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Treatment of Vegetable Oil Refining Wastes

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TREATMENT OF VEGETABLE OIL REFINING WASTES

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14. ABSTRACT

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Key Words: vegetable oil industry, vegetable oil, refining, industrial wastewater, waste characterization, reduction, removability, treatment technologies

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TREATMENT OF VEGETABLE OIL REFINING WASTES

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1. INTRODUCTION

Vegetable oils and fats are essential to human as a source of nutrient, but they are also used in animal feed, for medicinal purposes, and for certain technical applications. There are numerous vegetable oils derived from various sources. Soybean, sesame, sunflower, corn, canola, and cotton seeds are the most commonly used raw materials for the production of edible oil (1). Their yields, compositions and physical and chemical properties determine their usefulness in various applications aside edible uses.

There are numerous technological processes carried out to obtain refined vegetable oils from seeds. Until the 19th century, vegetable oils were extracted from oil seeds through mechanical or hydraulic means. Today, vegetable oils are obtained by different pressing methods, solvent extraction or a combination of these (2). The selection of the extraction process depends primarily on the oil content of the source material, the amount of residual oil in the meal allowed, the amount of protein denaturation allowed, the amount of investment capital available, and local environmental laws concerning emissions of volatile organic compounds (VOCs).

A basic process chart for vegetable oils and related products is given in Figure 1. Oilseeds are dehulled, cracked and flaked, and prepared for oil extraction. Hexane is used to dissolve the oil in the prepared oilseed or similar input and then recovered in a desolventizing (evaporation) process and recycled for reuse in the process (3, 4).

[Insert Figure 1 here]

Crude vegetable oil obtained at these facilities is then transferred to a refining facility where they are prepared for human consumption or prepared for use in animal feeds. Refined edible oil is a process where free fatty acids are volatized, condensed and recovered simultaneously with vacuum decolouring operation.

Processes in vegetable oil refining, such as filter backwash, acidification of soapstock, and washing of equipments produce big amounts of wastewaters (5). These wastewaters have high chemical oxygen demand (COD) and oil and grease levels, along with elevated phosphorus and dissolved solids concentrations (6).

2. REFINING

Crude oils are not usually considered to be edible before the removal of numerous nonglyceride compounds through operations collectively known as refining. The refining processes remove undesirable materials such as phospholipids, monoacylglycerols, diacylglycerols, free fatty acids, colour and pigments, oxidised materials, flavour components, trace metals, sulfur compounds, trace solvent residue, and water, but, may also remove valuable minor components which are antioxidants and vitamins such as carotenes and tocopherols. Unfortunately, some of the refining operations are not very selective and remove some beneficial compounds along with the targeted undesirable ones. However, some oils, such as olive, tallow, and lard, have been consumed without refining.

Figures 2 show a general diagram and processing steps involved in the refining of vegetable oils. There are two major types of refining: chemical and physical. The major steps involved in chemical refining include degumming, neutralizing, bleaching, and deodorizing. Physical refining removes free fatty acids (FFA) and flavors by distillation, to combine the steps of neutralization and deodorization into one operation.

[Insert Figure 2 here]

Conventional chemical refining involves degumming for the removal of phospholipids, neutralization for the removal of FFA, and bleaching for decolorization and deodorization. Water is added during degumming to hydrate any gums present and the mixture is then centrifuged for separation. Non-hydratable gums are removed using phosphoric or citric acid before water is added and separation takes place in a centrifuge.

In physical refining, the crude oil is degummed and bleached, and then steam stripped to remove FFA, odor, and VOCs all in one step. This replaces chemical reaction mode using an alkali (caustic soda) in chemical refining. A physical pretreatment is used to achieve low phospholipid content by degumming and using bleaching earth. Following this, FFA can be stripped from the physically pretreated oil using steam distillation in a vacuum at temperatures of around 250^{o}C and refined by the oil flowing over a series of trays countercurrent to the flow of the stripping steam (7). Previous neutralization stages are eliminated because the neutralization and deodorization are combined. A scrubber is then used to condense the greater part of the fat from the vapors as a water-free product.

The advantages of physical refining method over the chemical refining are listed as follows;

- better yields
- high quality of fatty acids as by-products
- good oil stability
- simultaneous distillation of fatty acids and deodorization
- lower cost of equipment
- simplicity of operation

Ultimately, the marketing of a refined vegetable oil depends on the specifications met at the end of the processing (8). The typical steps followed by the industry in the refining of vegetable oils are discussed below.

2.1. Degumming

Degumming is a water-washing process to remove phosphatides. At this step, free fatty acids are converted to water soluble soaps, soap-stock. Phosphatides can hydrate from moisture in the air during storage or in the headspace, thus, phosphatides becomes insoluble in the oil, and precipitate, resulting an oil that is unattractive because of unpleasant sludge or gums (7). It is vital to remove the phosphatides content in the crude oil because the presence of this component will result in undesirable flavor and color, and shorten the shelf life of oil. Phosphatides, also known as lecithin, are important food emulsifiers and have an economical value. Therefore, they should be recovered where possible.

During degumming, the phosphatide portion of oil is either removed or conditioned by the addition of phosphoric acid or citric acid. Hot water is added to hydrate any gums present in crude oil prior to centrifugal separation. Non-hydratable gums are removed by converting them first to a hydratable form using phosphoric or citric acid, followed by the addition of water. This causes the separation of phosphatides from oil and they are removed after certain settling time. Occasionally, segregated gums are not directly removed but with soap-stock formed during neutralization (9). During degumming, caustic soda preheated to between 90°C and 110°C is added to the oil to saponify the FFA. The dosage of phosphoric acid is normally within the range of 0.05–0.1% of oil weight and the acid concentration is about 80-85%. Excessive use of phosphoric acid should be avoided since it increases phosphorus acid concentration that may cause further refining problems. However, degumming is not as reliable for bleached oils. Degumming may be conducted either as a separate process or concurrently with neutralization.

2.2. Neutralization

FFA naturally present in oil causes acidity which should be neutralized. Neutralization is the most important operation in refining edible oils. The neutralization process consists of three steps such as neutralization, washing, and drying. Neutralization is achieved by accomplishing a reaction between the FFA and caustic soda (sodium hydroxide) to form soap referred to as soap-stock. The chemical reaction (9) involved in this operation is given in Equation 1.

$$\underset{\text{fatty acid}}{\underline{\text{R-COOH }}}+ \text{NaOH} \longrightarrow \underset{\text{soap-stock}}{\underline{\text{R-COONa}^{+}}} + H_2O \qquad (1)$$

The soap-stock is then removed by precipitation followed by sedimentation or centrifugation and may be further processed into acid oils by splitting. Soap-stock is a valuable byproduct of refineries in that it can be acidulated with sulfuric acid to produce a marketable product. When re-acidified, the fatty acids (95% fatty acids) will separate in settling basins as 35-40% free liquid, called acid oil, from an emulsified layer (high in phosphatides) and a water layer. To regain fatty acid from soap-stock, the soap-stock is heated to between 70°C and 100°C and reacts with sulfuric acid to reform the fatty acids. The fatty acids are insoluble in water and float to the surface where they are skimmed. The mineral salts and any water soluble material remains in the water layer that is neutralized and discharged to the waste treatment facilities. The chemical reaction (9) taken place in this step is shown in Equation 2.

$$\underset{\text{soap-stock}}{\underline{\text{R-COONa}^{+}}} + H_2SO_4 \longrightarrow \underset{\text{Fatty acid}}{\text{R-}\underline{\text{COOH }+\ }}Na_2SO_4 \qquad (2)$$

The oil from caustic refining contains trace amounts of soaps and sodium hydroxide; hot water is added to the oil and agitated to remove them. The oil and water from this process is a weak (1% to 3%) soap solution with a relatively high pH. The oil from water washing contains trace amounts of water that can clog the filter during the subsequent filtration operations.

In vacuum drying, the oil is heated under a vacuum to remove this trace moisture. There is no significant waste stream from this process. Citric acid may be used instead of phosphoric acid, which brings a range of advantages, including reduced phosphorus load in the wastewater and a slight reduction in the amount of sludge. Enzymatic degumming uses enzymatic hydrolysis of the phosphatides. Environmental benefits from this approach include reduced consumption of phosphoric and sulfuric acid, as well as caustic soda, water, and energy. Efficiency of neutralization depends on using the proper amount of sodium hydroxide, proper mixing, proper temperature, sufficient contact time, and efficient separation.

2.3. Bleaching and Filtration

Vegetable oils are commonly treated with bleaching earth after alkali or physical refining and before hydrogenation and final deodorization. However, bleaching can be applied at different stages of the edible oil refining operation, for example, after water or acid degumming. The aim of bleaching is to remove red-pigments (carotenoids, xanthophyll, and gossypol), or green colors (chlorophyll), metals (nickel or iron), residual soaps, phospholipids from the oil or fat as well as the breakdown of peroxides prior to deodorization (7).

In this stage, the oil is taken into cylindrical tank and mixed with bleaching material called bleaching earth, and then, heated up to 90^{o}C with steam under vacuum. Thus, the moisture from oil is evaporated and oil becomes dry. The dried oil is treated with bleaching earths or clays such as bentonite, diatomaceous earth, attapulgite, montmorillonite, and carbon (9) at about 1-2%. During this stage, trace metal complexes such as iron and copper, pigments, phosphatides and oxidation products are removed by adsorptive effect of the bleaching earth. Then, the mixture of oil and bleaching agent is filtered a standard plate and frame press for separation. The clear oil obtained is bleached oil and is very much lighter in color than the neutralized oil. The oil charge is dehydrated under vacuum to avoid any further deterioration due to oxygen. In this operation, the colored pigments in oil are adsorbed by certain bleaching agents under specific conditions. Used bleaching material is called spent earth. Spent bleaching earth contains some entrained oil, as much as 30–50%. The spent bleaching earth is removed in pressure filters and blown with steam to reduce its oil content to about 20%. It is possible to reduce the oil content to about 1% if the cake removed from the filter is extracted with a solvent.

2.4. Hardening

The aim of hardening is to raise the melting point of the oil for use in shortening or margarine manufacture by the addition of hydrogen to unsaturated oil molecules over a nickel catalyst. The degree of hardening is determined by the temperature, pressure and quantity of hydrogen gas added to the reaction. The catalyst is filtered out of the oil after the reaction is complete. No significant wastewater is generated by hydrogenation.

2.5. Deodorization

The final step in refining fats and oils is deodorization. The oil after bleaching is practically pure, but it contains small amounts of original odoriferous matter and also the chemicals used during neutralization process. The filtered oil is channeled into the deodorizer for the deacidification and deodorization treatment. Deodorization is mainly aimed to remove compounds responsible for undesirable odors and flavors, such as residual free fatty acids (especially low molecular weight fatty acids), aldehydes, ketones, and alcohols from crude degummed and/or alkali refined edible oils and fats after bleaching. This process utilizes a combination of high temperature heating about 200^{o}C, under vacuum (2-4 mmHg) and direct steam injection of about 2.5-4.0 % by weight of oil (10). The volatile materials are evaporated off with some carrier (commonly direct steam). This oil is then cooled and clarified through a Filter Press to get sparkling oil. The purpose of deodorization is to make oil blend and tasteless. During this process, FFA in the form of fatty acid distillate is removed as refining waste, at the upper section of deodorizer. Apart from FFA, carotenoids pigments, primary and secondary oxidation products are also being removed as it may contribute to off-flavors.

3. ENVIRONMENTAL IMPACTS

The major problem met by vegetable oil industry is wastewater, both quantitatively and qualitatively. Wastewater generation in an edible oil industry can be divided into two categories:

- Wastewater generated directly from processes e.g. neutralization, washings etc.

- Wastewater generated from auxiliary systems e.g. cooling and vacuum systems etc.

Wastewater generated from both sources varies significantly in pollution load and concentration. Process wastewater contains high amounts of BOD, COD, oil & grease, TSS, TDS, and nickel while wastewater generated from the auxiliary systems is huge in quantity and relatively higher in temperature. It sometimes contains traces of VOCs. Boiler condensate recovery system is not efficient in some, and practically non-existent in most.

Most of the water used for neutralization and deodorization in vegetable oil processing facilities end-up as wastewater with a high organic load. The complexity of wastewater sources makes such wastewater hard to treat. The sources of wastewater can be listed as cleaning of greasy floors and equipment, leakages, heat exchangers, gas scrubbers, barometric condensers, process water from the refining plant and soap-stock splitting effluents. Typically vegetable oil refinery wastewater contains used chemicals including alkalis such as caustic soda and sodium carbonate; heavy metals from bleaching earth; acids such as phosphoric acid, citric acid, and sulfuric acid; Ni-catalysts; and methylates. Also, pesticides used during the growth of vegetable oilseed have been found in vegetable oil processing industrial wastes. Additionally, vegetable oil refinery wastewater contains chemical compounds like phenol, heavy metals from bleaching earth, catalysts used in the hydrogenation process, oxidizable substances and fats and oils to lesser degree. Because of quantity and characteristic variations and complexity, wastewater treatment to meet the desired effluent standards is complicated, and the selection of wastewater treatment method depends on many local conditions and, therefore, cannot be standardized.

Solvents such as acetone, ethanol, and methanol are sometimes used instead of, or to supplement, hexane in the extraction process. Hexane can cause health problems in relatively low concentrations and other dangerous chemicals, including strong acids and bases, present significant health and safety hazards.

