equilibrium clay concentration at the oil droplet surface was varied from $1.52 \times 10^{-5} \text{ g cm}^{-2}$ to $5.5 \times 10^{-5} \text{ g cm}^{-2}$, volume fraction of oil in emulsion was varied from 0.184 to 0.492, oil viscosity varied to include Bayol-35 (2.4 mPa s), light mineral oil (44 mPa s) and heavy mineral oil (142 mPa s), amount of added fresh oil was varied from 0 to 80g, and stirring speed was varied from 200 rpm to 800 rpm on demulsification are Studied. It was found that when both the oil droplet diameter and the initial clay concentration in the water were kept constant, the demulsification rate exhibited a minimum at a clay contact angle of about 90 Celsius. However, when the clay concentration at the oil droplet surface was kept constant for different clay contact angles, the demulsification rate increased monotonically with an increase in the contact angle. Having a larger oil droplet and high volume fraction of oil in the concentrated emulsion and a large amount of fresh oil addition gave a higher demulsification rate. Raising the clay concentration at the oil droplet surface led to a slower demulsification rate. The viscosities of both the fresh oil and the oil in the primary emulsion had little influence on the demulsification rate.

Yan and Masliyah (1996) studied the demulsification of oil-in-water emulsions stabilized by kaolinite clays treated with different asphaltene concentrations by the addition of fresh oil under the action of stirring. Controlling parameters are pH of aqueous phase of 0, 1, 2, 3, 4, and 5, and different fresh oil of Heptane, Bayol-35, Heptol, and Toluene. Clay concentration analysis showed that when the emulsion was mixed with the fresh oil, the clay concentration of the resulting flocs became higher than that of original emulsion, leading to higher clay coverage at the oil droplet surface and

difficulties for further demulsification. If the flocs were centrifuged, the clay concentration in the centrifuged flocs was about four times that of the original emulsion. It was not efficient to desorb the clays from the oil droplet surface by diluting the emulsions with fresh water because of the hysteretic behavior involved in the clay desorption. By modifying the clay surface properties with a higher aqueous phase pH or by using asphaltene-soluble solvents as fresh oil, the clays were desorbed from the oil-water interface, leading to a higher demulsification rate.

Yan and Masliyah (1997) studied the continuous demulsification of solids-stabilized oil-in-water emulsions by the addition of fresh oil. Controlling parameters on the coalescence are emulsion residence time varied from 0 s to 3600 s, equilibrium initial clay concentration at the oil droplet surface varied from 0 to 10×10^{-4} kg/m², oil droplet diameter varied from 40 μ m to 140 μ m, clay contact angle varied from 40° to 140°, initial oil volume fraction in prepared emulsion varied from 0.1 to 0.4, ratio of flow rate of the added fresh oil to that of the oil in the emulsion varied from 1 to 4, mixing speed varied from 500 rpm to 900 rpm, and aqueous phase pH varied from 4.5 to 7.5 on Oil Recovery. It was found that the variation of the oil volume fraction in the emulsion decreased exponentially with the emulsion residence time in the mixer. The demulsification rate constant decreased with increasing the clay concentration at the oil droplet surface as the clays offered a strong barrier to oil droplet coalescence. The demulsification rate constant exhibited a minimum at a clay contact angle of about 90°. Having a larger oil droplet, a higher volume fraction of oil in the emulsion, and a higher ratio of fresh oil to the emulsion oil led to a higher demulsification rate constant. An optimum mixing speed of 600 rpm was obtained due to poor mixing at a lower mixing speed and emulsification at a high mixing speed.