Other than liquid waste, solid waste and air emissions are also generated. Solid wastes include spent earth, filters cloth, and spent catalyst. Spent earth and spent catalyst are in slurry form and are combined together to extract before their final disposal. Also, during production of vegetable oil, some by- products, such as oils for animal feed or pharmaceutical products, are often produced by further processing of residues. This processing can reduce solid waste production, including fractions like spent bleaching earth that can be reused for energy production through direct incineration or biogas production either on-site or at another location. Citric acid and phosphoric acid can generally be used interchangeably in degumming operations.

3.1. Water and energy consumption

An average 1,000 metric tons per day vegetable oil refinery can consume as much as 75,000 m^3 of fresh water annually. Water comes in contact directly with the oil during a number of processes used within the typical refinery. The processes with the most significant water consumption are crude oil production; chemical neutralization and subsequent oil washing and deodorization (11). Table 1 gives information on water consumption and wastewater generation for some processes in the vegetable oil processing industry. For example, water is used:

- to remove phosphatides in the degumming process;
- to dilute the caustic in the chemical refining process;
- to further reduce unwanted constituents such as soaps, gums, and metal ions in the water-washing step.

Also, some water is consumed in other, indirect, applications, including:

- barometric condensing water in deodorization vacuum systems;
- boiler feed water;
- cooling tower make-up water;
- minor cooling applications using fresh water;
- centrifuge service water.

[Insert Table 1 here]

The energy consumption of vegetable oil processing facilities depends on the type of raw material, the equipment and the manufacturing processes. Heating to produce steam for process applications (especially for soap splitting and deodorization), cooling, drying, milling, pressing, evaporation and distillation are the major energy consuming steps. Some amount of energy is lost either during the cooling of the product for the subsequent process, or in terms of heat contained by the wastewater.

About 200-500 kg steam is consumed per ton of processed seed (155-390 kWh/t) and the electricity consumption is in the range 25-50 kWh/t processed seed (90-180 MJ/t). Table 2 and 3 shows energy and steam consumption for some processes in crude vegetable oil refining in German installations (11), which can be considered as indicators of this sector's efficiency and may be used to track performance changes over time.

[Insert Table 2 here]

[Insert Table 3 here]

3.2. Wastewater Sources and Quantities

In a vegetable oil industry, wastewaters are mainly generated from the degumming, deacidification, deodorization and neutralization steps (12). Table 2 shows wastewater generation of some processes in the vegetable oil processing industry. Blown down of the boiler and wash water from the de-oiling of the bleaching earth also contribute to the effluent in small amounts (13). Characteristics of the wastewater depend mostly on the type of oil processed and the process implemented (14, 15). The volume of wastewater produced changes highly with the raw material processed and the technology applied, for example wastewater volumes produced during the oil production from palm fruit can often be limited to 3–5 m^3/t of feedstock (14).

Wastewater generated during oil washing and neutralization may have a high content of organic material and, therefore, a high biochemical oxygen demand (BOD) and COD (13). Wastewater may also have a high content of suspended solids, organic nitrogen, and oil and fat, and may contain pesticide residues from the treatment of the raw materials; therefore, wastewaters from this industry need special attention (16). The characteristics of vegetable oil refinery wastewaters produced at soap-stock shredding and deodorization stages are given in Table 4.

[Insert Table 4 here]

The extraction plant wastewater consists of condensate. About 500-600 m^3/d condensate water with 300-400 mg/L BOD is generated during heating oils and jacket steam throughout the refinery. This stream contributes about 150-200 kg BOD per day to the wastewater load. It is usually hot (80-90ºC), clean water and suitable to be recycled as wash water in the refining step. The pH of this water is near neutral between 6 and 8.

Wash water generated in the oil washing step is high in BOD and fat due to dissolved soaps. The stream will contribute 450 to 2,200 kg/day of fat or BOD_5 to the sewer load. If the oil is not degummed before caustic refining, some water soluble phosphatides will be removed in this step and will cause higher loads. This is generally the case when corn oil is being processed. Wash water and barometric condensing water offer nearly ideal conditions for water recovery using evaporation. Both of these applications give an oil-water effluent that is greater than 97% water with only a small amount of organics such as neutral oil, free fatty acids, soaps, light ends, and phosphatides.

Greasy cooling water can be a major source of BOD_5 depending on the operation of the deodorizer scrubber and atmospheric conditions. Any organic material that passes through the scrubber becomes emulsified in the greasy water in the vacuum system. The greasy cooling tower dissipates the heat of condensation of the steam primarily by evaporation of the greasy water. In cold weather the water loses more heat by convection which decreases the amount of evaporation necessary. When the amount of water entering the tower via steam condensation is greater than the wind drift plus evaporation, it becomes necessary to blow down the tower to the sewer. The organic material in the water is primarily short chain free fatty acids. Typical COD values range up to 3,000 mg/L. For an overflow of 110 L/day, 340 kg of COD would be discharged to the sewer based on 3,000 mg/L of fat.

Tank car washings vary from one to four cars per day. The effluent is characterized by high temperature, 70 ºC, and a variable amount of emulsified oil. The BOD_5 can be anywhere from 2,000 to 60,000 mg/L.

The refining of crude vegetable oils generates large amounts of wastewater. The neutralization step, in particular, produces sodium salts of free fatty acids (soap-stocks) which breaks down through the use of H_2SO_4 and generates highly acidic and oily wastewater (13). Its characteristics depended largely on the type of oil processed and on the process implemented are the high COD, oil and grease, sulphates and phosphates content resulting in both high inorganic as well as organic loading of the relevant wastewater treatment works.

The neutralized acidulation water flow and COD is highly variable based on the amount of flush water being used on the centrifuges and whether or not the oil is being degummed prior to the refining. The phosphatides which would be removed in degumming significantly increase the strength of the acidulation water due to their water solubility. Fresh water can increase the moisture content of the soap from 50% to 95% which does not affect the total BOD_5 load, but, it does reduce the residence time in treatment facilities and reduces the processing time which is necessary to achieve good oil separation. BOD_5 of this stream is very high (25,000 mg/L) and the fat is relatively low (300-500 mg/L). This is the only waste stream from the refinery that is not composed primarily of hexane soluble material.

A typical day in vegetable oil processing facility would yield loadings of 1,800 kg/day BOD and 30 kg of fat based on 75,000 L at a 25,000 mg/L BOD_5 and 400 mg/L fat. Table 5 presents effluent guidelines for vegetable oil processing (14). These guidelines can be reached under normal operating conditions in properly planned and operated facilities through the application of pollution prevention and control techniques. Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in use of publicly operated sewage collection and treatment systems or, if discharged directly to surface waters, on the receiving water use classification.

[Insert Table 5 here]

There are some precautions for the prevention of process wastewater which are listed below:

- Emulsion breaking techniques (e.g. dissolved air flotation (DAF)) should be used to remove high BOD and COD oils from wastewater;
- Condensates should be recycled;
- Grids is needed to be used to protect drains in the production area and to prevent solid wastes and concentrated liquids from entering the wastewater stream;
- The dose and application of cleaning chemicals should be carefully determined and applied;
- Cleaning-in-Place procedures should be carefully prepared and applied to help reduce chemical, water, and energy consumption in cleaning operations;
- Cleaning solutions (e.g. through a soap-splitting process) should be properly treated and discharged to separate oil and fatty acids from the water phase and then through a fat trap;
- Phosphoric acid may be replaced with citric acid in degumming operations if feasible, thus, the phosphorus load in the wastewater is reduced and a small reduction in sludge quantities occurs.

3.3. Wastewater Treatment

Treatment of industrial wastewaters is difficult, and generally requires chemical or physicochemical treatment prior to biological treatment or discharge to a sewer system. Wastewaters from the vegetable oil refining processes fall in this category. The operating conditions and processes carried out influence the amount and characteristics of the by-products and wastes produced. The wastewater varies both in quantity and characteristics from one oil industry to another. The composition of wastewater from the same industry also varies widely from day to day (17). These fluctuations may also be attributed to different types of oils processed. Because of quantity and characteristic variations and complexity, wastewater treatment to meet the desired effluent standards is complicated, and the selection of wastewater treatment method depends on various local conditions and, therefore, cannot be standardized. Treatability studies becomes very important at this point and must be performed to describe wastewater characteristics before selecting any pre-treatment process to treat wastewater containing emulsified oil and grease wastewater. Thus, an oil-grease removal process can be designed efficiently and effectively (18).

Oily wastewater treatment in many respects is similar to the treatment domestic of wastewater. Firstly, settleable solids are removed in domestic wastewater treatment plant. Similarly, for the treatment of vegetable oil refining wastewaters, the separation of free floating oil from disperse emulsified and soluble fractions are performed at first stage wastewater treatment. At second stage of the treatment, oil/water emulsions are broken and dispersed oils are removed. Typical treatment technology is chemical treatment. In some applications, tertiary treatment is also used to remove finely dispersed and soluble oil fractions. Ultrafiltration, biological treatment and carbon adsorption may be used as a tertiary treatment method.

Physicochemical (skimming of oil, air floatation, flocculation, coagulation) treatment to remove colloidal pollutants followed by biological treatment to degrade dissolved organics are most commonly used techniques applied to vegetable oil refining wastewater effluent (18).

Primary treatment used in the vegetable oil sector generally includes grease traps, skimmers or oil water separators for separation of floating solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers (11). The purpose of primary treatment is to remove free floating oil and grease and suspended solids. This will also reduce the BOD and COD concentration. High correlation in terms of correlation coefficient (R^2) has been determined between COD with O&G on a large scale by Saatci et al.

(19) as 0.92 and by Aslan (20) as 0.90 for sunflower oil refining wastewaters and 0.81 for corn oil refining wastewaters indicating that a decrease in O&G may highly reduce the COD values. This can be achieved either by gravity settling or by dissolved air flotation (DAF).

Further, secondary treatment is applied and either chemical or biological processes are used. In general, the waste water is well suited to biological treatment. biological treatment, typically anaerobic followed by aerobic treatment (activated sludge, trickling filters and rotating biological contactors) for reduction of soluble organic matter (BOD); biological nutrient removal for reduction in nitrogen and phosphorus; chlorination of effluent when disinfection is required; dewatering and disposal of residuals; in some instances composting or land application of wastewater treatment residuals of acceptable quality may be possible (11).

The basic process of chemical treatment is coagulation (21, 22). The efficiency of treatment depends on the ratio of free oil to emulsified oil. The free oil can be easily removed from wastewater by physical processes using coagulating agents, e.g. alum and ferric chloride for phase separation (23). Additional engineering controls may be required to contain and neutralize nuisance odors (24, 25).

3.3.1. Unit operations in wastewater treatment of vegetable oil refining

The wastewater to be treated should also be analyzed for total oil and grease, including determination of the free, emulsified, and dissolved oil fractions. Although oil/water separators are designed to remove free oil, they also remove solids. Therefore, the solids content of the wastewater is important in overall system design. Analyses should include TSS, volatile suspended solids (VSS), and settleable solids. These analyses will help determine the amount and frequency of settled materials that will need to be removed from the bottom of the oil/water separator and the advisability of providing grit removal upstream of the oil/water separator.

Oil traps are used in oily wastewater treatment to remove free floating oils (24). Oleophilic (oil attractive) plates attract and retain small oil droplets under laminar flow conditions. Stokes' Law, the physical law governing the rise and fall rate of a droplet or particle in a fluid stream, can predict the settling time of solid particles and the rise time of oil droplets, which have specific gravities higher or lower than that of the main fluid. The plates may be made of an oleophilic material, such as polyethylene, fiberglass, or nylon to promote coalescence of oil droplets. For this reason, the units are sometimes referred to as coalescing plate separators. Parallel or coalescing plate separators are usually recommended only for light oil loadings when a higher level of oil removal is required and when the wastewater stream contains low solids concentrations.

Gravity grease traps, centrifugal separators, and rarely electro-flotation methods are also used as the other removal methods for free fats present in the oily wastewater. The majority of oil/water separators used is conventional gravity separators that rely on the different densities of oil, water, and solids for successful operation. The wastewater is fed to a vessel sized to provide a quiescent zone of sufficient retention time to allow the oil to float to the top and the solids to settle to the bottom. For the construction of gravity grease traps durable construction materials must be used because the wastewater of vegetable oil refining industry has high sulfate content due to it's the use of acids at some steps of the production. In a recent study, it was demonstrated that gravity separation procedure, in which the wastewater was kept in quiescence in a separation column and collecting the aqueous phase from the bottom, yielded oil and grease removals over 90% and COD removals between 58 and 90% after 24 h (26). This is a proper procedure as a primary treatment for vegetable oil refinery wastewaters and it would improve overall efficiency of wastewater treatment plant.

3.3.2. Flotation

Flotation processes are designed to remove all suspended particles, colloids, emulsions, and even some ions or soluble organics that can be precipitated or adsorbed on suspended solids (SS) (27). It is widely used in the treatment of oily wastewaters. In practice, the natural flotation process differs from the flotation with air. In the first case, the material particles lighter than the water (oils, greases) eventually associated with gas bubbles have the tendency to raise to the stationary liquid surface. In the flotation process with air, the material particles heavier than the water are transported to the liquid surface by attaching them with air bubbles (28). In the second case, the air could be introduced in water in very fine bubbles by the mechanical agitation flotation with dispersed air (29). The separation of materials lighter than water, e.g. edible oil/fat, can be enhanced by using flotation. This technique does not facilitate the separation of emulsified fat-oil-grease (FOG) from wastewater and, hence, is used in the vegetable oil refining sector for the removal of free FOG (11).

Flotation requires the generation of small bubbles which can be produced by dispersing air into the wastewater, applying a vacuum to the wastewater, dissolving air into pressurized wastewater and then releasing the pressure. Oil is usually removed from wastewater mainly by using the dissolved-air flotation (DAF) technique for bubble generation. The other flotation techniques are namely dispersed or induced air and electrolytic flotation, which are less frequently used (30). Brief information on each technique is provided below.

a) Dispersed (induced) air flotation (IAF)

This method is widely used for oil-water separation (oily sewage). In this technique, air bubbles are formed by mechanically dispersing air injected under rotating impellers or sparged by diffuser. The technology makes use of the centrifugal force developed (31, 32).

b) Vacuum flotation

In this system, air is first dispersed into the wastewater to achieve saturation conditions · Partial vacuum is then applied to the wastewater. This results in the generation of small air bubbles that attach themselves to the solid particles and make them rise. Typically, a cylindrical tank maintained under vacuum and continuously fed with wastewater is used for this purpose (29).

c) Dissolved air flotation (DAF)

DAF is very common method used for removal of suspended solids, oils and other contaminants by introducing small air bubbles into the wastewater containing the suspended solids/free oil to be floated (33). The fine air bubbles attach themselves to the chemically conditioned particles and as they rise to the surface, the solids float to the surface with them, where they are mechanically skimmed and removed from the tank. The air is dissolved under pressure 3 - 6 bar. The air is introduced into a recycle stream of treated wastewater after passed through a DAF unit. This supersaturated mixture of air and wastewater flows to a large flotation tank in which the pressure release and generation of numerous small air bubbles occurs. Mechanical skimming or suction withdrawal is used to remove the thickened solids/oil particles attached the air bubbles. Chemicals such as polymers, aluminium sulphate or ferric chloride can be used to enhance flocculation and therefore, the adhesion of bubbles (11). Flotation units can be provided with a recycle to prevent the incoming solids to be subjected to the shearing action of the pressurizing pump. By using this technique, free FOG, BOD/COD, SS, nitrogen and phosphorus levels are reduced.

d) Electroflotation

Electrochemical processes are investigated in several studies to treat oily wastewater (34-37). Briefly, in this process, bubbles are generated to carry the pollutants such as sludge and fine particles to the top of the solution where it can be more easily concentrated, collected and removed. An electrochemical reactor consists two sets of iron electrodes, anodes and cathodes, in which treatment is done in 2–20 min with intense iron dissolution. The electrodes are placed a few millimeters apart from each other and submerged in the wastewater that is to be treated for oil contamination. The cathode and anode is connected to the negative and positive outlets of a dc power supply, respectively. When direct current is applied to water through the electrodes, the energy barrier is overcome, and water molecules are broken down into hydrogen and oxygen gases. The reaction is observed through the hydrogen bubbles that evolve from the cathode and oxygen bubbles that originate from the anode. On the other hand, when the anode is made of metals having lower oxidation potentials than water, the anode is dissolved to produce metal ions instead of generating oxygen. These ions then react with hydroxyl ions, the by-products of hydrogen generation, to produce metal hydroxides (37). The reactions involved are given in Equations 3-5 (38).

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \frac{O_2}{\text{Air}} \rightarrow Fe^{3+}_{(aq)} + e^{-} \tag{3}$$

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \tag{4}$$

$$Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Fe(OH)_{3(s)} \tag{5}$$

As a result of the reactions, the emulsion is destabilized, and the colloidal oil particles begin to coalesce. Ultimately, the destabilized oil droplets absorb into the highly dispersed ferric hydroxide colloid formed by the reaction between the electro-generated Fe(III) and hydroxyl ions. Finally, the oil-rich sludge floats to the top where it is removed by skimming. It also contributes to coagulation by neutralizing any negatively charged colloidal particles, which have been reported to be more compact than sludge obtained by chemical methods (39). Ibanez et al. (40) revealed that the oil–water emulsion was actually broken down by the charge neutralization of ferric ions (Fe(III)) generated by the anodic dissolution of the iron electrode. The sunflower-seed oil and water emulsion was clarified within minutes of electrochemical treatment. It is mostly preferred due to its fast rate of pollutant removal with little sludge generation, compact size of equipment, simplicity in operation, and low capital and operating costs (36).

3.3.3. Coagulation-Flocculation

The choice of removal method for FOG from wastewater depends on oil form such as free or emulsified present. If oil is present in free form the methods mentioned above can be used for its removal. However, if oil in wastewater is in emulsified form, these emulsions must be broken by physico-chemical methods (41). Chemical treatment of an emulsion is usually directed toward the destabilization of the dispersed oil droplets or the destruction of emulsifying agents present in a first stage followed by the removal of the separated oil (37). Coagulation and flocculation is used for this purpose.

Coagulation and flocculation are often used interchangeably, but they refer to two distinct processes. Coagulation refers the process by which colloidal particles and very fine solid suspensions are destabilized so that they can begin to agglomerate if the conditions are appropriate. On the other hand, flocculation is the process by which destabilized particles actually conglomerate into larger aggregates so that they can be separated from the wastewater.

Most solids suspended in water possess a negative charge and, since they have the same type of surface charge, repel each other when they come close together. Therefore, they will remain in suspension rather than clump together and settle out of the water. Coagulation and flocculation processes are used to remove the suspended solids portion from the water. The suspended particles vary considerably in source, composition charge, particle size, shape, and density. Correct application of coagulation and flocculation processes and selection of the coagulants depend upon understanding the interaction between these factors. The small particles are stabilized (kept in suspension) by the action of physical forces on the particles themselves (28).

Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the wastewater to promote destabilization of the colloid dispersion and agglomeration of the resulting individual colloidal particles. The addition of some common coagulants to a wastewater not only produces coagulation of colloids but also typically results in the precipitation of soluble compounds, such as phosphates, that can be present in the wastewater. In addition, coagulation can also produce the removal of particles larger that colloidal particles due to the entrapment of such particles in the flocs formed during coagulation.

The choice of chemicals used for coagulation and flocculation depends upon the nature of the suspended solid to be removed, the raw water conditions, the facility design, and the cost of the amount of chemical necessary to produce the required effluent quality, as well as the intended disposal route for the sludges.

Final selection of the coagulant should be made by jar testing and plant scale evaluation. Common coagulant chemicals used in wastewater treatment are aluminum salts, ferric sulfate, ferric chloride, ferrous sulfate, sodium aluminate, and lime ($Ca(OH)_2$ or CaO (quicklime)). The first four will lower the alkalinity and pH of the solution while the sodium aluminate and lime will add alkalinity and raise the pH (42, 43). Also, polymers (cationic polymers, anionic and non-ionic polymers) which are long-chained, high-molecular-weight, organic chemicals are widely used, especially as coagulant aids together with the regular inorganic coagulants. Polymers are effective over a wider pH range than inorganic coagulants. They can be applied at lower doses, and they do not consume alkalinity. However, they are generally much more expensive than inorganic coagulants.

3.3.4. Biological Treatment

Despite the high efficiency of COD removal by physicochemical treatment at the beginning of the WWTP biological treatment is needed due to presence of lipids in the form of colloidal suspension (44). Biological treatment is mainly used to remove biodegradable organics and SS through biological methods. Adsorption of pollutants to the organic sludge produced will also remove non-biodegradable materials, e.g. heavy metals. Organic nitrogen and phosphorus can also be partially removed from the waste water.

Biological treatment options are aerobic processes using dissolved oxygen; anaerobic processes without oxygen supply and anoxic processes using biological reduction of oxygen donors. These systems can be used alone or in combination, based on the characteristics of the wastewater and the requirements before discharge. Mostly, aerobic and anaerobic biological treatment systems are used in the oil industry effluents.

Aerobic and anaerobic fats and oils removal by microorganisms have been reported in several studies (45-47). The conventional biological processes such as aerobic and anaerobic digestion require a BOD to COD ratio to be 0.6 (48). However, vegetable oil industry effluents usually have BOD/COD ratios between 0.15 and 0.2 indicating the requirement of a proper pretreatment before the biological step (49-52).

a) Aerobic Treatment

The success of the aerobic treatment depends upon sufficient oxygen levels required by the organisms to sustain their life. For an efficient operation of aerobic reactors to degrade oil and grease, it is very important to maintain good oxygen transfer (51). Activated sludge systems and biofilm processes such as fixed-bed or trickling filter processes are examples of the aerobic treatment.

Activated sludge systems consist of two tanks as shown in Figure 3. In the first tank, air is pumped by means of diffusers from the bottom of the tank into a mixture of wastewater and biological sludge (microorganisms). Air rises to the top in the form of bubbles, creating good agitation and also meeting the desired oxygen demand of the microorganisms. Microorganisms convert wastewater organics into end products such as carbon dioxide, water and an active mass of microbes (biologic floc) called activated sludge or biomass. This biomass is transferred into the next tank, where the absence of agitation allows the biomass to settle. The biological solids are subsequently separated from the treated wastewater and returned to the aeration process as needed (53).

[Insert Figure 3 here]

Activated sludge and wastewater mixture in the aeration tank is called mixed liquor. After a predetermined hydraulic retention time, which varies from several hours to an excess of 10 days, based on an organic loading rate or food to microorganisms (F/M) ratio of about 0.1-0.15 kg BOD/kg MLSS per day, the mixed liquor is directed from the aeration tank to a secondary clarifier where the activated sludge is settled out (Figure 3). The hydraulic retention time (HRT) or sludge age and F/M ratio can all vary as a function of the influent (raw wastewater) characteristics, e.g. composition, availability and degradability of organic substances, and the required final waste water quality. Most of the settled sludge is returned to the aeration tank (return sludge) to maintain a high population of microbes to allow efficient and rapid degradation of the organics. The excess sludge is diverted or wasted to the sludge handling system for treatment and disposal to maintain mixed liquor suspended solids (MLSS) at a required level, e.g. 3,000 mg/L (11). This system can be very effective if the level of total fatty matter is kept low after the pretreatment stage. The presence of fatty matter in the activated sludge systems will contribute not only higher BOD but the formation of foam which reduces the efficiency of the system.

The most common problem of activated sludge is the bulking of sludge indicating the poor settling characteristics of biological sludge. The presence of filamentous bacteria and/or excessive water bound within biological floc is known to be the reason of this problem. A typical solution for bulking problem is to use chemicals, i.e. chlorination, use of other oxidative chemicals or precipitation chemicals, to destroy all filamentous organisms that are not protected by activated sludge flocs. However, these methods are not very selective on microorganism and can terminate the whole biological activity (11).

The most important parameters of activated sludge system are HRT and the operating temperature. These parameters need to be carefully determined to ensure the breakdown of resistant organic substances. Additionally, separate compartment or selector is commonly used to prevent and control filamentous growth. The selector provides the selective growths of floc forming organisms by providing high F/M ratios at a controlled dissolved oxygen level. The contact time is generally 10-30 min.

The anoxic selector, which requires the presence of nitrate in the water, is often chosen in activated sludge systems for nitrification purposes. It reduces the oxygen requirements since nitrate-nitrogen is used as a terminal electron acceptor for the oxidation of influent biodegradable organics, and reduces the consumption of alkalinity during nitrification, by means of recovered alkalinity in the anoxic zone. Anoxic selectors can also be quite effective in controlling filament growth (11).

In fixed film aerobic processes such as trickling filters, the biomass grows as a film on the surface of packaging medium and the wastewater is evenly distributed across it. The trickling filter medium typically consists of rocks or various types of with filling material, such as slats, or plastic materials. The wastewater is distributed over the surface of media by a rotating arm. Rock filter diameters may range up to 60 m. As wastewater trickles through the bed, a microbial growth establishes itself on the surface of the stone or packing in a fixed film. The wastewater passes over the stationary microbial population, providing contact between the microorganisms and the organics. Oxygen is provided from the bottom to the biomass by blowing outside air. The treated wastewater is collected under the media and directed to a sedimentation tank from where a part of the liquid can be recycled to dilute the strength of the incoming wastewater (Figure 4).

[Insert Figure 4 here]

b) Anaerobic Treatment

Anaerobic processes are commonly used for the treatment of industrial wastewaters. Whereas aerobic processes effectively treat low strength wastes, anaerobic processes more effectively treat high strength wastes. These high strength wastes have COD levels greater than 2,000 mg/L. Anaerobic digestion occurs in a heated reactor with the absence of molecular oxygen that results in methane and carbon dioxide production (29). In comparing anaerobic processes and aerobic processes, anaerobic processes have distinct advantages including energy and chemical efficiency and low biological sludge yield, in addition to the possibility of treating high-strength wastewaters with a COD of 5,000 up to 40,000 mg/L, with the requirement of only a small reactor volume (54). The specific biomass loading of typical anaerobic processes treating soluble industrial wastewaters is approximately 1 kg COD utilized/(kg biomass-day). There is a wide range of anaerobic reactors with different organic loading rate (OLR), HRT, and influent COD ranges. Typical data of some anaerobic process is presented in Table 6.

[Insert Table 6 here]

As shown in Figure 5, anaerobic digestion has four steps which are hydrolysis, acidogenesis, acetogenesis and methanogenesis (57). The first step is the solubilization (hydrolysis) step in which hydrolytic microorganisms degrade insoluble polymer-type organics material such as polysaccharides and proteins by extracellular enzymes to monomers. This reduction results in no reduction of COD. Hydrolysis is the rate limiting step of overall anaerobic digestion because of the semi-rigid structure of the bacterial cells (57). In the second step, acid formers degrade soluble organics and they mainly form propionic and acetic acid and also alcohols, hydrogen and carbon dioxide. In the acidification stage, there is minimal reduction of COD. Third step is the acetogenesis in which acetogenic bacteria convert organic acids and alcohols into acetic acid. Finally methanogenic organisms, methanogens, convert the organic acids into methane and carbon dioxide. At this final step, about 70% of methane is produced from acetic acid (57).

[Insert Figure 5 here]

Methane organisms, methanogens, are very sensitive to pH fluctuations and they function over a pH range of 6.6–7.6 with an optimum near pH 7.0 (57). There are two distinct classes of methanogenes, namely, Methanothrix and Methanosarcina. Under standard temperature and pressure conditions, the degradation of 1 kg of COD or ultimate BOD results in 0.35 m^3 of methane production (57). The methane produced has a high calorific value and can be re-used as fuel, e.g. elsewhere in the process. The quantity of cells produced during methane fermentation will depend on the strength and character of the waste and the retention of the cells in the system.

Anaerobic digestion can be operated in mesophilic (30-38ºC) or in thermophilic (50-57ºC) conditions. Higher temperature operation leads to faster reactions and more biogas productions (29). Effect of temperature on biogas production is given in Figure 6.

[Insert Figure 6 here]

However, it is well-known that anaerobic digestion of oily wastes is not always easy and straight forward, since anaerobic bacteria are very sensitive to lipid-rich substances along with the intermediate compounds of oily wastes degradation process. Therefore, a treatability study together with determination of BOD and COD concentrations, pH, temperatures, and flow rates of the wastewaters is essential, especially for the wastewaters containing low-soluble compounds such as fats, oils, or greases or complex carbohydrates (57). Still, lipids are attractive substrates for anaerobic digestion and co-digestion due to the higher methane yield obtained when compared to carbohydrates.

In addition, anaerobic digestion has some limitations. The rate limiting step of hydrolysis is the most important limitation of anaerobic digestion. In some wastewaters most of the organics are located in the microbial cell and stable semi-rigid structure of the cell walls protects the cell from lysis. Therefore, high resistance to biodegradation leads to long HRT for the biological stabilization in digesters (56). Thus anaerobic digestion is a slow process because of the rate-limiting step of hydrolysis. However, the time required to initiate gas production can be reduced by adapting the bacteria to waste. These methods are normally employed strictly as pretreatment measures. Due to the slow microbial growth there is no phosphorus removal. No nitrification and denitrification occurs so nitrogen cannot be removed by anaerobic treatment. Some common operational problems experienced with anaerobic treatment processes are given in Table 7.

[Insert Table 7 here]

Foaming and bulking are other problems faced in anaerobic digesters. Some certain filamentous microorganisms lead to foaming and bulking which cause operational problems in anaerobic digesters such as reduced effective volume of the digesters and shortened digestion periods (58).

Anaerobic digestion is sensitive to shock loads and toxic materials (59). Methane formers can be easily affected by the unfavorable conditions which lead to a poor digestion. An anaerobic system alone would not satisfy a final wastewater quality high enough for discharge to a watercourse. Therefore, an aerobic system are usually installed after anaerobic reactors (Figure 7); so that, discharge limit values are satisfied by assisting in the breakdown of the remaining BOD and hydrogen sulphide is removed by well aeration. The energy gained from the anaerobic plant can be used to compensate the energy that is consumed in the aerobic plant.

[Insert Figure 7 here]

c) Membran Filtration

Membrane processes namely microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are also applied to treat oily wastewaters (15). Oil in wastewater presents in three forms such as free-floating oil, unstable oil/water emulsions, and highly stable oil/water emulsions. Membrane processes are ultimately utilized to remove stable emulsions, particularly water-soluble oily wastes (60). RO or NF is chosen when the salt content of the oily wastewater is too high.

Membrane systems or membrane bioreactors (MBR) are used in some variations on conventional activated sludge whereby a number of membrane modules, or cartridges, are placed within the body of the reactor vessel. After biological treatment, effluent is pumped under static head pressure to the membrane unit in which the solids and liquids are separated, the clean wastewater is discharged, and the concentrated mixed liquor is pumped back to the bio-reactor. The MBR can be operated in either aerobic or anaerobic mode (11).

An MBR is very efficient in biomass separation, allowing the biomass concentration within the upstream reactor to be up to ten times greater than the concentration normally attainable in a conventional suspended growth system. Secondary sedimentation is not required in MBR process and MLSS levels achieved can vary from 12 to 17,000 mg/L.

However, MBR system has very high operational cost especially the energy cost of pumping. This cost may be minimized by applying gravity feed of the wastewater. Another drawback of these systems which is the most common one is fouling. In order to control this problem, aeration and backwashing have been tried, but, these cause an additional production of wastewater. DAF can be used to scour and clean the membrane surfaces to prevent biofouling (11).

The space requirement for this system is very low compared to conventional activated sludge. This system is ideal for higher strength, acidic and lower volume wastewaters. It is more useful in situations where a long solids retention time is required to reach the necessary biological degradation of the pollutants. Likewise, wastewater containing not readily degradable compounds, e.g. phenols, pesticides, herbicides and chlorinated solvents, and high organic pollution which are present in vegetable oil refining wastes can be treated with MBR.

3.4. Solid Wastes and By-Products

Vegetable oil processing activities also generate significant amounts of organic solid waste and by-products, such as empty fruit bunches (EFBs) and waste palm kernels. The amount of waste generated depends on the quality of the raw materials and the use or reprocessing of the discarded materials into commercially viable by-products. Other solid wastes from the vegetable oil manufacturing process include soap-stock and spent acids from chemical refining of crude oil; spent bleaching earth containing gums, metals, and pigments; deodorizer distillate from the steam distillation of refined edible oils; mucilage from degumming; and spent catalysts and filtering aid from the hardening process. Solid wastes resulting from vegetable edible oil refining plants can be classified as follows:

- General waste,
- Tin cans and scrap,
- Filter cloth,
- Spent bleaching earths,
- Soap-stock,
- Lecithin,
- Spent Nickel,
- Deodorizer distillate

- Sludge from wastewater treatment plant.

General waste includes waste pipe, angle iron, steel, cans, plastic, glass bottles and papers. A portion such wastes is sold for recycling the rest is temporarily stored in the factory area and sent to landfills (61). Tin cans and scrap waste, used containers, caps and cans are the wastes resulting from production area. Some factories purchase cans from subcontractors so that these kinds of wastes are not produced in such factories. These wastes are temporarily stored in the factory area, and then sold for recycling. The amount of scrap constitutes 2-10% of total amount of tin.

Filter cloths are used in filter presses at winterization and bleaching steps during the refining of oil. When first installed filter cloth can be used 4-6 times. Then, it has to be removed and washed before re-use. In this way before being discarded, a filter cloth can be re-used 2-3 times (16).

Spent bleaching earths (SBE) is generated at the vegetable oil refining industry after bleaching of crude oil. The annual world generation of SBE is between 1.5 and 2.0 million tones based on the world edible oil production of 128.2 million metric tons in 2007 (61) and 1.2-1.6 kg of SBE generation per metric ton of edible oil production. SBE contains 20–40% by weight of oil, fat and colored pigments (62). This means that the bleaching earths, especially those containing poly-unsaturated fats, have self-flammable properties (63). Therefore, spent bleaching earths are listed as hazardous wastes and their disposal or treatment is difficult in the environment. Also, spent bleaching earths include color pigments like carotene, and chlorophyll and oxidation products which are present in the vegetable oil (9). In order to reduce their fat/oil contents, spent bleaching earth can be extracted with hexane and the oil present in them can be recovered and used as second quality oil for different purposes. By this way, the oil content of spent bleaching earth can be reduced to below 1%. Thus, bleaching earth becomes a solid waste consisting of inorganic chemicals. This still might be re-used as bleaching earth at the second quality oil production facilities (64).

Soap-stock is accepted as a by-product, which is generated from the alkali-refining of the vegetable oil, otherwise treated as waste. The soap-stock contains 50% total fatty matter and, therefore, it has a commercial value (8). But it also contains significant amount of phosphatides, pigments and other contaminants. Therefore, soap-stock cannot be used in good quality soap production. They chemically break down into acid oil. The breakdown can be accomplished by using a strong concentrated acid. This produced acid oil can be assessed by selling it to soap production factories (9).

Lecithin is formed at the degumming stage of the oil refining. Basically, it is a mixture of phosphatides and small amounts of water-soluble components like glycolipids and oligosaccharides. The gums from the centrifuge are processed by treating with H_2O_2 and then dried. After reduction of moisture, the product is cooled. Thus, lecithin is obtained and used in foods, and in cosmetic and pharmaceutical industries. The best quality lecithin can be produced from fresh oil (8, 9).

Spent nickel catalyst is generated from hydrogenation process of refined vegetable oil during the production of vanaspati (hard oil). The continuous use of nickel catalyst leads to high content of fat adherence to it (8).

Deodorizer distillate is the volatile organic material which is steam distilled in the deodorization of vegetable oil and hydrogenated vegetable oil. The distillate produced in the industry contains tocopherols and sterols, which are valuable raw materials for production of vitamin E and steroid drugs (8).

Wastewater treatment sludge consists of all chemical or biological sludges gathered from the bottom of sedimentation tanks of physico-chemical and/or biological treatment. Biological sludge production is clearly located in the aeration basin and sludge is composed of minerals (10-30%), biomass (20-50%) and non-biomass organics (20-40%). A portion of the sludge is returned to the biological treatment processes while the excess sludge is sold as a fertilizer or stored in landfills. Chemical sludge or lime sludge generated during the process after dewatering of producing wastewater has beneficial reuses (8). Although its contents varies depending on the chemicals used during the refining of oil, waste sludge from physicochemical treatment contains low molecular weight oils produced during refining of oils at the deodorization stage, esters, alcohols and other semi-volatile organic compounds found in oil, organic substances produced during chemical adsorption of long chain oil. After dewatering processes of this sludge, they can be stored in aboveground storage areas/landfills (64).

The following options can be applied to prevent and control solid wastes and by-products;

a) Waste kernels should be collected for fuel for steam and power generation at refineries. The waste kernel cannot be incinerated by typical crude oil mills since, unlike refineries, their boilers are not designed to handle the high silica content of the kernel;

b) Uncontaminated sludge and effluent from on-site wastewater treatment should be as fertilizer for agricultural purposes;

c) Contaminated sludge from wastewater treatment should be properly disposed at a sanitary landfill or by incineration. Incineration should only be applied in legalized facilities operating under international recognized standards for pollution prevention and control;

d) Production processes should be carefully designed and controlled to reduce product losses such as air humidity should be monitored and adjusted to prevent product losses caused by the formation of molds on edible materials;

e) Autoclave condensate should be recycled to remove vegetable oil;

f) Spent bleaching earth can be disposed of as follows;

    - A feedstock for brick, block, and cement manufacturing , and also as fertilizer, if not contaminated with heavy metals such as nickel, pesticide residues, and other contaminants;
    - After anaerobic digestion they can be spreaded on land;
    - If contaminated, they should be handled according to the waste management guidance;

g) Distillates (e.g. free fatty acids and volatile organic compounds), depending on the level of pollutants (pesticides and /or residues) can be used as follow;

    - Animal feed if uncontaminated;
    - A feedstock for chemical industry processes (e.g. antioxidants);
    - Fuel for energy production;

h) The nickel catalyst from hydrogenation should be either:

- Recycled and recovered for reuse as a nickel catalyst or as nickel metal, salt, or other use
- Stored and disposed of according to the waste management guidance.

3.5. Emissions to Air

Particulate matter (dust) and volatile organic compounds (VOCs) are the main emissions from vegetable oil processing. Dust results from the processing of raw materials, including cleaning, screening, and crushing, whereas VOC emissions are caused by the use of oil-extraction solvents, typically hexane (16). Table 8 presents emission guidelines for vegetable oil refining industry although it may change from location to location.

[Insert Table 8 here]

3.5.1. Volatile Organic Compounds

Solvent emissions results from various sources within vegetable oil processing plants, including the solvent-recovery unit, the dryer and cooler, and leaks in piping and vents. Small quantities of solvent may be present in the crude vegetable oil if the oil has been extracted by a solvent and will volatilize during the oil-refining process, particularly during deodorization.

The suggested management strategies to prevent and control VOCs are listed below as follows:

a) The efficient recovery of solvent by distillation of the oil from the extractor should be ensured;
b) Solvent vapors should be recovered where feasible, during vegetable oil extraction;
c) Re-boiler and a gravity separator should be to treat condensates with high solvent content in order to reduce solvent emissions and reduce the risk of explosions in the sewer.

The following techniques are recommended as management techniques to prevent and control dust and odors:

a) Proper maintenance of cleaning, screening, and crushing equipment, including any ventilation and air handling systems should be ensured to reduce emissions of fugitive dust;
b) Cyclones and/or fabric filters or electrostatic precipitators should be installed on selected vents, including dryers, coolers, and grinders to remove odor emissions;
c) Odor emissions (e.g. from soap splitting, cookers in the extraction process, vacuum systems, and pressurized systems) should be kept at a minimum by using a caustic, alkaline, or ozone scrubber system or the gas should be incinerated in a boiler plant or in separate incinerator system.

3.5.2. Exhaust Gases

Vegetable oil processing plants are large energy and steam consumers making use of auxiliary boilers for the generation of steam energy. Emissions related to the operation of these steam energy sources typically consists of combustion by-products such as NO_x, SO_x, PM, volatile organic compounds (VOCs), and greenhouse gases (namely CO and CO_2). Table 9 shows gaseous pollutants resulting from vegetable oil refining plants and their typical quantities together with their source. Recommended management techniques include adoption of a combined strategy which includes a reduction in energy demand, use of cleaner fuels, and application of emissions controls where required.

[Insert Table 9 here]

Oxides of Nitrogen (NO_x) are emitted from boiler stack and the generator exhaust. Continuous or intermittent exposure of humans to NO_x may cause certain illnesses, such as irritation in the respiratory tract and abnormal accumulation of fluid in the lungs leading to pulmonary edema. Direct exposure of NO_x to soil causes necrosis, vegetation loss and inhibition in plant growth. NO_x is undergone various photochemical and chemical reactions in the atmosphere and leads to the formation of photochemical smog and acid rain. Although, emissions of NO_x from generator are for short period of time, still the cumulative effects of NO_x at global scenario should not be ignored. Depletion of ozone at stratosphere level, formation of photochemical smog and acid rain may occur due to this.

Sulfur oxides (SO_x) results from the burning of solid or liquid fuels in the generator. The severity of SO_x effects depends on its concentration and the duration of exposure. Direct exposure to these oxides can be very harmful to human health, plants and vegetation. The harmful effects are dependent on the concentration and exposure duration. Photochemical smog and acid rain occurs due to indirect reactions of SO_x in the atmosphere.

Carbon monoxide (CO) is a colorless non-irritating gas. It is generated due to incomplete combustion. At high concentrations exceeding 5,000 ppm with an exposure of few minutes, this gas can be fatal for human or animal lives, by reacting with hemoglobin to form carboxyheamoglobin. At much lesser concentrations, but with a high duration of exposure, this gas may still be dangerous for human beings, as it may cause damages to visual perception, manual dexterity and the ability to learn. Concentration of CO from the methane cracking plants and the generator exhausts of the audited mills are very high. Therefore, its long-term impacts cannot be ignored.

Carbon dioxide (CO_2) is generated in large quantities during natural gas cracking in edible oil mills. In some mills this is collected and sold to beverage industry. While in others this gas is exhausted into the atmosphere. According to laboratory results of gas cracking plant exhaust, the concentration of CO_2 in the exhaust is about 500 times of its concentration in clean air. CO_2 is a greenhouse gas and its higher concentration in the atmosphere is responsible for global warming

Particulate matter covering a large variety of particles varies in size and chemical composition. It has adverse effects on human respiratory system. It lowers the aesthetics value of a place as well as general visibility at high concentrations. The general corrosion reactions on building materials, due to the presence of NO_x and SO_x in the air, may also get catalyzed due to the presence of particulate matter (16).

4. CASE STUDY

In this study, a vegetable oil factory (Kirlangic Oil Factory) was selected as representative of this sector and its effluent was investigated. The production capacity of Kirlangic Oil Factory Yarımca Facilities, Kocaeli, Turkey is 40,000 ton/year for sunflower-corn oil and 15,000 ton/year for olive oil. Also, fatty acids are produced as a byproduct at about 3,000 ton/year. Sunflower, corn and olive oil is gone under the full refining process, except the winterization process. Hydrogenation process is not applied.

4.1. Solid wastes

Solid wastes are bleaching earth used in the bleaching process (bentonite, tonsil, diatoms, etc.), perlite used in winterization process produced during the refining of crude oil, chemical and biological wastewater treatment plant sludge, scrap arising during the production of PVC plastics, tins, paper and cardboard wastes.

Bleaching earth is used at the refining process used by 1-2%. Bleaching earth includes color, glue, iron, nickel, and oxidized compounds (64). According to analysis carried out in 2002, the amounts of bleaching earth used during the processing of corn, sunflower, and soybean oil were reported as 26,208 ton/year, 26,732 ton/year, 1,399 ton/year, and 1,842 ton/year, respectively. According to the same year data, the amount of oil found in bleaching earth was 14%. These results indicated that the amount of oil in the bleaching earth was at recoverable levels; hence, bleaching earth has been sold to the second quality oil-producing companies (64).

Perlite is used in the factory during winterization. Perlite contains triglycerides in general. Also, perlite contains silicon oxide and sodium oxide due to its chemical nature. According to analysis carried out in 2002, the amounts of perlite used during the processing of corn, sunflower, and soybean were reported to as

21,840 ton/year, 26,732 ton/year, 1,105 ton/year, and 1,842 ton/year, respectively. According to the analysis conducted in 2002, the fat content of perlite was found as 25%. These results indicated that the amount of oil in the perlite was at recoverable levels; hence, perlite has been also sold to the second quality oil-producing companies (64).

Sludge is produced the WWTP of the factory during chemical and biological wastewater treatment; hence, it has biological and chemical properties. Chemical treatment sludge contains lime, iron (III) chloride and polyelectrolyte and low molecular weight oils, esters, alcohols and other semi-volatile organic compounds found in oil, organic material produced as a result of chemical adsorption of long-chain fats. Sludges from biological treatment contain microbial biomass known as activated sludge and organic matters. According to data obtained in 2002, sludge produced from chemical and biological wastewater treatment was about 140 ton/year and 60 ton/year, respectively, which were sold to Gubretas Company (64).

Other plastic bottles and can scraps, paper, and cardboard along with other solid waste are produced at different amounts in the year and they are stored temporarily/separately in the factory area. Then, they are sold to the recycling companies.

4.2. Factory and Gas Pollutants Emission Sources

The sources of emissions in the factory can be listed as boilers used for the production of steam, cooling towers used to cool the equipment and machines used for the production of PVC. There are three steam boilers in operation. Two of them are located in the boiler room; these boilers are in operation and produce all the steam needed. One of the boilers works continuously while the other is backup. The other boiler is used in the refining section used for the production of heat and high pressure steam needed for the removal of odor. In two of these four boilers fuel oil grade 4 is used as fuel while in the boiler diesel fuel is used. Dry flue-gas flow measured at the chimney of the main and auxiliary boiler was 6000 Nm^3/h, and that of the steam boiler was 300 Nm^3/h (64).

On the other hand, there was cooling tower emissions of due to absorption of volatile organic compounds produced as a result of the oil deodorization process to the water used for the cooling of the equipment during refining. The flows of tower fan and dry flue gas were 66,350 m^3/h and 61,400 Nm^3/h, respectively (64).

The other emissions sources of the factory are the chimneys of two machines used in the production of PVC bottles, which emits chemicals resulting from the decomposition of the additives in PVC due to the effect of heat and pressure. Emissions from factory chimneys includes gaseous pollutants such as CO, CO_2, SO_2, NO_2, dust, oil and unsaturated fatty acids, saturated and unsaturated aldehydes, ketones (such as acetone), phenols, total nitrogen (as NH_3), total sulfur (as H_2S) and HCl (64).

At the factory, emissions such as CO, SO_2, NO_x and dust burning results from boiler chimneys. Process dust emissions result from the two PVC machines. Organic materials in the form of unsaturated fats, fatty acids, aldehydes, ketones, and phenol emissions are only due to the cooling tower. Inorganic chlorine emissions results from the two PVC bottle production machines. Total nitrogen in the form of NH_3 and total sulfur in the form of H_2S results from the cooling tower (64).

4.3. Wastewater Characterization

Factory wastewaters consist of industrial wastewater and municipal wastewater each at about 60 m^3/d. Industrial wastewaters include wash water coming from segregators, wastewaters coming from deodorization and extraction wastewaters resulting from soap-stock shredding unit. Domestic wastewater results from wastewaters coming from toilet, shower and dining halls. Since deodorization unit is operated as closed loop, it discharges wastewater at certain times during the cleaning of the system. On the other hand, soap-stock and washing water is continuously produced and discharged to the treatment during the vegetable oil production. Also, a small amount of the waste water during washing of filters used in production occurs. Filter washing is done at certain times of the year. The amount of wastewater produced at this factory from refining unit, soap-stock shredding, and wash water, deodorization unit and other processes are 36, 10, and 14 m^3/d (64).

Aslan (20) carried out a study to characterize wastewater produced during the refining of corn oil and sunflower oil in Kirlangic Oil Factory. For this purpose, triplicate samples were taken from the inlet of equalization basin 1 at different times of production of both types of oil. Due to the completion of olive oil refining in very short time, wastewaters from olive oil refining are mixed with other wastewater. For this reason, the characterization study was not carried for olive oil wastewaters. The characterization results of corn and sunflower oil wastewaters are presented in Table 10 and Table 11.

[Insert Table 10 here]

[Insert Table 11 here]

4.4. Analysis of Wastewater Treatment Plant Efficiency

Wastewater volume at the treatment plant is 4 m^3/h. Emulsified oils, floating substances, and acid oil present in wastewater physically separated from wastewater by grease traps and two submersible pumps connected in series with self-leveling pool balancing. During the chemical treatment suspended and colloidal substances are removed from the wastewater by the addition of coagulants and flocculants. After the chemical treatment, wastewater is treated in a two-stage biological treatment system consisting of a facultative and a completely mixed extended aeration activated sludge system.

In order to determine, during the production of sunflower and corn oil which are produced at different times the efficiency of the treatment, triplicate samples were taken from 4 different points as indicated in Figure 3 and analyzed. Wastewater samples taken from point 1, 2, 3, and 4 represents the inlet of the wastewater treatment plant, the outlet of chemical treatment, the output of the first stage biological treatment (facultative treatment), second stage of the biological treatment (completely mixed aeration basin).

Wastewater samples except for point 1 were the supernatant of each treatment stage taken at the outlet weir of the treatment unit (20). Average values of the measured parameters and results of the analysis of wastewater samples are given in Table 12 and Table 13. Sampling points were indicated in accordance with statements given the above. Soluble COD and soluble BOD_5 are shown as SCODs and $SBOD_5$.

[Insert Table 12 here]

[Insert Table 13 here]

As presented in in Table 10 and 11, pH values of the wastewater indicates that factory wastewaters resulted during the production of corn and sunflower oil refining have an acidic character. The pHs of corn and sunflower oil refining wastewaters were 2.79 and 4.1 respectively. Corn oil refining wastewater is more acidic because it has higher amount of fatty acids in crude oil of corn oil and accordingly, higher production of soap-stock during the refining, hence, higher amount of acid use for the production of acid oil compared to sunflower oil.

It is clear from COD results of the plants that wastewater of the factory are heavily polluted. In corn oil refining wastewaters, total COD values were ranging from 11,581-15,449 mg/L and in sunflower refining wastewaters, total COD values were ranging from 8,344-9,202 mg/L Also, the sulfate content of the wastewater is very high, 11,000-12,000 mg/L (Table 10 and 11). The reason for this is due to that during vegetable oil refining effluents at neutralization stage soap-stock are decomposed with sulfuric acid for the production of acid oil. The chemical equation for this reaction is given in Equation 2. Phosphorus content of the wastewater is also high which is due to that crude oil has phosphorous compounds in its structures and due to the use of phosphoric acid at the degumming stage. It can be seen that wastewaters resulted during sunflower oil as well as corn oil refining are highly colored due to the extraction of oil from vegetables together with color pigments and the presence of natural organics. Vegetable oil refining wastewater has high color content because it contains a lot of dissolved organic matter. However, the color content of such wastewaters content has not been taken much attention in the literature. It is observed that corn oil refining wastewaters have more polluting load and more acidic character when compared to sunflower oil refining wastewater.

When the results of are examined it can be seen that BOD_5 values are quite low when compared to corresponding COD values. This result indicate that there might be some hidden BOD which cannot be completely determined in five days and needs longer period for accurate measurement, and therefore, BOD_5 is inadequate in characterization of this kind of wastewaters.

The BOD_5/COD ratios of the factory wastewaters are 0.15 and 0.2 for corn oil and sunflower oil refining wastewaters (20). Aslan et al. (52) investigated the biodegradability of vegetable oil refinery wastewaters and concluded that they have a low BOD_5/COD ratio and they concluded that these wastewaters cannot be treated only by biological treatment. Furthermore, their transport presents high risk of clogging in pumps and piping. In addition, COD/N/P (C/N/P) ratio of corn oil and sunflower oil refining effluents calculated from the average values of the total COD, TKN, and total phosphorus ratio were found as 52/3/1 and 22/3/1, respectively. These ratios indicate that there is no nutrient deficiency for wastewater microorganisms in terms of N and P. However, very low BOD_5/COD ratios suggest that only biological treatment is not enough for treatment of the factory wastewaters.

4.4.1. Caustic neutralization and physical treatment

In soap-stock unit, wastewaters produced during soap-stock chopping in the reaction tanks, containing a strong acid (pH = 0-1), are taken into the reaction tank 4 as shown in Figure 8a. This tank is dosed with caustic from the top and the air is provided from the bottom of the tank for the reaction of caustic with wastewater to adjust desired pH. The wastewater is then sent to the pumping pit.

[Insert Figure 8 here]

During the production at oil refining stage, wash water coming from separators reaches to the soap-stock unit after leaving the system. The pH of these waters is around 9-11. As shown in Figure 8.b, these waters are taken into tank 3 and sulfuric acid is added and heated by steam in order to facilitate the separation of oil and soap residues from water. The effluent of this tank is then directed to another tank, upgrade pit, and here, pH of the water is automatically adjusted to pH range of 3-5 by the addition of caustic. This operation is performed during the continuous stream of water. If the flow rate is appropriate the pH adjustment is not required. If the pH of the water is not suitable, caustic may be added manually by the operators to adjust pH. pH adjusted wash waters and soap-stock extraction unit wastewaters are taken into equalization basin 1 and 2. Here, oil water separation from these wastewaters is achieved by screens and by extending hydraulic retention time of the huge volume of the wastewater.

In addition, by considering that the wash waters and rain waters of the factory field may also contain some oil residues, these waters are collected in transfer basins after passing them through grease trap placed at the output of the rain water collection channel. From there, they are taken into either equalization basin or aeration tank. Acid oils and fatty substances are separated from the wastewater by the help of the screens placed in two equalization basins and these substances pumped back to acid oil and reaction tanks as accumulated over time.

4.4.2. Chemical treatment

Wastewaters gone under physical treatment becomes ready for chemical treatment. In such wastewaters, pollutants are mostly suspended and colloidal organic and inorganic substances and to a lesser degree some oil particles. Most of the suspended particles possess a negative charge and, since they have the same type of surface charge, repel each other when they come close together. Therefore, they will remain in suspension rather than clump together and settle out of the water. The amount of oil present in the wastewater makes this situation even worse.

Chemical treatment methods applied to the system involves the addition of iron (III) chloride ($FeCl_3$), anionic polyelectrolyte chemicals and limes to the wastewater, so that, they stick together and form heavy clusters (flocs) in a polymerized hydrates form. The precipitation of these flocs provides removal of them from wastewater. Thus, the COD of the wastewater is targeted to be at the lowest level before biological treatment.

In WWTP of Kirlangic Oil Factory, wastewaters are taken in to the first rapid-mix chamber. Wherein $FeCl_3$ purchased as a 40% solution is dosed as 10% solution. Thus, colloidal substances present in wastewater interact with $FeCl_3$ and form positively charged $Fe(OH)_3$. Then, the wastewater is taken to second rapid-mix chamber where neutralization done by lime dosing to form more stable flocs. Wherein, the pH of the wastewater is brought to the range of 7-8 by the addition of 5% lime slurry. After rapid-mix, wastewater containing stable flocs is taken into slow mixing tank. In this tank, the microflocs are brought into contact with each other through the process of slow mixing. Collisions of the microfloc particles cause them to bond to produce larger, visible flocs called pinflocs. The floc size continues to build through additional collisions and interaction with inorganic polymers formed by the coagulant or with organic polymers, 0.002% of the anionic polyelectrolyte, added. Macroflocs are formed. After this process, wastewater is directed to the chemical precipitation basin where formed macroflocs are settled down at the bottom of the basin. Also, foams formed on the surface of the basin during chemical precipitation are skimmed by scrapers and sent to the equalization basin. The effluent free from flocs is taken into CTP tank for final pH adjustment. There, the pH of the wastewater is brought to the suitable range for biological treatment (pH 7-9).

As known, iron (III) chloride has an acidic character. The studies also showed that it drops pH about 2 unit. Therefore, the necessity of pH adjustment range to ensure the efficiency of treatment requires using of lime in high amounts which causes increased levels of sludge formation. Due to the good quality of the wastewater produced in soap-stock unit and the long retention time of the wastewater in the equalization basin at the first stages of treatment resulted in a clear wastewater free from most of the colloidal substances, the use of lime in chemical treatment is deemed appropriate both economically and in terms of creating less sludge. Therefore, in the present system, only the lime has been used as a coagulant

4.4.3. Biological treatment

Wastewater is gone under biological treatment after chemical treatment. Domestic wastewater of the factory is also taken directly to the biological treatment. Urea and diammonium is added to the wastewater to ensure a sufficient amount of nitrogen and phosphorus phosphate which is necessary for microorganisms in biological treatment. Carbon source is the organic matter present in the wastewater. Biological treatment is carried out in two stages: a facultative and completely mixed extended aeration tanks consisting of two independent compartments are served for this purpose. In the first stage, some portion of the biological and chemical load of the wastewater is removed in the facultative aeration tank by aerobic microorganisms present at the upper level of the tank to which oxygen is provided with the help of the surface aerators and by anaerobic microorganisms present at the lower/bottom level of the tank. Then, wastewater is taken into the first biological clarification basin and the biomass is removed from wastewater by settling. The supernatant of partially treated wastewater is directed from this tank to the second completely mixed tank. The concentration of biomass settled as the waste sludge is measured frequently and is recycled to the facultative aeration pond. The excess sludge is removed from the system when the biomass concentration increased.

In the second stage, the organic pollution load of wastewater are removed by aerobic microorganisms in a completely mixed aerated tank which is mixed by diffused air provided by the surface and submerged aerators placed at the top and bottom of the tank, respectively. The mixture of wastewater and activated sludge is sent to final sedimentation tank and the excess waste activated sludge settled to the bottom of the tank is removed while a part of it is recycled back to the aeration tank. After sedimentation pool of clear supernatant is discharged. There is a sand filtration unit at the WWTP before clear supernatant storage tank, but in the current case it is not needed to be used.

4.4.4. Sludge removal and dewatering process

Sludge produced in this WWTP consisted of two different character; chemical and biological sludge. Sludge coming from chemical treatment was stored in the sludge thickener for a while for thickening and settlement purposes. Supernatant above the thickened sludge is recycled back to the chemical treatment while bottom thickened sludge is taken into bags and wherein the sludge is more concentrated. The excess sludge coming from biological treatment is taken into sludge drying bed which is a kind of big tank. Sludge dried there is sold to a fertilizer company together with the sludge of chemical treatment at certain times. Treatment plant flow diagram and the sampling points taken for wastewater characterization are shown in Figure 9. Table 14 shows the sizes of the tanks and basins in the treatment plant.

[Insert Figure 9 here]

[Insert Table 14 here]

According to the results of that study, corn oil refining wastewater treatment efficiency was 98.1%, 98.5%, 98.2%, 95.47%, and 86.8% for total COD, BOD_5, oil-grease, TSS and color removal, respectively, while treatment efficiency for total COD, BOD_5, oil-grease, TSS and color removal was 97%, 97.4%, 99.27%, 91%, and 48.2% for sunflower oil refining wastewater. It is clear from the findings that the concentrations of all wastewater pollutants parameters were decreased at all levels of the treatment plant. The study data reveals that the degree of chemical treatment itself is not efficient enough for the removal of such pollutants. For this reason, only chemical treatment for edible oil refining wastewater is not enough, the treatment system must be considered in conjunction with biological treatment.

Wastewater treatment plant of factory operates in a very efficiently and it is a good model for the treatment of vegetable edible oil refinery wastewaters. However since the MLSS concentration of wastewaters discharged from the plant is higher than the discharge limits; it is necessary to re-operate sand filter.

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Table 1 - Water consumption and wastewater production (9)

Inputs per unit of product	**Water**	**Wastewater**
Crude oil production (m^3/t raw material)	0.2–14	0.2–14
Chemical neutralization (m^3/t product)	1–1.5	1–1.5
Deodorization (m^3/t product)	10-30	10-30
Hardening (m^3/t product)	2.2-7	N.D.
Chemical Refining (m^3/t product)	0.25-0.8	14-35

N.D.: No data

Table 2 - Energy consumption in crude vegetable oil refining (9)

Processing Step	**Total Energy Consumption**	**Steam Consumption[1]**	**Electricity Consumption**
	(MJ/t final product)	**(MJ/t final product)**	**(MJ/t final product)**
Neutralization	145-330	112-280	22-44
Soap Splitting	620-2,850*	560-2,800*	11-36*
Deodorization	510-1,350	420-1,120	60-150
Hardening	400-1,000	N.D.	N.D.
Bleaching	N.D.	N.D.	N.D.
	(kWh/t final product)	**(kWh/t final product)**	**(kWh/t final product)**
Neutralization	40-92	31-78	6-12
Soap Splitting	172-792*	156-778*	3-10*
Deodorization	142-375	117-311	17-42
Hardening	111-278	N.D.	N.D.
Bleaching	N.D.	N.D.	N.D.

[1]:MJ/t=2.8xkg steam/t; *: MJ/t soap or kWh/t soap; N.D.: No data;
Final product=refined vegetable oil

Table 3 - Example of semi-continuous deodorization (12)

Parameter	**Industry benchmark**
Latent heat steam (kJ/g)	2,000
Amount of feedstock (kg)	1,000
FFA removal (kg steam)	0.35
Stripping steam (kg steam)	5
Motive steam (kg steam)	35
Total (kg steam)	65
Heating (kg steam)	24.2
Electricity (KWh)	5

Note: Semi continuous deodorization, 0.2% FFA, 0.5% stripping steam, and average electricity consumption; FFA, free fatty acid.

Tablo 4 - Characteristics of vegetable oil refinery wastewaters (18)

Parameter	**Soap-stock shredding**	**Deodorization**
pH	2	4-7
Temperature (°C)	80-90	20-30
BOD (mg/L)	13,400	600
COD (mg/L)	22,300	2,000
Total sulphate (mg/L)	40,000	-
Total phosphorus (mg/L)	2,500	-

Table 5 - Effluent levels for vegetable oil processing (12)

Parameter	**Guideline Value**
pH	6 – 9
BOD_5 (mg/L)	50
COD (mg/L)	250
Total nitrogen (mg/L)	10
Total phosphorus (mg/L)	2
Total suspended solids (mg/L)	10
Oil and grease (mg/L)	50
Temperature increase (ºC)	<3[b]
Total coliform bacteria (MPN[a] / 100 mL)	400
Active Ingredients / Antibiotics	To be determined on a case specific basis

[a]:MPN = Most Probable Number

[b]:At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity

Table 6 - Typical process and performance data of anaerobic wastewater treatment processes (9)

Process	**Input COD mg/L**	**HRT (h)**	**OLR (kg COD/m^3.day)**	**COD removal (%)**
Anaerobic Lagoons	N.D		0.6-1	
Anaerobic Contact process	1,500-5,000	2-14	0.5-5.3	75-90
Fixed-bed reactor	10,000-70,000	24-48	1-15	75-85
UASB	5,000-15,000	4-12	2-12	75-85
Expanded bed reactor	5,000-10,000	5-10	5-30	80-85
Fluidized bed reactor	N.D	N.D	40-60	N.D
Internal circulation (IC) reactor	N.D	N.D	31	N.D

N.D.: No data

Table 7 - Some common operational problems experienced with anaerobic treatment processes (9)

Problem	**Solution**
Lack of macro-nutrients	BOD:N:P ratios are normally maintained at 500:5:1
pH	The pH is maintained at 6.8 – 7.5
Temperature	The optimum temperature for mesophilic bacteria is 35-37 ºC
Lack of micro-nutrients	Minimum quantities of micro-nutrients are maintained, especially for Fe, Ca, Mg and Zn, according to the specific process employed
Physical blockage of the reactor inlet pipework	Effective screening and primary treatment is essential
Overloading	Care needs to be taken to ensure the original hydraulic, solid and organic loading design rates do not exceed the manufacturer's recommendations

Table 8 - Air emission levels for vegetable oil processing (12)

Parameter	**Guideline Value**
Dust (mg/Nm^3)	10 (dry dust) 40 (wet dust)
Hexane / VOCs (mg/Nm^3)	100

Table 9 - Gas pollutants resulting from vegetable oil refining plants from different sources (12)

Parameter	**Boiler**	**Generator**
CO (mg/Nm^3)	40-130	2,060
CO_2 (mg/Nm^3)	2-205	0.8
NO_x (mg/Nm^3)	60-125	1,300
SO_2 (mg/Nm^3)	-	110
Smoke (Ringlemann scale)	-	5
Particulate Matter (mg/Nm^3)	-	275

Table 10 - Characterization of wastewater formed during corn oil refining at Kirlangic Oil Factory (64)

Parameter	Minimum	Maximum	Mean	Standard Deviation
pH	2.72	2.85	2.79	0.07
COD (mg/L)	11,580	15,450	12,880	2,225.7
Soluble COD (SCOD) (mg/L)	5,140	6,700	5,680	884.7
BOD_5 (mg/L)	1,250	2,278	1,932	591.2
Soluble BOD_5 ($SBOD_5$) (mg/L)	1,100	1,207	1,135	61.78
TSS (mg/L)	1,058	2,990	2,850	1,077.3
TKN (mg/L)	1,125	1,458	1,261	174.7
NH_3 (mg/L)	38	62	48	12.5
Total P (mg/L)	275	775	583	269.6
Oil-grease (mg/L)	307.8	498.6	375	107.2
Sulfate (mg/L)	11,900	12,300	12,006	257.2
Color (Pt-Co)	868	1,700	1,161	467.1

Table 11 - Characterization of wastewater formed during sunflower oil refining at Kirlangic Oil Factory (64)

Parameter	Minimum	Maximum	Mean	Standard Deviation
pH	3.5	4.5	4.01	0.5
COD (mg/L)	8,345	9,700	9,215	756.1
SCOD (mg/L)	5,195	5,560	5,385	182.8
BOD_5 (mg/L)	1,500	1,900	1,850	327.9
$SBOD_5$ (mg/L)	1,450	1,800	1,550	217.9
TSS (mg/L)	1,516	1,985	1,733	236.5
TKN (mg/L)	458.3	625	517.6	93.2
NH_3 (mg/L)	18	51	29.6	18.5
Total P (mg/L)	52	420	1,77.3	210.2
Oil-grease (mg/L)	533	760.2	664.3	117.6
Sulfate (mg/L)	10,800	11,750	11,416	534.1
Color (Pt-Co)	224	272	242	21.6

Table 12 - Analysis results of corn oil refining wastewater samples taken from all treatment steps of WWTP at Kirlangic Oil Factory (64)

Sampling point / Parameter	1	2	3	4
pH	2.79	5.92	7.23	7.7
COD (mg/L)	12,880	8,015	1,705	225
SCOD (mg/L)	5,680	3,535	1,470	198
BOD_5 (mg/L)	1,932	1,375	620	27
$SBOD_5$ (mg/L)	1,135	783.5	290	19
TSS (mg/L)	2,850	1,074	129	127
TKN (mg/L)	1,261	564.5	250	228
NH_3 (mg/L)	48	84.5	15.5	1.6
Total P (mg/L)	583	3.65	2	1.4
Oil-grease (mg/L)	375	13.4	7.75	6.7
Sulfate (mg/L)	12,006	8,983	7,051	4,585
Color (Pt-Co)	1,161	821	683	151

Table 13 - Analysis results of sunflower oil refining wastewater samples taken from all treatment steps of WWTP at Kirlangic Oil Factory (64)

Sampling point / Parameter	1	2	3	4
pH	4.01	7.49	7.39	8
COD (mg/L)	9,215	5,047	1,770	265
SCOD (mg/L)	5,385	3,170	1,425	190
BOD_5 (mg/L)	1,850	1,095	220	44
$SBOD_5$ (mg/L)	1,550	960	51	18
TSS (mg/L)	1,733	267	261.6	152.6
TKN (mg/L)	517.6	270.8	395.8	215
NH_3 (mg/L)	29.6	10.5	11.5	11.4
Total P (mg/L)	177.3	7.15	4.1	1.7
Oil-grease (mg/L)	664.3	12.8	7.6	3.9
Sulfate (mg/L)	11,416	9,640	7,750	5,050
Color (Pt-Co)	242	186	180	125

Table 14 - The sizes of the tanks and basins in WWTP (64)

Tanks	**Equalization basin (2)**		**Equalization basin (1)**	**Aeration tank 1st Compartment**
	A1	**A2**		
Depth (m)	3.50	3.25	3.60	4.00
Width (m)	4.50	4.50	3.00	5.00
Length (m)	5.23	9.25	7.00	10.50
Volume (m^3)	82	135	76	210
1cm water height volume (L)	240	415	210	525

Tanks	**Rapid mixing**	**Slow mixing**	**DAF**	**CTP**	**Polyelectrolytes**	**Fe (Cl)$_3$**	**Lime**	**Sedimentation basin 1 and 2**
Diameter (m)	1.10	1.90	3.0	2.0	1.0	1.00	1.50	4.0
Depth (m)	1.50	1.50	3.0	2.0	1.0	1.20	1.50	4.0
Volume (m^3)	1.40	2.80	21.0	6.0	0.78	0.94	2.50	50.0
1cm water height volume (L)	13.0	15.0	70.0	30.0	7.85	7.80	17.0	125.0

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Figure 9 - Kirlangic Oil Factory WWTP Flow Chart

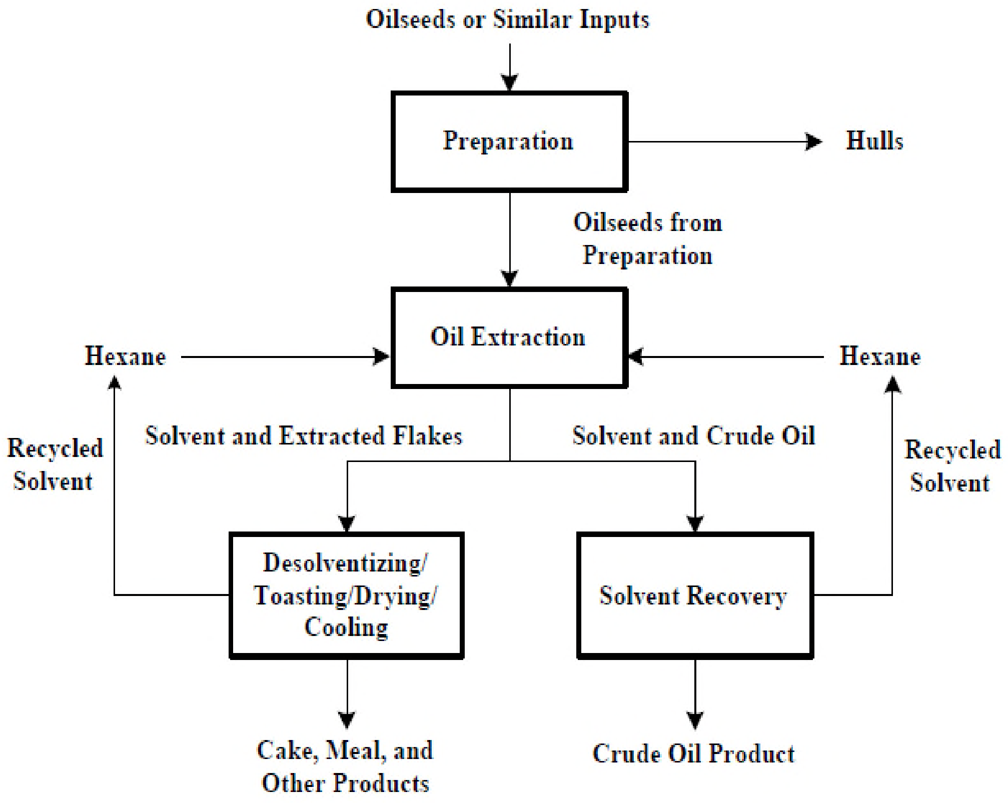


Figure 1 - A simple solvent extraction process for vegetable oils (3)

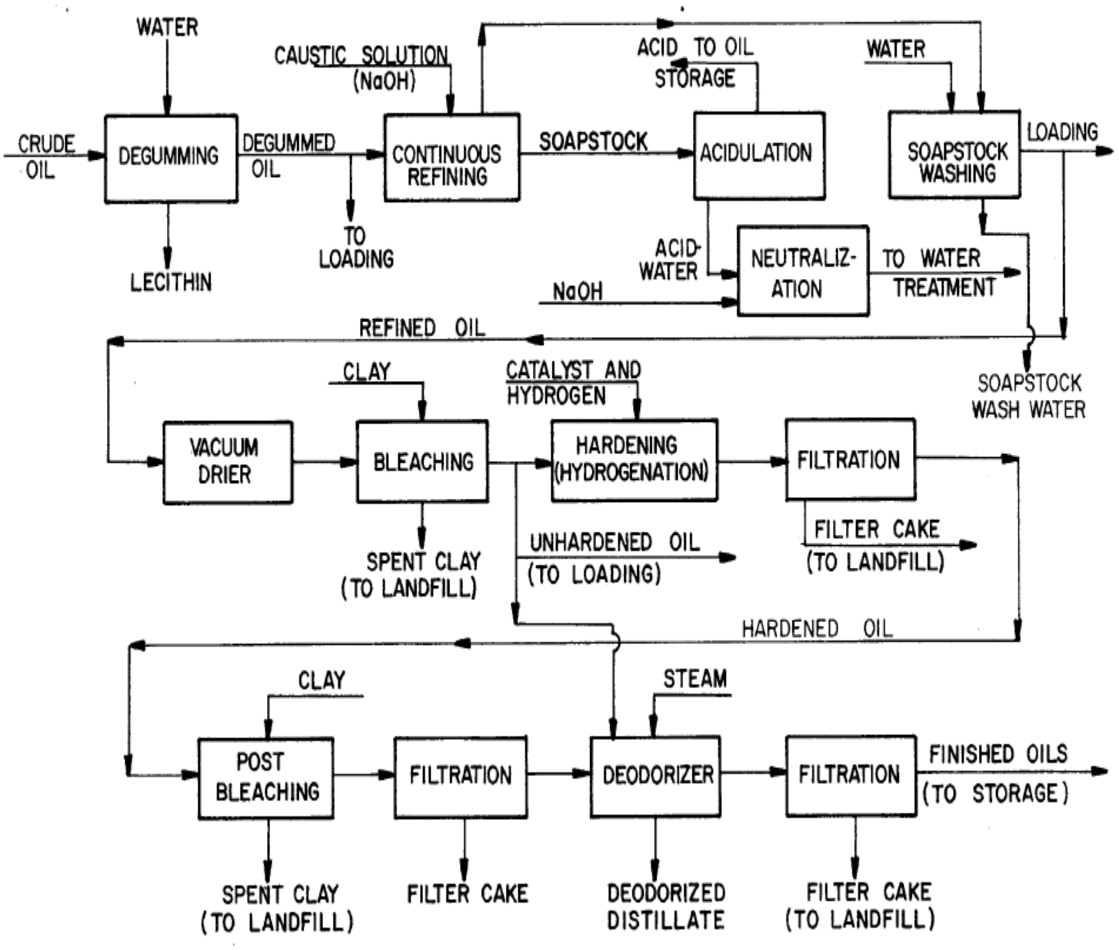


Figure 2 - Oil refining flow diagram (4)

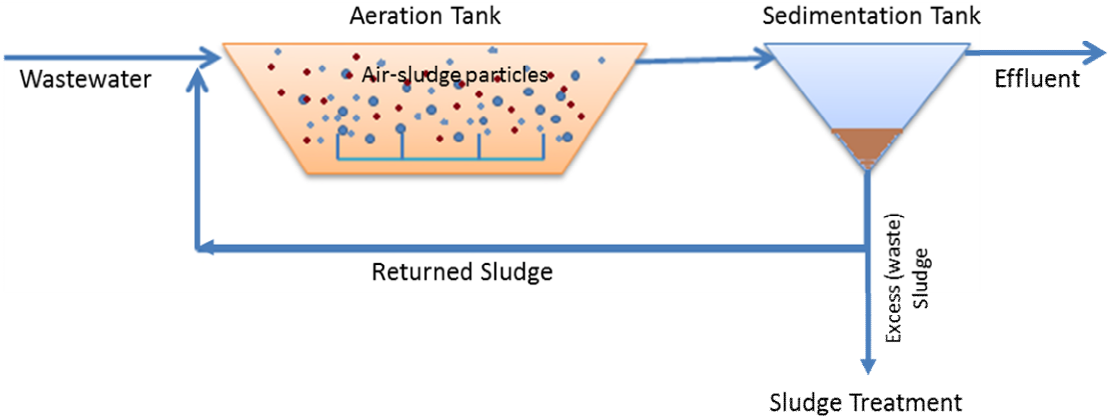


Figure 3 - Activated sludge diagram

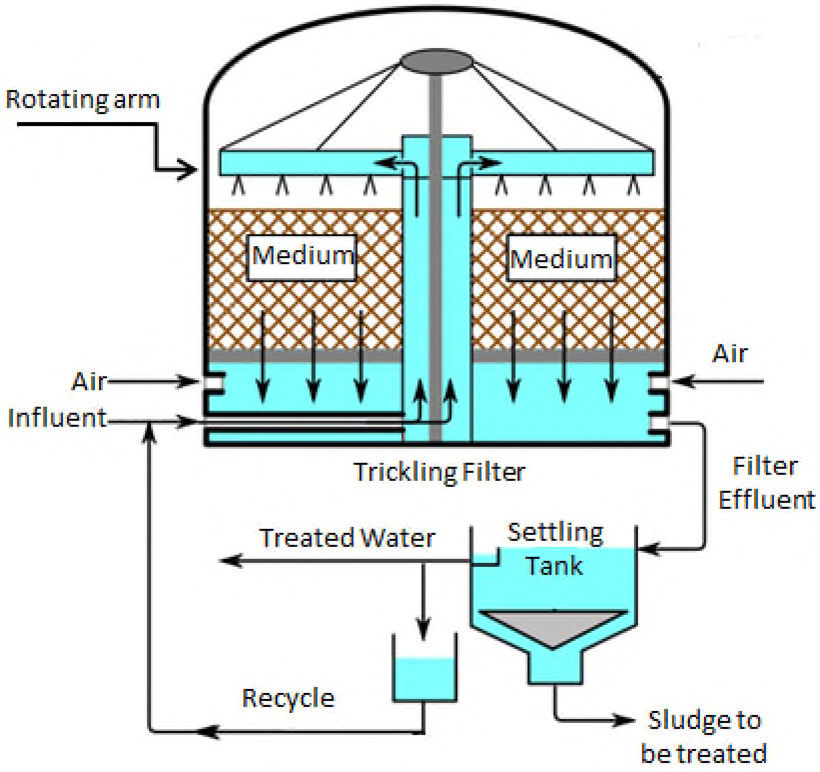


Figure 4 - A schematic representation of a trickling filter system (50)

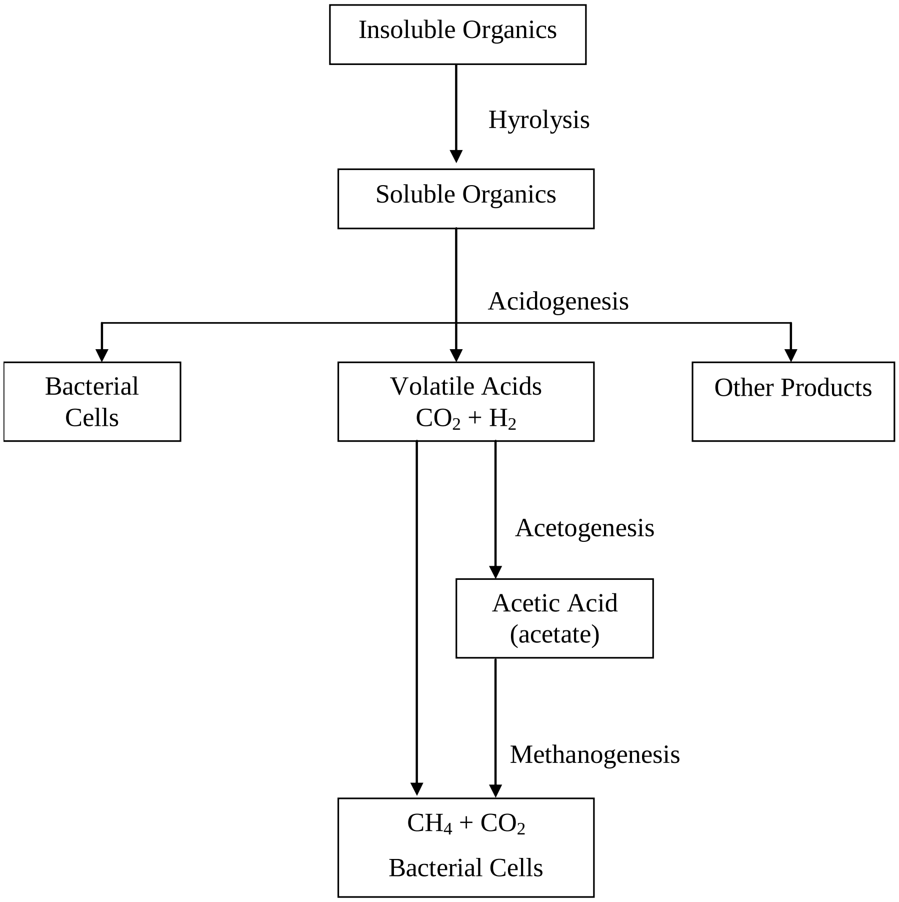


Figure 5 - Anaerobic degradation route (57)

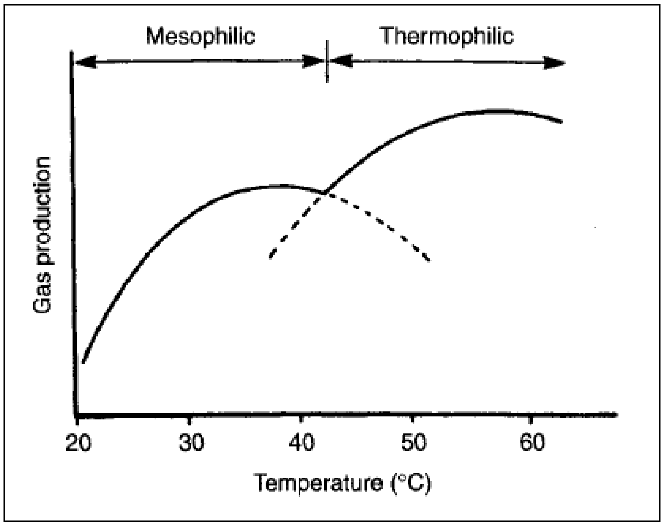


Figure 6 - Effect of temperature on biogas production (53)

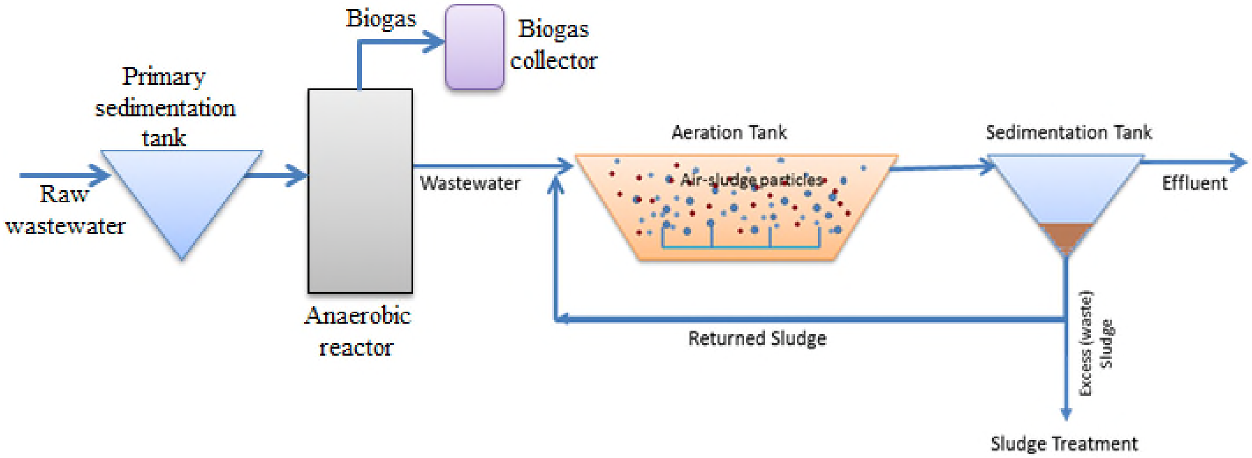


Figure 7- Anaerobic–aerobic treatment method

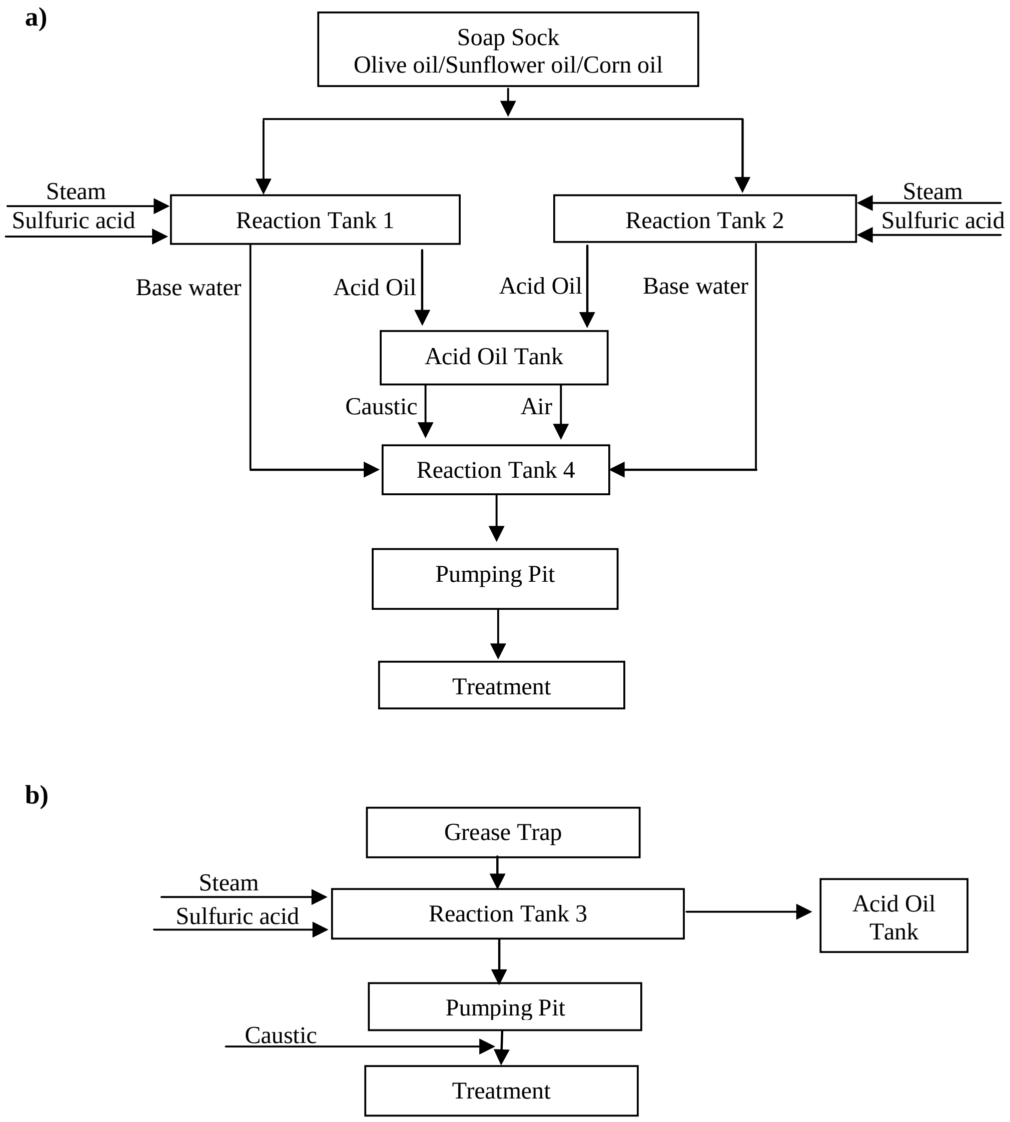
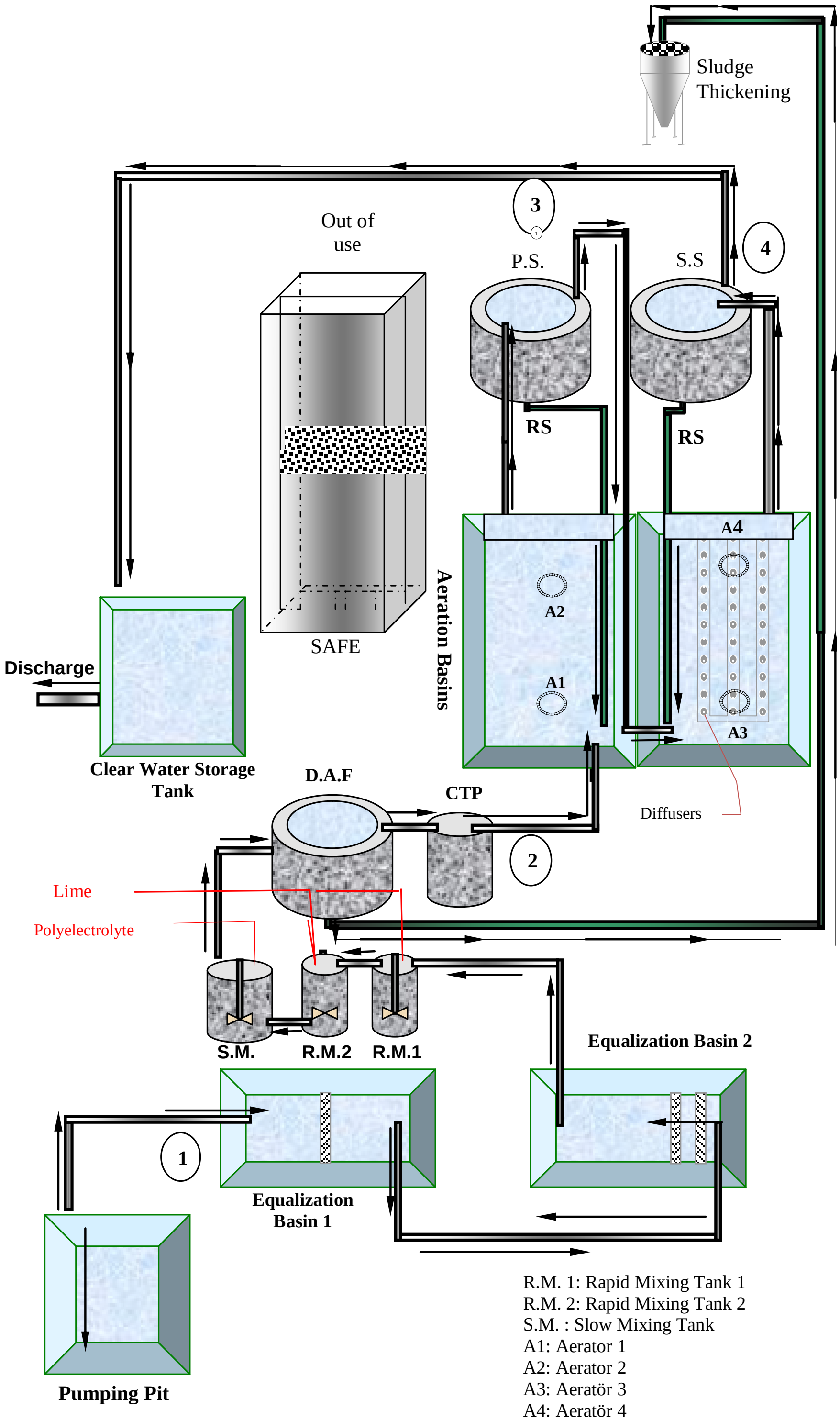


Figure 8 - a) Refinery soap-stock processing, b) Refinery wash water processing (64)



R.M. 1: Rapid Mixing Tank 1
R.M. 2: Rapid Mixing Tank 2
S.M. : Slow Mixing Tank
A1: Aerator 1
A2: Aerator 2
A3: Aeratör 3
A4: Aeratör 4
RAS: Recyled sludge
P.S.: Primary sedimentation
S.S.: Secondary sedimentation

Figure 9 - Kirlangic Oil Factory WWTP Flow (64)